INFORMATION TO USERS

This was produced from a copy of a document sent to us for microfilming. While the most advanced technological means to photograph and reproduce this document have been used, the quality is heavily dependent upon the quality of the material submitted.

The following explanation of techniques is provided to help you understand markings or notations which may appear on this reproduction.

1. The sign or “target” for pages apparently lacking from the document photographed is “Missing Page(s)”. If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting through an image and duplicating adjacent pages to assure you of complete continuity.

2. When an image on the film is obliterated with a round black mark it is an indication that the film inspector noticed either blurred copy because of movement during exposure, or duplicate copy. Unless we meant to delete copyrighted materials that should not have been filmed, you will find a good image of the page in the adjacent frame.

3. When a map, drawing or chart, etc., is part of the material being photographed the photographer has followed a definite method in “sectioning” the material. It is customary to begin filming at the upper left hand corner of a large sheet and to continue from left to right in equal sections with small overlaps. If necessary, sectioning is continued again—beginning below the first row and continuing on until complete.

4. For any illustrations that cannot be reproduced satisfactorily by xerography, photographic prints can be purchased at additional cost and tipped into your xerographic copy. Requests can be made to our Dissertations Customer Services Department.

5. Some pages in any document may have indistinct print. In all cases we have filmed the best available copy.

University Microfilms International

300 N. ZEEB ROAD, ANN ARBOR, MI 48106
18 BEDFORD ROW, LONDON WC1R 4EJ, ENGLAND
Nalepa, Christopher John

Part I. The Effect of Structure and Temperature on the Photochemistry of Cyclic and Bicyclic Azoalkanes. Part II. The Synthesis and Thermal Rearrangement of 1-Vinylbicyclo(2.2.0)Hexane

Rice University

University Microfilms International 300 N. Zeeb Road, Ann Arbor, MI 48106
RICE UNIVERSITY

PART I

THE EFFECT OF STRUCTURE AND TEMPERATURE ON
THE PHOTOCHEMISTRY OF CYCLIC AND
BICYCLIC AZOALKANES

PART II

THE SYNTHESIS AND THERMAL REARRANGEMENT
OF 1-VINYLBICYCLO[2.2.0]HEXANE

by

CHRISTOPHER J. NALEPA

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE

DOCTOR OF PHILOSOPHY

APPROVED, THESIS COMMITTEE:

Paul S. Engel, Professor of Chemistry
Chairman

Wilbur E. Billups,
Professor of Chemistry

Barry F. Dunning,
Associate Professor of Physics

HOUSTON, TEXAS

APRIL 1981
Abstract

Part I

The photochemistry of 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO) and 11 of its derivatives has been investigated; the syntheses of two new derivatives of this class are described. Introduction of either radical stabilizing substituents at the bridgehead position or strained rings anti to the azo moiety have been found to increase the photoreactivity of the normally photoinert DBO skeleton by up to 70 fold as measured by the quantum yield of nitrogen formation. Strained rings syn to the azo function have little effect. The increase in photoreactivity with structural changes is accompanied by a corresponding decrease in fluorescence lifetimes and quantum yields. The quantum yield of nitrogen formation has been found to correlate with the activation parameters for thermal decomposition of the azoalkanes; that is, the compounds that are labile photochemically are relatively labile thermally and vice versa. This is taken as evidence that a barrier to photochemical nitrogen loss from $S_1$ exists which can be lowered with suitable structural changes. Strained rings syn to the azo moiety and bridgehead methyl substitution exert little effect on photoreactivity but do affect the fluorescence quantum yield and lifetime relative to DBO; this is accounted for by slight changes in the rate of intersystem in these relatively photoinert DBO derivatives.

An investigation of products from photolysis of two DBO analogues, one with monovinyl and the other with divinyl bridgehead substitution, revealed the complete lack of formation of the corresponding bicyclo [2.2.0]hexanes, the product expected from simple collapse of the 1,4
biradical. To account for this lack of ring closure product, it is proposed that these compounds could decompose via a one bond homolysis to form a diazene radical as a discrete intermediate. This species then collapses to the most stable product.

The effect of temperature on the photoreactivity and photo-photophysics of several cyclic and bicyclic azoalkanes is described. For azoalkanes whose quantum yields for nitrogen formation are less than unity at room temperature, it has been found that raising the temperature at which the photolysis is performed can be an effective means of increasing photoreactivity. A simple model in which the rate constant for excited state nitrogen loss is treated with the Arrhenius equation yields activation parameters for nitrogen loss. For the compounds investigated here, these values fall between 0-10 kcal mol⁻¹. At least for the 2,3-diazabicyclo[2.2.2]oct-2-ene derivatives investigated, those which are more photoreactive exhibit lower activation energies than those which are relatively photoinert.

Part II

The synthesis and thermal rearrangement of 1-vinylbicyclo[2.2.0]hexane is reported. A synthesis of this compound via a route involving a tosylhydrazone decomposition was unsuccessful but a novel tosylhydrazone fragmentation reaction was discovered in its stead. In addition, a photochemical cleavage of the strained 1,4 bond in 1-acetylbicyclo[2.2.0]hexane was discovered.
Acknowledgements

I would like to thank Dr. Paul S. Engel for suggesting this work and for his guidance and instruction which helped see it to completion. I would also like to thank Ms. Treacy L. Woods for her assistance with the biacetyl quenching experiments and the computer data analysis. Studies of the fluorescence lifetimes of the bicyclic azo compounds would have been impossible without use of the excellent facilities at the Center for Fast Kinetics Research (CFKR) in Austin, Texas and the advice of Dr. M. A. J. Rodgers. Finally, I would like to thank my wife and family for their patience and understanding during the period of time this work was undertaken.
Table of Contents-Part I

A. Introduction .................................................................1

B. Synthesis of Azo Compounds
   1. 2,3-Diazabicyclo[2.2.2]oct-2-ene (DBO) Derivatives ..........12
   2. Tetrahydropyridazine Derivatives ..............................24
   3. 1-Pyrazolines .........................................................24

C. Photochemistry of DBO Derivatives-Results
   1. Absorption and Emission Spectra .................................26
   2. Nitrogen Quantum Yields ..........................................28
   3. Fluorescence Quantum Yields and Lifetimes ......................33
   4. Location of the Triplet Energy of 1-Vinyl-DBO ..............33
   5. The Solvent Dependent Photochemistry of 1,4-Dimethyl-DBO.......38
   6. Investigation of the Products from Photolysis of 1-Vinyl-
      DBO, 1,4-Divinyl-DBO, and 1,4-Dimethyl-DBO ..................39

D. Photochemistry of DBO Derivatives-Discussion ......................42

E. Photochemistry of Tetrahydropyridazine Derivatives .............53

F. Effect of Temperature on Azoalkane Quantum Yields ...............56

G. Other Studies of Cyclic and Bicyclic Azoalkanes
   1. The Search for Phosphorescence from Two Bridgehead
      Halogen Analogues of DBO .........................................70
   2. Triplet Sensitized Photochemistry of Cyclic and Bicyclic
      Azoalkanes ..........................................................72
   3. Thermolysis of a DBO Derivative Possessing an Endo
      Cyclopropyl Group .................................................76

H. Experimental .............................................................79
Table of Contents-Part I (Cont'd)

I. Spectra.................................................................117
J. Appendices..............................................................124
K. References and Notes...............................................131

Table of Contents-Part II

A. Introduction..........................................................143
B. Attempted Synthesis of 1-Vinylbicyclo[2.2.0]hexane via a Tosyl-
   hydrazone Decomposition...........................................148
C. Synthesis of 1-Vinylbicyclo[2.2.0]hexane via the Wittig
   Reaction.................................................................154
D. Thermal Isomerization of 1-Vinylbicyclo[2.2.0]hexane...........158
E. Experimental............................................................162
F. Spectra.................................................................172
G. References and Notes...............................................176
Table of Tables—Part I

1. Absorption and Emission of **DBQ** Derivatives..........................27
2. Quantum Yields for Direct Irradiation of **DBQ** Derivatives........30
3. Nitrogen Quantum Yields for 1-Vinyl-**DBO** and 1,4-Divinyl-**DBO**
   Employing Various Actinometer Systems...............................31
4. Fluorescence Quantum Yields and Lifetimes of **DBO** Derivatives....34
5. Rate Constants for Quenching of Ketone Phosphorescence with
   **DBO**........................................................................35
6. Rate Constants for Quenching of Biacetyl Phosphorescence by
   **DBO** and 1-Vinyl-**DBQ**.................................................36
7. Solvent Dependent Photochemistry of 1,4-Dimethyl-**DBO**...........38
8. Rate Constants for Photochemical Processes in **DBO** Derivatives....51
9. Quantum Yields for Direct Irradiation of Tetrahydropyridazine
   Derivatives........................................................................53
10. The Effect of Temperature on $\Phi_r$ for several 1-Pyrazolines........60
11. Temperature Dependent Fluorescence Data for 67.......................62
12. The Effect of Temperature on $\tau_f$ of 67................................64
13. The Effect of Temperature on $\Phi_r$ for Several Cyclic and Bicyclic
    Azoalkanes........................................................................64
14. Activation Parameters for Photochemical Nitrogen Loss from
    Various Azoalkanes.........................................................67
15. Triplet Sensitized Quantum Yields of Cyclic Azoalkanes in
    Solution..........................................................................73
16. Rates of Decomposition of Endo-Cp at Several Temperatures........77
17. The Effect of Strained Rings on Thermolysis of **DBQ** Derivatives...77
Table of Tables-Part II

1. Variation of the Ratio 28:29 with Reaction Time.................149
2. Solution Phase Decomposition of 1-Vinylbicyclo[2.2.0]hexane......159
3. Activation Parameters for Thermolysis of Small Ring Compounds....159
A. Introduction

Cyclic azo compounds have long been used as precursors to biradicals and the products derived from them. Upon irradiation with ultraviolet light, five membered cyclic azo compounds (1-pyrazolines) lose nitrogen to afford 1,3 biradicals which then collapse to cyclopropanes. Photolysis of six membered cyclic azo compounds (2,3,4,5-tetrahydropyridazines) likewise affords 1,4 biradicals which undergo competitive ring closure and 2,3 bond rupture to mixtures of cyclobutanes and olefins, respectively. A possible side reaction in the photolysis of these compounds is phototautomerism, a formal 1,3 migration of an α hydrogen to nitrogen (see 1-2 below). Phototautomerism, for example, is the major process for compounds 1, 3, and 4.

Since cyclic azo compounds are quite popular synthetic precursors, one might assume that their photoreactivity is uniformly high.
Photoreactivité as measured by the quantum yield of nitrogen evolved, $\phi_r$, however, is strongly correlated to ring size. Five membered systems like 5 and DBH (2,3-diazabicyclo[2.2.1]hept-2-ene) generally exhibit high quantum yields.\(^9\) The corresponding six membered systems (6 and 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO)) are in contrast amazingly photoinert. Note that in the monocyclic compounds above, full substitution at the $\alpha$ carbons prevents phototautomerism; this side reaction is also blocked in the bicyclic systems because the resulting hydrazone would violate Bredt's rule.

In recent years, several examples have appeared in the literature in which syntheses employing azo compounds as key precursors have either failed completely or proceeded only under special conditions. Most of these compounds have contained the DBO framework. Snyder's failure to obtain cubane from photolysis or thermolysis of azo precursor 7 is the classic example,\(^{13}\) although other "reluctant"
azo compounds are known (8-10). The photoinertness of these compounds is so striking that much work has been done to find methods to effect their photodecomposition.

Compound 10 is a particularly noteworthy case.16 Whereas prolonged photolysis in a variety of solvents failed to decompose it to a measurable extent, photolysis under special conditions (gas phase, 800 C) did result in conversion to several cyclopentadiene dimers in high yield. Recent application of these same conditions to compound 7, however, failed to produce cubane.17 Benzene, the only volatile organic compound found, was obtained in 50% yield. Studies are still continuing regarding the photoreactivity of 7. It has been found that photolysis in pentane solution employing 185 nm light results in efficient conversion to cyclooctatetraene.18 It will be shown in this thesis that performing solution phase photolyses at temperatures greater than ambient may be an additional method for increasing the photoreactivity of these "reluctant" azo compounds.

Not all syntheses using the often uncooperative six membered azo system are unsuccessful or require special conditions. Tanida, et al.19,20 photolysed two compounds containing strained rings anti to the azo moiety.21 Photolysis of Exo-Cp in ether produced 11a and 11b in good yield but similar treatment of CB was reported to give a major amount of nonvolatile material along with compounds 12a-c.

\[
\text{EXO-Cp} \xrightarrow{\text{hv, ether, -20°C}} 11a \quad 20\% + \quad 11b \quad 60\%
\]
Further work by Martin, et al. on CB identified an additional photoprodut as the reactive cis,trans-1,4-cyclooctadiene 13. Since 13 is the major product in most solvents, it is likely that the nonvolatile material referred to by Tanida, et al. arises from further reaction of this substance under their isolation conditions. Unfortunately, lack of quantum yield data by both Martin and Tanida preclude any comparison of the photoreactivity of these compounds with that of the parent DBO. It would be interesting to see what effect the strained rings in Exo-Cp and CB have on their photoreactivity.

Roth and Erker photolyed the di-methylene azo DM, thereby generating the tetramethylenethane derivative. Stabilization of the incipient diradical might be expected to increase the photoreactivity of this system. No quantum yield data were disclosed, however.

Pacquette and Epstein utilized an azo precursor to generate cis-bicyclo[5.2.0]nona-2,5,8-diene and monitor its facile Cope
rearrangement. Conversion of 15 to 16 was reported as quantitative but lack of quantum yield data once again precluded comparison with DBQ. Systems analogous to 15 have been irradiated to afford novel products in several laboratories.25

In view of the popularity of six membered azo compounds as synthetic precursors, it was thought that a quantitative study of a series of them would be of considerable value.40 It was hoped that such a study would uncover some of the factors governing their photoreactivity (i.e. ring strain, incipient radical stability, stereoelectronic factors, reaction exothermicity) and would therefore aid the understanding of the reasons behind the successes and failures encountered when using these systems as synthetic precursors. It was also deemed of interest to see if their photoreactivity was uniformly low or if suitable structural changes could increase the quantum yield of nitrogen loss. Additionally, the mechanism of nitrogen loss upon direct irradiation of these compounds was in some doubt and it was hoped to shed further light on this matter. An account of some of this mechanistic work will now be presented.

Clark and Steel11 have investigated the photochemistry of DBQ quite thoroughly. They found that in the gas phase, the fate of excited DBQ was fluorescence from the n,π* singlet state and inter-
system crossing to the triplet from which decomposition occurred. Quantum yields for these processes were determined to be $0.56 \pm 0.1$ and $0.50 \pm 0.1$, respectively.

These conclusions were based upon two lines of evidence. The fluorescence quantum yield was insensitive to changes in pressure (addition of inert gas) whereas the decomposition yield varied markedly, decreasing with increasing pressure. This indicated that the emitting and decomposing states were not the same. Furthermore, DBO effectively quenched the fluorescence of naphthalene and the phosphorescence of benzaldehyde and benzophenone but only in the case of naphthalene could sensitized emission be observed.

Clark and Steel then explored the photochemistry of DBO in isoctane solution. The quantum yield as measured by the formation of C$_6$ hydrocarbons ($\phi^C_6$) in the triplet sensitized photolysis equalled the yield measured by the disappearance of DBO and was 0.014. In the direct photolysis, however, a discrepancy between the yields measured by these two methods appeared (0.022 and 0.068, respectively). The discrepancy was attributed to build-up of hydrazine DBO-H arising from photoreduction of the azo linkage. Support for this explanation is found in the observation that the bridgehead dichloro
derivative photoreduces in hexane.\textsuperscript{27} By determining the fluorescence quantum yield as 0.20, and making the assumption that $\phi_f + \phi_{isc} = 1$ (as it is in the gas phase), Clark and Steel determined that ca. 50% of the C\textsubscript{6} yield in the direct photolysis occurs from S\textsubscript{1} with the remainder from T\textsubscript{1}. Thus the amount of C\textsubscript{6} hydrocarbons produced from the triplet manifold of DBO in the direct photolysis is equal to $\phi_{isc} \times \phi_{C6 \text{ (triplet)}} = (1.0 - 0.2)(0.014) = 0.011$ or half the actual value obtained. The following scheme summarizes the rich direct photochemistry of DBO.\textsuperscript{28}

\[
\begin{array}{c}
\text{DBO} \\
\xrightarrow{hv} \\
\xrightarrow{\text{isoctane}} \\
\xrightarrow{20\%} \\
\xrightarrow{hv_f} \\
\xrightarrow{20\%} \\
\xrightarrow{75\%} \\
\xrightarrow{4\%} \\
\xrightarrow{1\%} \\
\xrightarrow{1\%} \\
\xrightarrow{99\%} \\
\xrightarrow{\text{hydrazine}} \\
\xrightarrow{\text{DBO}} \\
\xrightarrow{\text{N}_2 + \text{Me}_2 \text{N} + \text{C}_2 \text{H}_4} \\
\text{Di-Me}
\end{array}
\]

Studies by Turro, et al.\textsuperscript{29} on the photochemistry of the bridgehead dimethyl analogue of DBO (Di-Me) in various solvents contrast to the work discussed above. It was found that as the solvent was varied from acetonitrile to methanol, the quantum yield for azo dis-
apperance, $\phi_{-\text{azo}}$, stayed about the same (ca. 0.2) while the fluorescence quantum yield decreased dramatically from 0.7 to 0.01. In methanol-d$_1$, the fluorescence yield increased to 0.1 but $\phi_{-\text{azo}}$ was once again unchanged. The scheme below was used to rationalize the results.

$$\text{Di-Me} \xrightarrow{\text{hv}} S_1^v \xrightarrow{\text{hv}_f} S_1 \xrightarrow{\text{MeOH}} \text{Di-Me}$$

Decomposition was postulated to occur from a state with excess vibrational energy ($S_1^v$) which preceded the fluorescing state ($S_1$). The role of methanol and methanol-d$_1$ is to offer an additional mode for deactivation of $S_1$ through the formation of an excited state complex. Since this solution phase mechanism for Di-Me differed from that of DBO, and since these were the only bicyclo[2.2.2]oct-2-enes whose photochemistry was examined in detail, it was not clear which mechanism was the rule and which the exception. Further mechanistic work was clearly warranted on other members of this bicyclic class.

Few studies had likewise been done on monocyclic six membered azo compounds. Because these compounds do not fluoresce, the mechanistic work has involved product studies.

A key study was done by Berson and Olin. They found that direct irradiation of 17-19 yielded products whose stereochemistry was the same as that produced upon thermolysis. Interestingly, the similar photochemical and thermal behavior of this series was cited as a breakdown of the familiar Woodward-Hoffman rules. These rules
would predict conrotatory ring opening photochemically and disrotatory opening thermally, if loss of nitrogen occurred by a [4+2] cycloreversion. The results obtained were interpreted as being most consistent with photodecomposition from a vibrationally excited ground state, S\textsuperscript{v}.

Bartlett and Porter\textsuperscript{26} looked at the effect of spin multiplicity on the ratio of products produced from either meso or d,l \textsuperscript{20}. The degree of retention of configuration from direct decomposition of meso or d,l \textsuperscript{20} was 95 and 97%, respectively. Corresponding values for thioxanthone triplet sensitized decomposition were 61 and 65%. The differing degrees of retention from the direct and sensitized reactions (a spin correlation effect) argues against much decomposition
from the triplet state in the direct photolysis of these compounds. If the minor lack of retention in direct photolysis is caused by reaction from the triplet manifold, this pathway comprises only ca. 10% of the total amount of decomposition.

It has already been mentioned that photolysis at temperatures greater than ambient has been found to be an effective method of increasing the photoreactivity of several azo compounds. A survey of the literature reveals that the temperature dependency of photochemical reactions has not received much attention. The effect of temperature has been studied on the photochemical cis-trans isomerization of stilbene and some of its derivatives, fluorescence of indole derivatives, [2+2]photoadditions of olefins to enones, and the α cleavage reaction of ketones. Although many years ago temperature dependent photochemistry was discovered for acyclic azoalkanes in the gas phase, it has been only just recently that temperature effects have been reported of azo compounds in solution.

At the start of this work, Turro and coworkers at Columbia University monitored the effect of temperature on the fluorescence properties of the compound below. They found that increasing temperatures caused a decrease in fluorescence intensity, indicating that some temperature dependent process was competing with fluorescence. If
this process could be shown to be that leading to nitrogen forma-
tion, a new method for increasing solution phase photoreactivity
would be uncovered. Hence Professor Engel and I agreed to look at
the effect of temperature on the quantum yield of nitrogen produc-
tion for this compound and others.

The details of this investigation, as well as the effect of
structural changes on the photoreactivity of simple derivatives of
six membered cyclic and bicyclic azoalkanes, will now be presented.
In addition, the mechanistic implications of these results will be
discussed.
B. Synthesis of Azo Compounds

1. **DBO** Derivatives

   The most general method for gaining entry into the bicyclo[2.2.2] azo system is the [4+2] Diels-Alder reaction of a 1,3-cyclohexadiene with an azo ester. The resulting adduct is then transformed in a series of steps into the azo compound. This strategy is illustrated below.

   \[
   \text{Cyclohexadiene} + \text{Azo ester} \rightarrow \text{DBO}
   \]

   \(E=\text{CO}_2\text{Me, CO}_2\text{Et}\)

   1: hydrolysis
   2: oxidation

   Cohen and Zand\textsuperscript{41} first prepared **DBO** by this route but the synthesis suffers from the fact that a competing ene reaction to form 23 occurs to a major extent. This side reaction is not uncommon when using azo esters\textsuperscript{66} and the resulting bicyclic adducts in addition are frequently viscous oils and thus difficult to work with and purify. These problems are circumvented by the use of the more reactive triazolinediones \textsuperscript{24,42} as dienophiles. Competing ene adducts are not

   \[
   \begin{aligned}
   24 & \quad a: R=\text{Me} \\
   & \quad b: R=\text{Ph}
   \end{aligned}
   \]

   formed and the resulting compounds are crystalline.\textsuperscript{43} Furthermore, the cycloaddition occurs readily at room temperature and the reac-
tion can be conveniently performed by adding a solution of the red triazolinedione to the diene until the color faintly persists. Scheme 1 illustrates the syntheses of some of the compounds used in this work by the triazolinedione route.45

Several aspects of Scheme 1 bear comment. The cycloaddition with 1,4-dimethylcyclohexa-1,3-diene 25b was actually performed with a mixture of 1,3 and 1,4 dienes produced from Birch reduction of p-xylene and isomerization using potassium tert-butoxide in DMSO. Since it has been shown that 24a can react with 1,4 dienes,32 care was taken to insure that enough dienophile was added to react with the 1,3 diene present in the mixture but not so much that the slower reaction with 1,4 diene occurred to give undesired products. No special problems were encountered when running the cycloaddition with compounds 25a and 25c. With 25d, undesired adduct 3147 was initially obtained as the major product along with minor amounts of 27d. However, by raising the reaction temperature to 100° C, a temperature at which the valence isomerization 25d ⇌ 26d occurs more readily,48 27d was formed almost exclusively. The hydrogenations of all adducts proceeded smoothly but some problems were encountered in the hydrolysis reaction.

Application of the Snyder procedure49 (KOH-isopropanol) to bridgehead dimethyl adduct 28b led only to recovery of starting material. More vigorous conditions (NaOMe-DMSO)44 were therefore required to effect hydrolysis of the urazole ring. The methyl group in 28b apparently restricts easy access to the carbonyl by base. In the case of 28c, the hydrolysis reaction was carried out using the more vigorous conditions because the relative merits of the Snyder
Scheme 1

\[ \text{R} \]  
\[ \text{25} \]  
\[ \text{26} \]  
\[ \text{27} \]  
\[ \text{28} \]  

a: \( R = H \)  
b: \( R = \text{Me} \)  
c: \( n = 1 \)  
d: \( n = 2 \)  

\[ \text{28a,d} \]  
[ \overset{\text{KOH}}{\Delta} \]  
[ \overset{\text{CuCl}}{\text{NH}} \]  
[ \overset{\text{NH}_4\text{OH}}{\text{DBO, CB}} \]  

1) \( \text{NaOMe, DMSO} \)  
2) \( \text{CuX}_2 \)  

b: \( X = \text{Cl} \)  
c: \( X = \text{Br} \)  

\[ \text{30} \]  

\[ \text{31} \]
procedure (high yields and convenience) were not apparent at the time. This procedure would now seem to be the method of choice for hydrolysis of 28c.

Overall yields from adducts 27 to azo compounds were 22% (Di-Me), 63% (DBO), and 64% (CB). Since Exo-Cp is unstable at room temperature, it was not isolated but generated in situ when needed. The overall yield from 27c to Exo-Cp precursor 29c was 67%.

Three other azo compounds (Mono-Me, MV, and DV) were synthesized by other workers in this laboratory via the triazolinedione route.

![Chemical Structures]

Mono-Me  MV  DV  DM

The syntheses of all three have been described in detail elsewhere and will not be recounted here. Additionally, a sample of the cuprous chloride precursor to DM was obtained. The synthesis of this compound has also been described.

Scheme 2 shows the synthesis of a compound possessing a cyclopropyl group in the endo orientation (CPCB). This route was published by Allred and Voorhees but no experimental methods were disclosed. The key feature of this synthesis is the use of the exo oriented cyclobutane ring in 32 to block the addition of diazomethane from that side of the double bond. It was felt that this compound was particularly worthy of synthesis because the cyclopropyl group was oriented differently than Exo-Cp and the molecule possessed a large amount of
Scheme 2

\[ \begin{align*}
25d & \quad \xrightarrow{\text{CH}_2\text{N}_2, 80^\circ, 2X} \quad 26d \quad \xrightarrow{\text{E} = \text{N} = \text{N}, 100^\circ} \quad \text{E} = \text{CO}_2\text{Me} \\
35 & \quad \xrightarrow{\text{NH}_4\text{OH}} \quad \text{CPCB}
\end{align*} \]

strain.

The literature route to CPCB was resorted to when attempts to synthesize it starting from triazolinedione adduct 27d were unsuccessful. Stirring 27d in the presence of an excess of diazomethane (room temperature, four days) led to quantitative recovery of starting material. An attempt at adding carbene produced from the cuprous chloride decomposition of diazomethane\textsuperscript{52} similarly failed.

Addition of diazomethane to 32 proved difficult also. However, it was discovered that by carrying out the reaction under forcing conditions (80\(^\circ\) C, sealed bottle, overnight) 33 could be obtained although the reaction had to be repeated in order to convert 32 completely to product.\textsuperscript{53} The rest of the synthesis was straightforward. Overall yield from 32 to CPCB was 6% with the hydrolysis and oxidation (34 + CPCB) proceeding in particularly low yield (20%).

Investigations into the photochemistry of CPCB revealed that the cyclobutyl ring was masking any effect of the cyclopropyl ring.
What was really needed was the compound without the cyclobutyl ring, **Endo-Cp**, a previously unknown compound. The route eventually developed to this compound is shown in Scheme 3.

**Scheme 3**

\[ \text{27a} \xrightarrow{\text{KOH}} \text{36} \xrightarrow{\text{37a} + \text{37b}} \]

Hydrolysis of **27a** by a modification of a published procedure\(^5\) yielded azoxy compound **36** in good yield (88%). This compound underwent a particularly facile 1,3 dipolar addition with diazomethane to afford a mixture of regioisomers **37** in 71% yield after chromatography on fluorisil. That the product consisted of a mixture of regioisomers was indicated by the broad melting point (87-94° C) of the purified material and the presence of seven pairs of resonances in the \(\text{C}^{13}\) nmr spectrum of the crude material. Comparison of the proton nmr of **37** with **39**\(^5\) revealed no upfield shift of the protons on the methylene bridge. This lends support to the endo assignment of stereochemistry. Exo orientation, which places the protons of the methylene bridge in close proximity to the azo moiety, would be expected to shift these protons upfield.\(^5\) Further evidence in support of the
stereochemical assignment is discussed below.

The relative ease of diazomethane cycloaddition and the exclusive endo orientation are noteworthy and suggest a directing effect of the azoxy moiety. While the reasons for this effect are unclear at this time,\textsuperscript{69} it has obvious applications to organic synthesis and should be explored further.

Denitrogenation of 37 was readily accomplished by irradiation in acetonitrile through a pyrex filter. In this manner, the long wavelength (324 nm) pyrazoline absorption could be selectively irradiated without affecting the shorter wavelength (230 nm) azoxy chromophore, affording 38 in slightly impure form. Comparison of the nmr spectrum of this material to authentic azoxy 40\textsuperscript{56} revealed the complete absence of the latter material. Hexachlorodisilane, ordinarily an effective deoxygenating reagent,\textsuperscript{54,56} was found to produce inconsistent results when applied to the transformation $38 \rightarrow \text{Endo-Cp}$. This is apparently due to the failure to obtain 38 in pure form. Lithium aluminum hydride, however, did furnish \text{Endo-Cp} in 18\% yield after preparative gas chromatography.

An alternative route to \text{Endo-Cp} was briefly explored. Addition of diazomethane to 27\textsubscript{a} using the forcing conditions developed
during the synthesis of CPCB yielded two products in the ratio 61:39 which could be separated by preparative tlc. The slowest moving band, consisting of the minor component, was assigned the endo configuration (41a) on the basis of nmr evidence. Comparison of the nmr of this material with that of 28a revealed no upfield shift of the protons on the methylene bridge. In contrast, the nmr of 41b did show an upfield shift of these protons of 0.25 ppm. In 41a the azo moiety is far removed from the methylene bridge protons whereas in 41b this group is in close proximity and causes the observed upfield shift. While 41a could presumably be transformed into Endo-Cp, this route was abandoned when the synthesis by the azaoy route was achieved.

The synthesis of two bridgehead halogen compounds is shown in Scheme 4. Luttke and Schabacker have previously described the synthesis of Di-Cl and Scheme 4 differs from theirs only in that hexa-chlorodisilane is used for the transformation 42 + 43. It was hoped that by using this reagent, a one step conversion of 42a to Di-Cl could be achieved. Greene and Gilbert, for example, have shown that the compound below is reduced directly to azo 6 with this reagent.
Surprisingly, treatment of 42a with greater than two equivalents of hexachlorodisilane gave 43a in quantitative yield, even after refluxing overnight. Since Snyder has shown that this reagent is effective for removal of the oxygen atom from compounds such as 36 and 39,56 and even deoxygenates at -30°C,54 it follows that the N-O bond in 43a must be strengthened. This would be the case if electron withdrawal causes resonance form 44a, which places negative charge nearer the electronegative chlorine atom, to be more important for 43a than 36 or 39. Increased contribution from this resonance form, which lends some double bond character to the N-O bond, would be expected to increase its resistance to cleavage. The synthesis of the previously unknown Di-Br was readily accomplished starting from 42b.58

An attempt to synthesize the bridgehead diiodo compound 48 starting from the known diene 4559 is outlined on the next page. The reaction of triazolinedione 24a with a mixture of 43 and its 1,4 diene isomer furnished 46, a white crystalline material, in 79% yield. Since this adduct underwent slow decomposition to a black complex mixture which was acidic to litmus, it had to be hydrogenated im-
Initially of 47. Attempted hydrogenation at one atmosphere using palladium on carbon or Adam's catalyst led to extensive decomposition of 46 and little hydrogen uptake. This compound could be hydrogenated successfully, however using diimide and the product was stable to long term storage.

Unfortunately, attempts to convert 47 to the azo compound failed. Thus hydrolysis with KOH in isopropanol afforded a complex mixture which upon oxidation with cupric chloride did not yield the cuprous chloride complex. Similarly, no complex formed upon hydrolysis with sodium methoxide in DMSO. A try at making the azoxy compound 49 led to recovery of starting material in 70% yield. The inability to transform 45 to azo is reminiscent of the difficulties encountered at this step in the synthesis of the bridgehead dimethyl compound Di-Me, and in view of the greater steric bulk of iodine compared to methyl, it is not altogether surprising that suitable conditions were not found for this transformation.

Other attempts at synthesizing DBO derivatives will be briefly described. Reaction of the bis-oxime of cyclohexane-1,4-dione 50
with hydrogen cyanide using the conditions developed by Porter and Hellerman\textsuperscript{61} for cyclohexanone oxime yielded a light tan solid (mp 169-170\degree \text{C} (dec)) in 95\% yield which was identified as \textit{51} (presumably a mixture of meso and \textalpha,\textbeta stereoisomers) on the basis of ir and mass spectral data. Oxidation of \textit{51} with chlorine\textsuperscript{62} was expected to give a mixture of bis-\alpha-cyanonitroso compounds \textit{52} the cis form of which was expected to yield \textit{53} by a facile internal dimerization\textsuperscript{27} Compound \textit{53} could then be transformed into \textit{54} by the chemistry outlined in Scheme 4. Upon oxidation of \textit{51} with chlorine, a light blue solid was isolated. Comparison of the uv and ir of this material with \textit{40a} and \textit{40b}, however, revealed no evidence for the cis diazoxy moiety and the synthesis of \textit{54} by this route was abandoned.

Heyman and Snyder\textsuperscript{63} have described an efficient synthesis of bicyclic azoalkanes utilizing dibenzylazodicarboxylate \textit{56} as a dieneophile and an attempt was made to synthesize \textit{58} by the route shown on the next page starting from the known diene \textit{55}.\textsuperscript{64} Upon photolysis of \textit{55} and \textit{56}, a complex mixture was obtained (five spots by tlc) and this synthesis was likewise scrapped.
Several attempts were made to exchange the halogens of Di-Cl and Di-Br with lithium using both lithium-sodium alloy and tert-butyllithium as exchange reagents. If the bridgehead dilithiated compound could be produced, it might be possible to react the compound with various electrophiles to afford bridgehead substituted azo compounds not obtainable by other methods (note the preceding failed syntheses). Unfortunately, all attempts to form 59 led to recovery of starting material as shown by UV. If any 59 had formed, quenching with methanol would have yielded DBO, a compound easily discernable by UV from Di-Cl and Di-Br (see sec. C.1.).
2. Tetrahydropyridazine Derivatives

The compounds of this class which were examined in this work are shown below. Since compounds 61 and 62 are thermally unstable, they were generated from their respective precursors just prior to use. Azo 6 was made in one step by oxidative cyclization of 2,5-

\[
\begin{align*}
6 & \quad 60 & \quad 61 & \quad 62 & \quad 63 \\
\end{align*}
\]

\[
\begin{align*}
\text{NCO}_2\text{Me} & \quad \text{NCO}_2\text{Me} \\
64 & \quad 65 & \quad 66 & \quad 60, 61 \\
\text{H}_2 \text{Pd/C} & \quad \text{KOH} \\
\text{CH}_2\text{N}_2 & \quad \text{t-BuOCl}, -78^\circ \\
\text{CuCl} &
\end{align*}
\]

diamino-2,5-dimethylhexane\(^{57}\) while 62 was produced by tert-butyl hypochlorite oxidation of the hydrazine 63.\(^{67}\) Compounds 60 and 61 were synthesized according to the procedures of Bishop.\(^{68}\)

3. 1-Pyrazolines

Several 1-pyrazolines (below), examined for possible temperature dependent photochemistry, were available from previous studies

\[
\begin{align*}
5 & \quad 67 & \quad 68 \\
\end{align*}
\]
studies in this laboratory. Their syntheses have been described.
C. Photochemistry of DBO Derivatives—Results

1. Absorption and Emission Spectra

The initial investigation of the photochemistry of these derivatives started with a study of their absorption and emission characteristics in benzene solution. Table 1 summarizes the data (for actual spectra, see Appendix I). All of the compounds exhibit unsymmetrical absorption envelopes and most display $\pi^\pi^*$ maxima around 380 nm with extinction coefficients in the range 190–290 l cm$^{-1}$ mol$^{-1}$. These extinction coefficients, which are an order of magnitude higher than for the similar transition in trans azoalkanes and ketones, results from the fact that while the $\pi^\pi^*$ transition is symmetry forbidden in the latter compounds, the transition is allowed in cis azoalkanes with polarization perpendicular to the molecular plane.

The unusually low extinction coefficient for DM, suggestive of an interaction between the methylene groups and the azo chromophore, is particularly noteworthy in view of an opposite effect in ketone 69. This latter compound displays an unusually intense $\pi^\pi^*$ absorption relative to the parent 70. Further evidence for an interaction in DM arises from the uncharacteristic steep rise in absorption at wavelengths shorter than 350 nm. The nature of this absorption is un-
Table 1
Absorption and Emission of DBQ Derivatives^a

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorption</th>
<th>Emission</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda_{\text{max}}^b$</td>
<td>$e_{\text{max}}^c$</td>
</tr>
<tr>
<td>DBQ</td>
<td>379</td>
<td>264</td>
</tr>
<tr>
<td></td>
<td>369(s)</td>
<td>152</td>
</tr>
<tr>
<td>Mono-Me</td>
<td>382</td>
<td>272</td>
</tr>
<tr>
<td>Di-Me</td>
<td>384</td>
<td>254</td>
</tr>
<tr>
<td>Endo-Cp</td>
<td>379</td>
<td>214</td>
</tr>
<tr>
<td></td>
<td>368(s)</td>
<td>114</td>
</tr>
<tr>
<td>CB</td>
<td>385</td>
<td>226</td>
</tr>
<tr>
<td></td>
<td>372(s)</td>
<td>122</td>
</tr>
<tr>
<td>CPCB</td>
<td>383</td>
<td>289</td>
</tr>
<tr>
<td></td>
<td>372(s)</td>
<td>150</td>
</tr>
<tr>
<td>Exo-Cp</td>
<td>378^f</td>
<td>190^e,f</td>
</tr>
<tr>
<td></td>
<td>368(s)</td>
<td>100</td>
</tr>
<tr>
<td>MV</td>
<td>381</td>
<td>238</td>
</tr>
<tr>
<td>DV</td>
<td>382</td>
<td>245</td>
</tr>
<tr>
<td>DM</td>
<td>380</td>
<td>120^e</td>
</tr>
<tr>
<td></td>
<td>371(s)</td>
<td>80</td>
</tr>
<tr>
<td>Di-Cl</td>
<td>366</td>
<td>128</td>
</tr>
<tr>
<td>Di-Br</td>
<td>366</td>
<td>129</td>
</tr>
</tbody>
</table>

a) in benzene unless otherwise noted  
b) in nm  
c) 1 mol\(^{-1}\)  
d) singlet energy, kcal mol\(^{-1}\)  
e) approximate value  
f) in ethyl acetate at -78° C  
g) in hexane at ca. 0° C
The azos containing bridgehead halogens show a hypsochromic (blue) shift of 13 nm in the absorption maximum relative to DBO. This shift is consistent with studies done on α-halogenated cycloalkanones and steroidal ketones in which axial substituents were shown to produce shifts to shorter wavelength in the n,π* transition of about 5 nm relative to unsubstituted model compounds by an inductive effect.74

Interestingly, all compounds lacking bridgehead substituents in Table 1 exhibit fine structure in the form of a shoulder at ca. 370 nm. This can be assigned to the (0→1) transition.11 The separation between the absorption maximum (0→0 transition) and the (0→1) transition is about 800 cm⁻¹. Compounds containing bridgehead substituents show no fine structure. Some of the compounds also contain a slight hint of structure near 340 nm. Since this is separated from the absorption maximum by about 3000 cm⁻¹, it probably corresponds to a C-H stretch.

The fluorescence spectra of these compounds are unstructured. There is no clear correlation of emission maximum with molecular structure although increasing ring strain in the system does seem to "sharpen" the fluorescence spectrum. Fine structure has been observed in the emission of some DBO derivatives.40

2. Nitrogen Quantum Yields

Nitrogen quantum yields for direct irradiation of the DBO derivatives are presented in Table 2. In several cases quantum yields for
the decrease of the azo absorption band ($\phi_{-azo}$) were also determined. Benzene was used as solvent because its poor hydrogen donating ability should prevent photoreduction of the azo linkage and production of light absorbing impurities during the photolysis. These problems have been noted when irradiating certain DBO derivatives in hydrocarbon solvents and ether.\textsuperscript{11,20,27}

Comparison of the $\phi_r$ and $\phi_{-azo}$ data in Table 2 shows that photoreduction is unimportant in benzene for these compounds. The nitrogen quantum yields further show that the addition of strained rings or radical stabilizing substituents into the bicyclo[2.2.2]azoalkane substructure can greatly increase the photochemical reactivity of the system. Addition of one or two vinyl groups (which can stabilize the incipient biradical) $\alpha$ to the azo chromophore, increases $\phi_r$ by almost two orders of magnitude (compare MV and DV with DBO). Methylene groups (DM) cause a similar rise in photoreactivity. Strained rings, too, were found to increase $\phi_r$, the effect being more pronounced with the compound containing the exo cyclopropyl group Exo-Cp ($\phi_r=0.85$) than the exo cyclobutyl group CB ($\phi_r=0.28$). Particularly noteworthy is the fact that the cyclopropyl group only increases photoreactivity in a certain orientation. The two compounds containing the cyclopropyl group in the endo orientation (Endo-Cp and CPCB) exhibit photoreactivity comparable to their counterparts lacking this structural feature.

The similar quantum yields of MV and DV were at first quite puzzling. It was felt that if one vinyl group increased $\phi_r$ to 0.9, a second vinyl group would surely increase $\phi_r$ to 1.0. However, a
Table 2

Quantum Yields for Direct Irradiation of DBO Derivatives

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$\phi_r^b$</th>
<th>$\phi_{\text{azo}}^c$</th>
<th>$\Delta H^+, \text{kcal mol}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DBO</td>
<td>0.013</td>
<td></td>
<td>45.0$^e$</td>
</tr>
<tr>
<td>Di-Me</td>
<td>0.024</td>
<td>0.023</td>
<td>43.7$^e$</td>
</tr>
<tr>
<td>Endo-Cp</td>
<td>0.022</td>
<td>0.022</td>
<td>45.9$^j$</td>
</tr>
<tr>
<td>CB</td>
<td>0.28</td>
<td>0.29</td>
<td>38.6$^f$</td>
</tr>
<tr>
<td>CPCB</td>
<td>0.28</td>
<td>0.26</td>
<td>40.8$^g$</td>
</tr>
<tr>
<td>Exo-Cp</td>
<td>0.85$^d$</td>
<td></td>
<td>21.5$^i$</td>
</tr>
<tr>
<td>MV</td>
<td>0.87</td>
<td></td>
<td>34.2$^k$</td>
</tr>
<tr>
<td>DV</td>
<td>0.86</td>
<td></td>
<td>28.8$^k$</td>
</tr>
<tr>
<td>DM</td>
<td>0.83$^l$</td>
<td></td>
<td>32.6$^h$</td>
</tr>
<tr>
<td>Di-Cl</td>
<td>0.020</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Di-Br</td>
<td>0.022</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) irradiated at 366 nm in benzene at room temperature; azo-tert-butane ($\phi_r=0.46$) was used as actinometer  
b) quantum yield for nitrogen formation  
c) from decrease in the azo absorption band  
d) in ethyl acetate at -78$^o$ C  
e) ref. 10  
f) ref. 46  
g) ref. 51  
h) based on a measured $k=9.7 \times 10^{-5}$ sec$^{-1}$ at 100.2$^o$ C and an assumed $\Delta S^+$ of 10 eu  
i) ref. 76  
j) this work  
k) ref. 44  
l) corrected for incomplete light absorption
second vinyl group had no effect on $\Phi_r$. The extremely feeble fluorescence from both compounds ($\Phi_f<0.01$, see sec. C.3.) suggested that perhaps $\Phi_r$ was not 0.9 for both of them but essentially 1.0 and prompted an investigation of the nitrogen quantum yields using several actinometer systems. Since several of the more common actinometer systems (potassium ferrioxalate and benzophenone-benzhydrol) employ solvents other than benzene, and because it has been shown that the amount of light absorbed by round tubes can differ according to the refractive index of the solvent, the photolysis tubes used in this study were placed within opaque sleeves with a small square window area exposed to the light. This arrangement presumably eliminated the problem. Table 3 sums up the results.

Table 3
Nitrogen Quantum Yields for MV and DV Employing Various Actinometer Systems

<table>
<thead>
<tr>
<th>Compound</th>
<th>Actinometer</th>
<th>$\Phi_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MV</td>
<td>Azo-tert-butane ($\Phi=0.46)$</td>
<td>0.87</td>
</tr>
<tr>
<td></td>
<td>Potassium Ferrioxalate ($\Phi=1.21$)</td>
<td>0.89</td>
</tr>
<tr>
<td></td>
<td>Benzophenone-Benzhydrol ($\Phi=0.68$)</td>
<td>1.0$^e$</td>
</tr>
<tr>
<td>DV</td>
<td>Azo-tert-butane</td>
<td>0.86</td>
</tr>
<tr>
<td></td>
<td>Potassium Ferrioxalate</td>
<td>0.89</td>
</tr>
<tr>
<td></td>
<td>Benzophenone-Benzhydrol</td>
<td>1.0$^e$</td>
</tr>
<tr>
<td></td>
<td>Benzophenone-DBH ($\Phi=0.97$)</td>
<td>0.96</td>
</tr>
</tbody>
</table>

a) irradiated at 366 nm in benzene at room temperature  b) ref. 77
c) ref. 78  d) ref. 79  e) see text  f) ref. 80
Using potassium ferrioxalate, \( \phi_r \) for \text{MV} and \text{DV} did not differ significantly from the values obtained when using azo-tert-butane as actinometer. Benzophenone-benzhydrol yielded quantum yields of 1.0 for both \text{MV} and \text{DV}, but this result was tainted by the build up of an absorbing impurity in this actinometer system.\(^82\) This was shown by the fact that the percent conversion as determined by uv was wavelength dependent. Therefore, a fourth actinometer system was tried. Determination of \( \phi_r \) employing the benzophenone sensitized decomposition of \text{DBH} to measure the light intensity, gave a quantum yield that supported the benzophenone-benzhydrol result.

The reason for the discrepancies among the various actinometer systems is unclear. The actual light output of the lamp, using 2,7-dimethyl-3,6-diazaacyclohepta-1,6-diene perchlorate and Corning glass filters to isolate the 366 nm line,\(^75\) was shown to be essentially monochromatic. This was done by monitoring the light output with a monochromator-photodiode arrangement (see Appendix II). No light from the nearby 335 and 405 nm lines of the mercury lamp was getting through the filters. With the possibility of impurity light ruled out, one is led to the conclusion that these results are indicative of experimental uncertainties in the quantum yield values for the various actinometer systems used here or (a much more likely possibility) reflect the magnitude of systematic error possible when using these secondary actinometer systems.

In summary, the photoreactivity of the \text{DBQ} system has been shown to be very structure dependent. While the quantum yields reported in Table 2 may be subject to a small systematic error, the rel-
ative values values are secure.

3. Fluorescence Quantum Yields and Lifetimes

Since DBO and its derivatives exhibited fluorescence, the quantum yield and lifetime for this process was determined (see Table 4). Several interesting trends are apparent. While the fluorescence quantum yield, \( \Phi_f \), and the fluorescence lifetime, \( \tau_f \), vary considerably with structure, their ratio, \( k_f \), remains virtually constant. This constancy of \( k_f \) has been noted in a recent study of various cyclic azo systems and appears to be general. \(^{40}\) The class of DBO derivatives which have low nitrogen quantum yields have the highest fluorescence quantum yields and the longest singlet lifetimes. Increasing strain in these relatively photoinert compounds is accompanied by decreases in \( \Phi_f \) and \( \tau_f \). Thus in going from Di-Me to DBO to Endo-Cp, \(^{145}\) \( \Phi_f \) decreases in the order 0.53, 0.39, and 0.097, respectively, accompanied by corresponding decreases in \( \tau_f \). The compounds with high nitrogen quantum yields, in contrast, have very low fluorescence quantum yields and extremely short fluorescence lifetimes (\(<2\) nsec). \(^{120}\) The bridgehead halogenated compounds form a third class of compounds with low fluorescence and nitrogen quantum yields and short fluorescence lifetimes. The mechanistic implications of these results will be discussed shortly.

4. Location of the Triplet Energy of 1-Vinyl-DBO

Since DBO does not phosphoresce (nor does any other azo compound for that matter), \(^{83}\) Clark and Steel \(^{11}\) used an indirect method
<table>
<thead>
<tr>
<th>Compound</th>
<th>$\phi_f^b$</th>
<th>$\tau_f^c$, nsec</th>
<th>$k_f$, sec$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DBO</td>
<td>0.39</td>
<td>434</td>
<td>$9.0 \times 10^5$</td>
</tr>
<tr>
<td>Mono-Me</td>
<td>0.44</td>
<td>500</td>
<td>$8.8 \times 10^5$</td>
</tr>
<tr>
<td>Di-Me</td>
<td>0.53</td>
<td>599</td>
<td>$8.8 \times 10^5$</td>
</tr>
<tr>
<td>Endo-Cp</td>
<td>0.097</td>
<td>155</td>
<td>$6.2 \times 10^5$</td>
</tr>
<tr>
<td>CB</td>
<td>0.18</td>
<td>302</td>
<td>$6.0 \times 10^5$</td>
</tr>
<tr>
<td>CPCB</td>
<td>0.051</td>
<td>98</td>
<td>$5.2 \times 10^5$</td>
</tr>
<tr>
<td>Exo-Cp</td>
<td></td>
<td>1.3$^d$</td>
<td></td>
</tr>
<tr>
<td>MV</td>
<td>0.00088</td>
<td>0.56</td>
<td>$1.6 \times 10^6$</td>
</tr>
<tr>
<td>DV</td>
<td>0.0014</td>
<td>0.53</td>
<td>$2.6 \times 10^6$</td>
</tr>
<tr>
<td>DM</td>
<td>0.0044</td>
<td>1.3</td>
<td>$3.4 \times 10^6$</td>
</tr>
<tr>
<td>Di-Cl</td>
<td>0.033</td>
<td>58</td>
<td>$5.7 \times 10^5$</td>
</tr>
<tr>
<td>Di-Br</td>
<td>0.032</td>
<td>60</td>
<td>$5.3 \times 10^5$</td>
</tr>
</tbody>
</table>

---
a) in degassed, purified benzene; $\lambda_{ex} = 337$ nm and $A_{337} = 0.3$; the fluorescence of MV, DV, Exo-Cp, and DM is so weak that some contribution from impurities cannot be ruled out$^{120}$  
b) relative to 9,10-di-phenylanthracene ($\phi_f = 0.96$)$^{85}$  
c) determined by M.A.J. Rodgers, CFKR, Austin, Texas  
d) in degassed toluene at $-78^\circ$ C
for determining the triplet energy ($E_T$) of this compound. The idea is to quench the phosphorescence of a series of triplet energy donors with the compound (quencher) whose triplet energy is unknown (in this case DBO) and to obtain the rate constant ($k_Q$) for this process from

$$3_b^* + Q \xrightarrow{k_Q} 3_Q^* + D$$  (1)

$$1/\tau = 1/\tau_o + k_q[D]$$  (2)

the familiar Stern-Volmer relationship (eq 2). In equation 2, $\tau_o$ is the phosphorescence lifetime of the donor in the absence of quencher, while $\tau$ is the lifetime in the presence of quencher. It is generally accepted that when $E_T$(donor) - $E_T$(acceptor) is 3 kcal mol$^{-1}$ or greater that quenching occurs at the diffusion controlled rate ($k_Q=10^{10}$ M$^{-1}$ sec$^{-1}$), while if this difference is less than this value, the rate decreases.$^{86,87}$ This falloff is usually quite rapid$^{88}$ and enables the triplet energy of the quencher to be readily obtained as long as donors of appropriate triplet energy are found.

Clark and Steel's$^{11}$ results regarding DBO are summarized in Table 5 and demonstrate the utility of the method. The dropoff of

<table>
<thead>
<tr>
<th>Ketone</th>
<th>$E_T$, kcal mol$^{-1}$</th>
<th>$k_Q$, M$^{-1}$ sec$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzophenone</td>
<td>68.5</td>
<td>$6.7 \times 10^9$</td>
</tr>
<tr>
<td>Biacetyl</td>
<td>54.9</td>
<td>$2.0 \times 10^9$</td>
</tr>
<tr>
<td>Benzil</td>
<td>53.7</td>
<td>$2.6 \times 10^8$</td>
</tr>
</tbody>
</table>

a) ref. 11  b) in benzene
k_Q is seen to occur between biacetyl and benzil. On this basis, Clark and Steel\textsuperscript{11} concluded that the triplet energy of DBO was 54.5 ± 1.5 kcal mol\textsuperscript{-1}.

Since the above results indicate that DBO quenches biacetyl phosphorescence at less than the diffusion controlled rate,\textsuperscript{84} it was decided to make use of this fact to determine the triplet energy of MV. If it could be shown that MV quenched biacetyl phosphorescence at the same rate as DBO and that the rate was less than diffusion controlled, the conclusion would be that the triplet energies of these compounds are the same.\textsuperscript{89} Table 6 shows the data obtained. The k_Q's

Table 6
Rate Constants for Quenching of Biacetyl
Phosphorescence by DBO and MV\textsuperscript{a}

<table>
<thead>
<tr>
<th>Compound</th>
<th>k_Q x 10\textsuperscript{-8} M\textsuperscript{-1} sec\textsuperscript{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>DBO</td>
<td>6.7\textsuperscript{b}</td>
</tr>
<tr>
<td></td>
<td>5.1\textsuperscript{b}</td>
</tr>
<tr>
<td>MV</td>
<td>4.4\textsuperscript{b}</td>
</tr>
<tr>
<td></td>
<td>4.3\textsuperscript{b}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} in benzene \textsuperscript{b} preliminary two point result

were obtained from least squares treatment of \(\tau\textsuperscript{-1}\) vs. azo for four points and are plotted in fig. 1. In addition, several preliminary experiments are included in Table 6.

The k_Q's of both DBO and MV are about the same and less than
Fig. 1. Quenching of biacetyl phosphorescence with DBO and MV.
the diffusion controlled rate.\textsuperscript{87} Therefore, $E_T$ for MV should be about 54.5 kcal mol$^{-1}$. Actually, because some decomposition of the extremely photoreactive MV may have occurred during the experiment, only an upper bound can be placed on the triplet energy of this substance.

5. The Solvent Dependent Photochemistry of 1,4-Dimethyl-DBO

Turro, et al.\textsuperscript{29} investigated the photochemistry of Di-Me in various solvents. While quantum yields for azoalkane disappearance ($\phi_{\text{-azo}}$) were obtained, no nitrogen quantum yields were disclosed. Because the mechanism suggested by Turro differed from the one set forth by Clark and Steel\textsuperscript{11} for DBO, we reinvestigated Di-Me (Table 7).

Table 7

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\tau_f$, nsec</th>
<th>$\phi_f$</th>
<th>$\phi_{\text{-azo}}$</th>
<th>$\phi_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetonitrile</td>
<td>780$^a$, 740$^b$</td>
<td>0.7$^{a,b}$</td>
<td>0.15$^a$, 0.019$^c$</td>
<td>0.016$^c$</td>
</tr>
<tr>
<td>Benzene</td>
<td>599$^c$, 660$^a$</td>
<td>0.53$^c$</td>
<td>0.023$^c$</td>
<td>0.024$^c$</td>
</tr>
<tr>
<td>Methanol</td>
<td>14$^a$, 30$^b$</td>
<td>0.01$^a$</td>
<td>0.25$^a$</td>
<td>0.0015$^c$</td>
</tr>
</tbody>
</table>

a) ref. 29  b) ref. 40  c) this work

Note that in changing the solvent from acetonitrile to methanol, a ten fold decrease in $\phi_r$ is obtained along with the decreases in $\phi_f$ and $\tau_f$. Thus although $\phi_{\text{-azo}}$ was reportedly not affected by changes
in solvent, this is clearly not the case for $\Phi_r$. The similarity of the $\Phi_{\text{azo}}$ and $\Phi_r$ values obtained in this work for the photolysis of Di-Me in acetonitrile and benzene indicates that the only reaction occurring in these solvents is simply destruction of the azoalkane into nitrogen and hydrocarbons. In methanol, however, this is apparently not the case as two attempts to remeasure $\Phi_{\text{azo}}$ by decrease in the azo absorption band failed due to the build up of an absorbing impurity. This result suggests that some of the azoalkane reacts without forming nitrogen in this solvent.

6. Investigation of the Products from Photolysis of 1-Vinyl-DBO, 1,4-Divinyl-DBO, and 1,4-Dimethyl-DBO

Generally, irradiation of bicyclo[2.2.2]azoalkanes leads to mixtures of ring closed products (bicyclo[2.2.0]hexanes) and ring opened products (olefins). As shown below, the photolysis of MV and DV could be expected to yield several novel hydrocarbons. In addi-

\[ \text{MV} \xrightarrow{\text{hv}} \text{[Molecule]} \rightarrow \text{[Product]} + \text{[Product]} + \text{[Product]} \]

\[ \text{DV} \xrightarrow{\text{hv}} \text{[Molecule]} \rightarrow \text{[Product]} + \text{[Product]} + \text{[Product]} + \text{[Product]} \]
tion to the "normal" products (71-74), several other products can arise from radical closure at the less substituted site of the allyl radical or from Cope rearrangement. Compounds 77 and 78 have recently been synthesized\textsuperscript{59} and the thermal reactions of 74 are currently under investigation.\textsuperscript{91}

Irradiation of MV (acetone-d\textsubscript{6}, -78\textdegree C, 366 nm) resulted in its efficient destruction. Triene 72 was the only product detected by nmr analysis and it was identified by comparison to authentic material.\textsuperscript{92} It was thought that perhaps 71 was a thermally labile intermediate on the pathway to 72. Eventual synthesis of 71, however, rules out this possibility (see part II of this thesis). Irradiation of DV (acetone-d\textsubscript{6}, room temp., 366 nm) by a post doctoral fellow in this lab likewise yielded only tetraene 74.\textsuperscript{93} Even irradiation at -78\textdegree C followed by low temperature nmr only gave evidence for 74. Utilizing the "ring closure" conditions of Martin and Hekman\textsuperscript{25a} (frozen benzene-d\textsubscript{6}, -20\textdegree C, 366 nm) again produced solely 74. Finally, irradiation of DV at 260 K in an argon matrix by O.L. Chapman and R.A. Hayes\textsuperscript{90} yielded an ir identical to that of authentic 74.

In contrast to the above results and more in keeping with the typical behavior of bicyclo[2.2.2]azoalkanes, photolysis of Di-Me (60\textdegree C, pentane) through pyrex yielded 79 and 80 in the ratio 27:73.\textsuperscript{94}
This result can be compared with Clark and Steel's photolysis of DBO in isooctane in which bicyclo[2.2.0]hexane and 1,5 hexadiene were produced in the ratio 42:58.
D. Photochemistry of DBO Derivatives—Discussion

The data obtained enable an evaluation of the two published mechanisms for photolysis of bicyclo[2.2.2]azoalkanes. Let us look at the results first in terms of the mechanism suggested by Turro, et al.\textsuperscript{29} for Di-Me (see p. 8). The salient feature of this mechanism is that the decomposing state ($S_1^*$) precedes the fluorescing state ($S_1$). Comparison of Tables 2 and 4 reveals that compounds with high $\phi_r$'s exhibit short fluorescence lifetimes while those with low $\phi_r$'s have long fluorescence lifetimes (for the moment let us not consider the bridgehead halogenated compounds). These data indicate that the process leading to nitrogen formation must be contributing greatly to deactivation of $S_1$ in the photoreactive compounds. The Turro mechanism, however, predicts that although increasing $\phi_r$ will lower $\phi_f$, it will not shorten $\tau_f$ and hence it cannot be used to explain the photochemistry of these compounds.

Looking more closely into the photochemistry of Di-Me, upon which the Turro mechanism was based, we found that $\phi_r$ decreased from 0.016 in acetonitrile to 0.0015 in methanol. An alternative interpretation of the solvent dependent photochemistry of Di-Me, consistent with the data in Table 7, is shown below. In this mechanism, metha-
nol decreases $\phi_f$ and $\phi_r$ by providing an extra deactivation pathway for $S_1$ through the formation of a methanol-excited state azo complex. This complex then reverts to ground state azo or yields a nitrogen containing product, presumably with the reduced form of the azo linkage 81. Note that similar species have been postulated in the photochemistry of DBO in isoctane 11 and have been isolated in the photolysis of Di-Cl in hexane 27.

A further argument against the Turro mechanism is the following. If the vibrationally excited state species ($S_1'$) is important in solution, it must be so in the gas phase. Steel's 11 results concerning the gas phase photolysis of DBO at low pressure revealed that $\phi_f + \phi_r = 1$ and that all the photodecomposition arises from a state (presumably $T_1$) derived from $S_1$ which is quenchable with added inert gas. Since a vibrationally excited state is unimportant in the gas phase photolysis of DBO, it is unlikely that it will be important in the solution phase photochemistry of Di-Me.

Let us now consider Clark and Steel's 11 mechanism for DBO to see if it can be extended to DBO derivatives as well. The mechanism is shown below. This mechanism offers promise at explaining the effect

\[
\begin{align*}
\text{DBO} & \xrightarrow{h\nu} S_1 & k_{\text{isc}} & T_1 & \xrightarrow{h\nu} \text{DBO} \\
& \quad \downarrow k_d & \downarrow & \quad \downarrow k_{\text{r}} & \quad \downarrow \text{DBO} \\
& \quad N_2 & N_2 & \text{DBO} & \text{N}_2
\end{align*}
\]
of structure on $\Phi_r$ and $\tau_f$ because there exists two pathways for nitrogen formation and both of these can compete directly for deactivation of $S_1$. If we designate $k_d$ as the process of internal conversion from $S_1 \rightarrow S_0$ and define $F$ as the fraction of triplet molecules yielding nitrogen, equation 3 for $\Phi_r$ can be derived. Increases in $\Phi_r$ as a result of structural changes can be attributed to either increases in $k_r$ or $k_{isc}F$.

$$\Phi_r = \frac{k_r}{(k_r+k_f+k_{isc}+k_d)} + \frac{k_{isc}F}{(k_r+k_f+k_{isc}+k_d)} \quad (3)$$

It is unlikely that the increases in $\Phi_r$ for the DBO derivatives are caused by increases in $k_{isc}F$. MV and DBO both have similar triplet energies (sec. C.4.) and singlet energies (Table 1). Since the rate of intersystem crossing generally depends upon the $S_1-T_1$ energy gap, it seems unreasonable to suppose that $k_{isc}$ is increased significantly in MV relative to DBO. The fraction of triplets going to nitrogen, $F$, actually is greater in MV ($\Phi_r$, triplet = 0.75) than DBO ($\Phi_r$, triplet = 0.014) but if the high direct quantum yield for MV was strictly the result of more triplet decomposition, no decrease in $\tau_f$ would be expected in contrast to the results. It is therefore quite reasonable to suppose that the increases in $\Phi_r$ with structure are the result of increases in the rate constant, $k_r$, for decomposition from $S_1$.

One other possibility exists for explaining the data, namely, that increases in $\Phi_r$ for some of the DBO derivatives are caused by an increased rate of internal conversion, $k_d$, to a decomposing vibration-
ally excited ground state. Note that these species were deemed important by Berson and Olin\textsuperscript{30} in some tetrahydropyridazine derivatives. By comparing MV to DBO once again, however, there is no reason to expect a vinyl group to enhance $k_d$ to a significant extent. Addition of a vinyl group to benzene, for example, does not enhance $k_d$.\textsuperscript{97}

Hence it is evident that structural changes can increase $\Phi_r$ by increasing $k_r$ and that Clark and Steel's mechanism accounts for the data. In order to explain why $\Phi_r$ is increased with structural changes, a look at a calculated potential energy diagram for photochemical nitrogen extrusion from cis diimide is particularly enlightening.\textsuperscript{98} Fig. 2 shows the diagram for one bond homolysis of this species.

Fig. 2. Potential energy curves for one bond photocleavage of cis-diimide. The dashed lines show the postulated effect of greater thermal lability.
While the published diagram for two bond homolysis shares many of the same features, the one bond diagram is shown because 1) the activation barriers are half that of the two bond and 2) product studies of MV and DV support the one bond homolysis scheme.

The most important feature of the potential energy curves is that they show an activation barrier to nitrogen loss. Upon irradiation into the \( n, \pi^* \) band of cis diimide, a barrier of 0.95 ev (22 kcal mol\(^{-1}\)) must be surmounted in order to achieve crossing point A leading to the dissociative surface to product. In view of this activation barrier, it might be expected that 1) thermally labile azoalkanes, i.e. those possessing lower activation barriers would exhibit higher \( \Phi_r \)'s than their less labile counterparts and 2) raising the temperature at which the photolysis is performed will increase \( \Phi_r \). The former possibility is observed experimentally (Table 2), while the latter is dealt with in section F.

Table 2 reveals that a correlation between thermal lability (\( \Delta H^\dagger \)) and photochemical reactivity does indeed exist. The compounds (DBO, Di-Me, Endo-Cp) which are very stable to thermolysis (\( \Delta H^\dagger > 41 \) kcal mol\(^{-1}\)) are those similarly stable to photolysis. As \( \Delta H^\dagger \) decreases below 41 kcal mol\(^{-1}\), photochemical reactivity starts to increase until for the relatively thermally labile compounds (\( \Delta H^\dagger < 35 \) kcal mol\(^{-1}\)), the quantum yields have increased to their maximum value of ca. 0.9. In terms of the potential energy diagram (Fig. 2), the effect of radical stabilizing substituents is to lower the barrier to crossing onto the dissociative surface so that this crossing now occurs at point B. This decrease in the energy of the barrier is re-
flected in an increase in $k_r$ and $\phi_r$. To take into account the above correlation, it is postulated that Clark and Steel's mechanism (p. 43) should be modified by including a thermal barrier for nitrogen loss from $S_1$.

Although the above description rationalizes the results very nicely, other possible relationships between structure and photoreactivity should be examined. Ring strain does not govern photoreactivity. If this were so, then surely CPCB ($\phi_r=0.28$) with the extra strained ring, would be as photoreactive as Exo-Cp ($\phi_r=0.85$). Endo-Cp ($\phi_r=0.022$), for that matter, which differs only in the orientation of the ring, would be expected to exhibit the high photoreactivity of Exo-Cp. The greatly differing photoreactivity of these latter two compounds further shows that reaction exothermicity ($\Delta H_r$) does not determine the photochemical reactivity of the DBQ system. Irradiation of both these compounds should produce the same diradical and therefore $\Delta H_r$ should be the same for both of them.99

\[ \text{Exo-Cp} \quad \xrightarrow{\text{hv}} \quad \text{N}_2 \quad \text{Endo-Cp} \]

It is of interest that the fact that some ring closed product was produced in the photolysis of Exo-Cp in contrast to the thermolysis at 25°C where only 1,4-cycloheptadiene formed, led Tanida and co-workers20 to conclude that participation of the cyclopropyl group occurred thermally but not photochemically. However, the high photo-
reactivity of this compound requires the participation of the cyclo-
propyl group in the transition state for photolysis.

As previously discussed by Pacquette and Epstein\textsuperscript{24} and Boyd, et al.,\textsuperscript{100} exo fused rings permit good overlap of the bent bond with the developing radical center while the endo orientation precludes overlap (below). In fact, in this latter case the developing radi-

cal center and the bent bond are orthogonal. CPCB is particularly il-
lustrative of this point. Even though the degree of bent bonding of the cyclopropane ring is three times that of the cyclobutane ring,\textsuperscript{101} only the cyclobutane ring is in the proper orientation to aid pho-
tolysis and the increased quantum yield of this compound relative to DBO is governed solely by this moiety. In conclusion, electronic fac-
tors (i.e. orbital overlap and radical stability) and not ring strain or reaction exothermicity determine the photoreactivity of DBO deri-

vatives.

Photophysically, however, strain does exert an influence, as previously pointed out (sec. C.3.). Addition of a cyclopropane ring endo to the azo moiety was shown to decrease \( \Phi_f \) and \( \tau_f \) while leaving \( \Phi_r \) essentially unchanged (compare CPCB with CB; Endo-Cp with DBO, Table 3). Since minor variations of \( k_r \) and \( k_f \) cannot account for the
observed decrease, it follows that either \( k_d \) or \( k_{isc} \) is increased by strain. Internal conversion \( (k_d) \) generally decreases with increasing rigidity of a system and since this would create an effect opposite to that observed, it appears likely that \( k_{isc} \) increases in the more strained compounds. Table 3 further reveals that bridgehead methyl substituents increase \( \Phi_f \) and \( \tau_f \) (compare **DBO**, **Mono-\text{Me}**, and **Di-\text{Me}**). This effect is analogous to that encountered in cyclic and acyclic ketones where a methyl substitution increases \( \tau_f \).\(^{114}\) The same explanation advanced for the ketones appears applicable here, namely, that bridgehead methyl substitution decreases \( k_{isc} \). Thus in the absence of significant changes in \( k_r \) or \( k_f \), \( k_{isc} \) will be the major factor determining \( \Phi_f \) and \( \tau_f \) and small changes in this rate constant will affect the photophysical properties of these **DBO** derivatives.

Not much attention has been focused up to this point on the bridgehead halogenated compounds **Di-\text{Cl}** and **Di-\text{Br}**. The above explanation holds for these compounds which exhibit relatively small \( \Phi_f \)'s and \( \tau_f \)'s. The increase in \( k_{isc} \) in this case can be rationalized as enhancement of the \( S_1-T_1 \) crossing as the result of spin-orbital coupling.\(^{102}\) What is puzzling, though, is that the photophysical properties of **Di-\text{Br}** are virtually identical with **Di-\text{Cl}**. If spin-orbital coupling is the reason behind the increase in \( k_{isc} \), one would expect **Di-\text{Br}** to have an even larger \( k_{isc} \) and a correspondingly lower \( \Phi_f \) and \( \tau_f \) than **Di-\text{Cl}**, in contrast to experimental fact. Hence another explanation may be advanced for the increase in \( k_{isc} \) in these compounds, namely that the halogens decrease the \( S_1-T_1 \) energy splitting and enhance \( k_{isc} \) in this manner and not by partially overcom-
ing the forbiddenness of the transition. In order to test this latter possibility, the energy of $T_1$ for these two compounds could be determined in a manner analogous to that of sec. C.4.

In summation of the above discussion, rate constants for the various processes occurring in DBO and its derivatives are collected in Table 8. Note that in terms of Clark and Steel's mechanism (p. 43), the $k_r$'s are actually upper limits as some decomposition may occur from the triplet manifold, especially in the less reactive compounds. In the more photoreactive compounds, $k_r$ is much greater than $k_{isc}$ so that little decomposition can occur via the triplet pathway. Similarly, the rate constant $k_{isc} = (1 - \phi_r - \phi_f) / \tau_f$ should be treated as a lower limit for the less reactive compounds. Note that from the data in Table 8, it seems that $k_{isc}$'s for the more reactive compounds are much greater than their less reactive counterparts. From the above formula, it can be seen that $k_{isc}$ is strongly dependent upon the value for $\phi_r$ when $\phi_r$ is high. In light of the discussion of possible systematic errors with $\phi_r$ values (sec. C.2.) and the biacetyl quenching study (sec. C.4.), it appears that the actual values of $k_{isc}$ for the photoreactive azos could be lower than the values shown in Table 8.

The lack of ring closed products from photolysis of MW and DV and the similar $k_r$'s for both of these compounds (Table 8) yield important information concerning intermediates on the pathway to products. If cleavage occurred by a two bond mechanism, one would expect that introduction of a second vinyl group onto the DBO skeleton would increase $k_r$ by the same amount as the first, a trend not observed. This result is consistent with breakage of one bond to form
the diazenyl radical in the rate determining step (82, p. 52). This radical has recently been proposed as an intermediate in the triplet sensitized decomposition of acyclic azoalkanes. Product studies of MV and DV are also consistent with breakage of one bond.

## Table 8

Rate Constants for Photochemical Processes in DBO Derivatives

<table>
<thead>
<tr>
<th>Compound</th>
<th>$k_r^b$</th>
<th>$k_f^c$</th>
<th>$k_{isc}^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DBO</td>
<td>$3.0 \times 10^4$</td>
<td>$9.0 \times 10^5$</td>
<td>$2.3 \times 10^6$</td>
</tr>
<tr>
<td>Mono-Me</td>
<td></td>
<td>$8.8 \times 10^5$</td>
<td></td>
</tr>
<tr>
<td>Di-Me</td>
<td>$4.8 \times 10^4$</td>
<td>$8.8 \times 10^5$</td>
<td>$1.6 \times 10^6$</td>
</tr>
<tr>
<td>Endo-Cp</td>
<td>$1.4 \times 10^5$</td>
<td>$6.2 \times 10^5$</td>
<td>$6.3 \times 10^6$</td>
</tr>
<tr>
<td>CB</td>
<td>$9.3 \times 10^5$</td>
<td>$6.0 \times 10^5$</td>
<td>$2.4 \times 10^6$</td>
</tr>
<tr>
<td>CPCB</td>
<td>$2.8 \times 10^6$</td>
<td>$5.2 \times 10^5$</td>
<td>$7.3 \times 10^6$</td>
</tr>
<tr>
<td>Exo-Cp</td>
<td>$6.5 \times 10^8$</td>
<td></td>
<td>$1.1 \times 10^8$</td>
</tr>
<tr>
<td>MV</td>
<td>$1.7 \times 10^9$</td>
<td>$1.6 \times 10^6$</td>
<td>$1.2 \times 10^8$</td>
</tr>
<tr>
<td>DV</td>
<td>$1.7 \times 10^9$</td>
<td>$2.5 \times 10^6$</td>
<td>$1.3 \times 10^8$</td>
</tr>
<tr>
<td>DM</td>
<td>$6.4 \times 10^8$</td>
<td>$3.4 \times 10^6$</td>
<td>$1.3 \times 10^8$</td>
</tr>
<tr>
<td>Di-Cl</td>
<td>$3.4 \times 10^5$</td>
<td>$5.7 \times 10^5$</td>
<td>$1.7 \times 10^7$</td>
</tr>
<tr>
<td>Di-Br</td>
<td>$3.7 \times 10^5$</td>
<td>$5.3 \times 10^5$</td>
<td>$1.6 \times 10^7$</td>
</tr>
</tbody>
</table>

a) from data in Tables 2 and 4  
b) calculated from $k_r = \phi_r / \tau_f$  
c) calculated from $k_{isc} = (1 - \phi_r - \phi_f) / \tau_f$  
d) these values are probably too high; see text
Stabilization of diyl 83 with vinyl substituents is not expected to affect the ratio of ring closure to ring opening, especially in view of the fact that this ratio is not affected by radical delocalization in the Norrish Type II photocleavage of ketones and monocyclic azoalkanes. The scheme below may rationalize the results.

\[ \text{R=H, CHCH}_2 \]

A vinyl group can be seen as stabilizing the diazenyl radical 82b, enabling it to assume an energy minimum on the pathway to product. This species then collapses directly to the most stable product. Since the diradical corresponding to 83 is not formed from MV, the ring closure typical of these species is not observed. In the case of DBQ, it appears that either diyl 82a behaves differently than 82b or that it does not lie on the pathway to products.

In order to substantiate the scheme above, an attempt should be made to observe the diazenyl radical from MV or DV. While no attempt has been made to do so, previous studies indicate that the lifetime of this species would be extremely short. The evidence for a diazenyl radical in the photochemistry of MV and DV is thus circumstantial; supported by product studies, fluorescence lifetimes, and theoretical calculations.
E. Photochemistry of Tetrahydropyridazine derivatives—Results and Discussion

Consistent with the results on DBO derivatives, it has been found that radical stabilizing substituents and strained rings can increase the photoreactivity of six membered monocyclic azoalkanes as well. Table 9 presents the results obtained in this series.

Table 9
Quantum Yields for Direct Irradiation of Tetrahydropyridazine Derivatives

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Phi_r$, solvent, temp.</th>
<th>$\Delta H^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Structure 1" /></td>
<td>6</td>
<td>0.0085, n-BuOAc, 30°C</td>
</tr>
<tr>
<td><img src="image2.png" alt="Structure 2" /></td>
<td>50</td>
<td>0.008, EtOAc, -78°C</td>
</tr>
<tr>
<td><img src="image3.png" alt="Structure 3" /></td>
<td>61</td>
<td>0.17, EtOAc, -78°C</td>
</tr>
<tr>
<td><img src="image4.png" alt="Structure 4" /></td>
<td>62</td>
<td>0.18, EtOAc, -78°C</td>
</tr>
</tbody>
</table>

a) at 366 nm  
b) average of values in ref. 10  
c) calculated from the data for 6, an assumed $\Delta S^\neq=11.3$ eu, and correction for lack of four methyl groups (cf. ref. 10)  
d) calculated from rate data for the 3,6-dimethyl analogue (ref. 30), an assumed $\Delta S^\neq=7$ eu, and methyl group correction (ref. 10)  
e) ref. 106
Photolyses of 50-62 were conducted in a Cary 17 sample compartment using a specially designed low temperature apparatus which allowed progress of the reaction to be monitored by uv. It should be noted that while phototautomerism is possible in 60 and 61, measurement of photoreactivity by nitrogen evolution and not the decrease in the azo absorption band as done in a previous study,68 eliminates any contribution from this possible side reaction to the results in Table 9.

Table 9 shows that strained rings and radical stabilizing substituents can enhance \( \Phi_r \) by a factor of 20. Unfortunately, due to the lack of fluorescence from these azoalkanes, we cannot look closely at the photophysical pathways leading to deactivation of \( S_1 \). Loss of nitrogen via a mechanism involving internal conversion to a vibrationally excited ground state followed by decomposition of this species, as has been proposed by Berson and Olin30 for derivatives of 61, cannot therefore be ruled out. Additionally, while the quantum yields in Table 9 correlate with reaction exothermicity,68 a correlation also exists between thermal reactivity (\( \Delta H^+ \)) and photochemical reactivity. Since this latter correlation obtained with the DBO derivatives, it seems most reasonable to interpret the effect of structure on these monocyclic azoalkanes in the same terms, namely, that radical stabilizing substituents lower an activation barrier to nitrogen loss thereby increasing \( k_r \) and \( \Phi_r \).

It is noteworthy that the decreases in \( \Delta H^+ \) which render compounds 61 and 62 unstable at room temperature cause \( \Phi_r \) to increase only to 0.2. This is in contrast to the DBO derivatives in which similar structural changes produced \( \Phi_r \)'s approaching 1. It is apparent that
due to the greater flexibility of the six membered monocyclic azos, radiationless decay competes effectively with $k_r$ even when thermal lability is greatly increased. An additional method of energy wastage which may be possible in these compounds is twisting about the azo linkage. This twisting may occur to the extent that a trans isomer (6′-t) is formed photochemically which then thermally reverts back to cis. In support of this idea, photochemical cis-trans isomerization is known in seven $^{107}$ and eight $^{108}$ membered azoalkanes. If this process occurs in 6, it should be possible to detect 6′-t by matrix ir. An attempt to do so, however, was unsuccessful.$^{90}$
F. The Effect of Temperature on Azoalkane Quantum Yields

This study was spurred by the discovery of Turro and coworkers that when solutions of certain azoalkanes were heated, fluorescence quantum yields decreased. For example, upon examining the temperature dependence of \( \Phi_f \) of 67, the following data were obtained (Fig. 3, lower points). While these data established that some process was competing with fluorescence, it did not establish its identity. If this process could be shown to be nitrogen loss, we would have a method of increasing \( \Phi_r \) without structural changes; we therefore undertook a study of the effect of temperature on the \( \Phi_r \) of this compound. These results (Fig. 3, top set of points) clearly show that the process competing with fluorescence is that leading to nitrogen loss. While a qualitative appreciation for the effect of temperature on \( \Phi_r \) and \( \Phi_f \) is gained from Fig. 3, the data can be mathematically treated to afford a more quantitative picture using the following model (Scheme 5).
Scheme 5.
A Model for the Temperature Dependence of
Azoalkane Quantum Yields

\[
\begin{align*}
&\text{Azo} \xrightarrow{h\nu} S_1 \\
&S_1 \xrightarrow{k_f} \text{Azo} + h\nu_f \\
&S_1 \xrightarrow{k_d} \text{Azo} + \text{heat} \\
&S_1 \xrightarrow{k_r} N_2 + \text{product(s)} \\
\text{Assume } k_r = A e^{-E_a/RT}
\end{align*}
\]

In Scheme 5, \( k_d \) may also include \( k_{isc} \). In addition to the assumption that \( k_r \) is temperature dependent and can be treated by the Arrhenius equation, the further assumptions are made that \( k_f \) and \( k_d \) are temperature independent. Using the above model, the following series of expressions are readily obtained (eqs 4-6). From eq 6, it is seen

\[
\Phi_r = \frac{k_r}{(k_r + k_f + k_d)}
\]

\[
1/\Phi_r - 1 = \frac{(k_f + k_d)}{k_r} = A/(k_f + k_d) \times e^{E_a/RT}
\]

\[
\ln[1/\Phi_r - 1] = E_a/RT + \ln[(k_f + k_d)/A]
\]

that a plot of \( \ln[1/\Phi_r - 1] \) vs. \( 1/T \) should yield a straight line of slope \( E_a/R \) and intercept of \( \ln[(k_f + k_d)/A] \) if the above assumptions are correct.

Since a quantitative comparison of some temperature dependent \( \Phi_r \) data will be made with some corresponding \( \Phi_f \) data, a derivation of
the latter method of obtaining \( E_a \)'s is warranted. The treatment is outlined below. Utilizing eq 9, a plot of \( \ln[1/\phi_f - 1 - k_d/k_f] \) vs.

\[
\phi_f = k_f/(k_r + k_f + k_d) \tag{7}
\]

\[
1/\phi_f - 1 - k_d/k_f = k_r/k_f = (A/k_f) e^{-E_a/RT} \tag{8}
\]

\[\ln[1/\phi_f - 1 - k_d/k_f] = \ln[A/k_f] - E_a/RT \tag{9}\]

\(1/T\) should yield a line of slope \(-E_a/R\). This will not always be true, however and this equation should be thought of in terms of three limiting cases.

Case 1. \( k_r \gg k_d + k_f \)

Here, \( k_r \) dominates the denominator of eq 7 and eq 9 can be simplified to give eq 10. A plot of \( \ln[1/\phi_f] \) vs. \( 1/T \) yields a line of

\[\ln[1/\phi_f] = (A/k_f) e^{-E_a/RT} \tag{10}\]

slope \(-E_a/R\). Note that no knowledge of \( k_d/k_f \), a quantity that is often unknown, is needed in this case. This case obtains for compounds with high \( \phi_r \)'s.

Case 2. \( k_r \ll k_d + k_f \)

In the denominator of eq 7, \( k_r \) is an unimportant contributor, and therefore changes in this quantity will have very little effect on \( \phi_f \). Even if \( k_r \) is changing rapidly with temperature, it will not affect \( \phi_f \) and thus \( E_a \) will be apparently zero. This is the case for azo compounds with low \( \phi_r \)'s.

Case 3. \( k_r = k_d + k_f \)

In this case, eq 9 must be used in its entirety. \( E_a \)'s can be
obtained by treating the quantity \((-1-k_d/k_f)\) as a factor whose value is varied until the best line is obtained. Compound \(67\), as we shall see, falls into this category.

In summation, while temperature dependent \(\phi_r\)'s yield \(E_a\)'s directly, temperature dependent behavior of \(\phi_f\) should be thought of in terms of three limiting cases. Before interpreting \(E_a\)'s from \(\phi_f\)'s one should identify which case obtains.

In Table 10, the effect of temperature on \(\phi_r\) for the 1-pyrazoline \(5, 67\), and \(68\) is shown; Table 14 gives activation parameters calculated from eq 6. Table 10 shows that in cases where the nitrogen quantum yield is less than unity, increasing the temperature at which the photolysis is performed is an effective means for enhancing photoreactivity. The data are plotted in Fig. 4 and it can be seen that in all cases reasonable straight lines are obtained, in support of the model and the assumptions of the temperature independence of \(k_f\) and \(k_d\).

Note that while \(67\) exhibits very temperature dependent photo-reactivity, \(5\) is temperature independent. Addition of the isopropylidine moiety thus creates a barrier to nitrogen loss (Table 13). In terms of the previous discussion on bicyclic and monocyclic six membered azoalkanes, it would not be expected that the radical stabilizing substituent would increase this barrier. This group, though, also stabilizes the molecule to thermal nitrogen loss. Engel and Shen\(^70\) have shown that \(k_{rel} (200^\circ C) 67:5 = 1:78\). Thus factors which stabilize this compound thermally stabilize it photochemically. The reason for this stabilization is unclear but as
Table 10

The Effect of Temperature on $\phi_r$ for Several 1-Pyrazolines\textsuperscript{a}

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>Temp. ($^\circ$C), $\phi_r$</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Run 1</td>
<td>Run 2</td>
<td>Run 3</td>
<td></td>
</tr>
<tr>
<td>67</td>
<td>CH$_3$CN</td>
<td>5.0</td>
<td>0.30</td>
<td>5.0</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td></td>
<td>31.7</td>
<td>0.66</td>
<td>31.7</td>
<td>0.68</td>
</tr>
<tr>
<td></td>
<td></td>
<td>52.5</td>
<td>0.89</td>
<td>52.5</td>
<td>0.89</td>
</tr>
<tr>
<td>67</td>
<td>Benzene</td>
<td>6.5</td>
<td>0.41</td>
<td>6.4</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>29.7</td>
<td>0.61</td>
<td>30.0</td>
<td>0.67</td>
</tr>
<tr>
<td></td>
<td></td>
<td>59.9</td>
<td>0.78</td>
<td>59.8</td>
<td>0.78</td>
</tr>
<tr>
<td>5</td>
<td>Benzene</td>
<td>6.5</td>
<td>0.98</td>
<td>6.5</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30.0</td>
<td>1.0</td>
<td>30.0</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>59.8</td>
<td>0.99</td>
<td>59.8</td>
<td>0.99</td>
</tr>
<tr>
<td>68</td>
<td>Benzene</td>
<td>29.7</td>
<td>0.53</td>
<td>30.0</td>
<td>0.57</td>
</tr>
<tr>
<td></td>
<td></td>
<td>59.9</td>
<td>0.67</td>
<td>59.8</td>
<td>0.63</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60.1</td>
<td>0.63</td>
<td>60.1</td>
<td>0.63</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Irradiation at 313 nm using DBH ($\phi_r = 1.0$)\textsuperscript{12} as actinometer
Fig. 4. Plots of Temperature Dependent Quantum Yield Data for Several l-Pyrazolines According to Equation 6 or 9.
pointed out by Engel and Shen,\textsuperscript{70} a required motion for extrusion of nitrogen in the transition state of 67 could be restricted due to a steric interaction of the \(\alpha\) methyls with the isopropylidene group. Alternatively, addition of the isopropylidene moiety may stabilize the ground state of 67 relative to 5. This latter possibility is currently under investigation in this laboratory.

Compound 67 offers the chance to compare \(E_a\)'s deduced from both nitrogen and fluorescence quantum yields. The fluorescence data are shown below (Table 11). Turro, et al.\textsuperscript{38} reported the \(E_a\) of this com-

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>(\Phi_f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-6.1</td>
<td>0.301</td>
</tr>
<tr>
<td>25.4</td>
<td>0.153</td>
</tr>
<tr>
<td>44.9</td>
<td>0.080</td>
</tr>
<tr>
<td>60.2</td>
<td>0.052</td>
</tr>
</tbody>
</table>

a) in acetonitrile, read from a graph in ref. 38

ound as 6.5 kcal mol\(^{-1}\), treating it as if the factor \(k_d/k_f\) were negligible for this compound. This is not the case, though (see below). Hence we used a computer program to determine the value of \((1 + k_d/k_f)\) which gave the best straight line with eq 9. This constant was determined to be 2.50 and yielded an \(E_a = 8.1\) kcal mol\(^{-1}\) and an A factor of \(2.4 \times 10^{12}\), in reasonable agreement with the values obtained from nitrogen quantum yields (\(E_a = 10.0\) kcal mol\(^{-1}\), \(A = 5.9 \times 10^{13}\), Table 14).
The fluorescence activation parameters are actually tied strongly to the value of the constant used in eq 9. \( E_a \) increases to 8.6 kcal mol\(^{-1} \) using a value of 2.64 for this constant, a value that is obtained from known data for \( {67}^{40} \). In fact, increasing the value of the constant to 2.92 yields \( E_a = 10.0 \) kcal mol\(^{-1} \) and an \( A \) factor of \( 4.5 \times 10^{13} \), in excellent agreement with the values obtained from the nitrogen quantum yields. It is therefore concluded that while temperature dependent \( \phi_f \)'s can yield activation parameters for photochemical nitrogen loss, determination of these parameters from \( \phi_r \)'s is perhaps the preferred method since it avoids the problem of subtracting factors.

Looking further into the temperature dependent photochemistry of \( {67} \), we determined the effect of temperature on its fluorescence lifetime in benzene. The data obtained (Table 12) can be fitted to eq 11. Once again, a computer program was written to determine the

\[
\ln \left[ \frac{1}{\tau_f} - (k_f + k_d) \right] = -\frac{E_a}{RT} + \ln A \quad (11)
\]

value of the constant (in this case, \( k_d + k_f \)) which yielded the best straight line. The constant was determined to be \( 2.01 \times 10^6 \) and yielded an \( E_a = 8.0 \) kcal mol\(^{-1} \) and an \( A \) factor of \( 5.4 \times 10^{12} \). These values can be compared with the corresponding values of 6.1 and \( 1.6 \times 10^{11} \) obtained from the \( \phi_r \) data (Table 14). The \( \tau_f \) data can be criticized on the same basis as the \( \phi_f \) data above.

Table 13 shows the effect of temperature on \( \phi_r \)'s of several bicyclic azoalkanes and a monocyclic six membered ring compound (6). Note that, with the exception of \( \text{CB}_{10} \), photochemical activation parameters cannot be obtained by the fluorescence method. Compound 6 does not
Table 12
The Effect of Temperature on $\tau_F$ of 67$^a$

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>$\tau_F$, nsec</th>
<th>$\tau_F$, nsec</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.3</td>
<td>207.9</td>
<td>206.8</td>
</tr>
<tr>
<td>12.9</td>
<td>156.7</td>
<td>154.7</td>
</tr>
<tr>
<td>16.7</td>
<td>148.0</td>
<td>145.3</td>
</tr>
<tr>
<td>22.9</td>
<td>122.9</td>
<td>110.5</td>
</tr>
<tr>
<td>32.0</td>
<td>85.6</td>
<td>81.6</td>
</tr>
<tr>
<td>40.0</td>
<td>65.9</td>
<td>65.5</td>
</tr>
<tr>
<td>51.7</td>
<td>40.1</td>
<td>38.6</td>
</tr>
</tbody>
</table>

a) in nitrogen purged benzene solution; determined at CFKR, Austin, Texas

Table 13
The Effect of Temperature on $\phi_r$ for Several Cyclic and Bicyclic Azoalkanes$^a$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>Temp (°C), $\phi_r$</th>
<th>Temp (°C), $\phi_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DBO</td>
<td>Benzene</td>
<td>6.2  0.0054  0.0056</td>
<td>29.8  0.016  0.017</td>
</tr>
<tr>
<td></td>
<td></td>
<td>47.9  0.040  0.041</td>
<td></td>
</tr>
<tr>
<td>Di-Me</td>
<td>Benzene</td>
<td>6.2  0.0093  0.0092</td>
<td>29.8  0.034  0.035</td>
</tr>
<tr>
<td></td>
<td></td>
<td>47.9  0.093</td>
<td></td>
</tr>
<tr>
<td>Di-Me</td>
<td>CH$_3$CN</td>
<td>7.0  0.0055  0.0055</td>
<td>44.6  0.024  0.025</td>
</tr>
<tr>
<td></td>
<td></td>
<td>67.0  0.066  0.066</td>
<td></td>
</tr>
<tr>
<td>CB</td>
<td>Benzene</td>
<td>7.0  0.15  0.15</td>
<td>29.3  0.32  0.31</td>
</tr>
<tr>
<td></td>
<td></td>
<td>49.3  0.515  0.525</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>n-BuOAc</td>
<td>30.7  0.0086</td>
<td>110  0.017$^b$</td>
</tr>
</tbody>
</table>

a) irradiation at 366 nm b) corrected for a minor amount of thermolysis
fluoresce and DBO and Di-Me correspond to case 2 \((k_r << k_f + k_d)\) and hence yield apparent \(E_a\)'s of zero by the fluorescence method.\textsuperscript{38} The data in Table 13 are plotted using eq. 6 in Fig. 5; activation parameters are given in Table 14.

Compounds Di-Me and DBO offer the most rigorous test yet for the model proposed to explain the temperature effects in azo compounds (Scheme 1). Since \(k_r\) is much smaller than \(k_f\) or \(k_d\) in these bicyclics, even a minor temperature dependence of \(k_f\) or \(k_d\) would be reflected in a non-linear behavior in the Arrhenius plots. This is not observed.

\(E_a\)'s are higher in the case of Di-Me and DBO than in CB (Table 14) in keeping with the previous suggestion that suitable substituents can increase \(\Phi_r\) in these compounds by lowering the barrier to nitrogen loss. MV, which has a higher room temperature \(\Phi_r\) than any of the compounds in Table 13, would be expected to have an even lower barrier. In fact, all data obtained to date suggests that neither this compound nor DV encounter any barrier to nitrogen loss. The quantum yield of MV was invariant upon heating from room temperature to ca. 45\(^\circ\)C in benzene solution. Furthermore, \(\Phi_r\) in hexane was unchanged upon cooling from room temperature to -78\(^\circ\)C. Additional evidence for the lack of a barrier was obtained from measurements of the fluorescence lifetimes of MV and DV at different temperatures in toluene solution. For MV, \(\tau_f = 2.4\) nsec at room temperature and 3.6 nsec at -78\(^\circ\)C. For DV, these quantities were 2.6 and 2.7 nsec, respectively. Although the lifetimes are about five times the benzene values, their near constancy with temperature further imply that MV and DV encounter
Fig. 5. Plots of Temperature Dependent Nitrogen Quantum Yield Data for Several Bicyclic Azoalkanes According to Equation 6.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>$E^b_a$</th>
<th>$\ln[(k_f+k_d)/A]$</th>
<th>$\tau_f^c$</th>
<th>$\phi_r^d$</th>
<th>$k_f + k_d^e$</th>
<th>$A$, sec$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>67</td>
<td>CH$_3$CN</td>
<td>10.0 ± 0.6</td>
<td>-17.3 ± 1.0</td>
<td>225</td>
<td>0.59</td>
<td>$1.8 \times 10^6$</td>
<td>$5.9 \times 10^{13}$</td>
</tr>
<tr>
<td>67</td>
<td>Benzene</td>
<td>6.1 ± 0.6</td>
<td>-10.7 ± 0.9</td>
<td>117</td>
<td>0.59</td>
<td>$3.5 \times 10^6$</td>
<td>$1.6 \times 10^{11}$</td>
</tr>
<tr>
<td>5</td>
<td>Benzene</td>
<td>0.0</td>
<td>$\leq 7^f$</td>
<td>$\leq 0.99$</td>
<td>$\geq 2.8 \times 10^6$</td>
<td>$\geq 1.4 \times 10^8$</td>
<td></td>
</tr>
<tr>
<td>68</td>
<td>Benzene</td>
<td>2.4 ± 0.2</td>
<td>-4.2 ± 0.4</td>
<td>3$^f$</td>
<td>0.54</td>
<td>$1.5 \times 10^8$</td>
<td>$1.0 \times 10^{10}$</td>
</tr>
<tr>
<td>DB0</td>
<td>Benzene</td>
<td>8.6 ± 0.3</td>
<td>-10.2 ± 0.5</td>
<td>434</td>
<td>0.013</td>
<td>$2.3 \times 10^6$</td>
<td>$6.2 \times 10^{10}$</td>
</tr>
<tr>
<td>Di-Me</td>
<td>Benzene</td>
<td>10.0 ± 0.3</td>
<td>-13.4 ± 0.5</td>
<td>599</td>
<td>0.024</td>
<td>$1.6 \times 10^6$</td>
<td>$1.0 \times 10^{12}$</td>
</tr>
<tr>
<td>Di-Me</td>
<td>CH$_3$CN</td>
<td>7.9 ± 0.3</td>
<td>-9.0 ± 0.5</td>
<td>740$^f$</td>
<td>0.016</td>
<td>$1.3 \times 10^6$</td>
<td>$1.1 \times 10^{10}$</td>
</tr>
<tr>
<td>CB</td>
<td>Benzene</td>
<td>7.7 ± 0.2</td>
<td>-12.1 ± 0.3</td>
<td>302</td>
<td>0.28</td>
<td>$2.4 \times 10^6$</td>
<td>$4.3 \times 10^{11}$</td>
</tr>
<tr>
<td>MV</td>
<td>Benzene</td>
<td>0.0</td>
<td>0.56</td>
<td>0.9</td>
<td>$1.8 \times 10^8$</td>
<td>$1.6 \times 10^9$</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>n-BuOAc</td>
<td>2.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) errors are the standard deviation  
 b) kcal mol$^{-1}$  
 c) in nsec  
 d) room temperature value  
 e) calculated from the formula $k_f + k_d = (1 - \phi_r - \phi_f)/\tau_f$  
 f) ref. 40
virtually no barrier to nitrogen loss.

It is of interest that temperature alters $\Phi_\text{r}$ of the monocyclic azo 6 very little. An 80° temperature rise causes only a two fold increase in $\Phi_\text{r}$. This corresponds to an $E_a$ of only 2.0 kcal mol$^{-1}$ and is in sharp contrast to the results with its bicyclic analogue Di-Me. The increased flexibility of 6 apparently makes $\Phi_\text{r}$ relatively insensitive to temperature changes. This result is consistent with the smaller effects that radical stabilizing substituents had on $\Phi_\text{r}$ in this system relative to the bicyclics.

Let us briefly discuss the A factors for these azo compounds. Table 14 reveals that these factors for all the azos are lower than expected for a rapid unimolecular decomposition. The A factors may therefore be a reflection of spin forbiddenness of the crossing of the singlet excited state surface with the triplet decomposing surface in Fig. 1.$^{111}$

In conclusion, nitrogen quantum yields for several classes of cyclic azo compounds have been shown to be temperature dependent and in accord with a simple model in which the rate of loss of nitrogen from the excited state is treated by the Arrhenius equation. This temperature dependence shows that raising the temperature of the photolysis can be an effective method for increasing the photoreactivity of azo compounds with quantum yields less than unity. This temperature dependence may further explain why no esr spectrum was obtained during low temperature photolysis of DB0$^{112}$ and why irradiation of the normethyl analogue of 67 (3) yielded an extremely feeble esr spectrum at low temperature.$^{113}$
G. Other Studies of Cyclic and Bicyclic Azoalkanes

1. The Search for Phosphorescence from Two Bridgehead Halogen Analogues of DBO

Although phosphorescence has been observed from azo compounds 84 and 85, no triplet emission has been observed from simple azo compounds. Engel, for example, could detect no phosphorescence from Di-Me at -196°C, even under conditions where the triplet was efficiently populated by sensitization. A recent attempt to detect phosphorescence from a series of cyclic and bicyclic azoalkanes at -196°C met a similar fate.

We decided, however, to see if phosphorescence could be observed from Di-Cl and Di-Br and therefore obtain the triplet energy of these compounds directly. These compounds were deemed worthy of study because each exhibited low direct photoreactivity (\(\phi_r + \phi_f = 0.07\)) implying efficient intersystem crossing, and furthermore possessed the halogen atoms. The halogens could presumably aid in the observation of phosphorescence by enhancing transitions between singlet and triplet states through spin-orbital coupling. The net effect we hoped would be an increase in the quantum yield of phosphorescence, a situation encountered in aromatic hydrocarbons.

Upon irradiation at 366 nm of solutions of Di-Cl and Di-Br
dissolved in an isopentane-methylcyclohexane glass (4:1) at $-196^\circ$ C, however, no measurable phosphorescence could be detected. This result is not completely surprising in light of the fact that although halogens can enhance the $T_1 \rightarrow S_0$ radiative transition in aromatic hydrocarbons, they also enhance the non-radiative deactivation of $T_1$.\footnote{115} The rate of this latter process is apparently so fast in most azo compounds that it precludes the observation of phosphorescence.\footnote{116}
2. Triplet Sensitized Photochemistry of Cyclic and Bicyclic Azoalkanes

The triplet state of cyclic azoalkanes can be populated by energy transfer from donors of suitable triplet energy.\textsuperscript{2,3} While many studies of the triplet photochemistry of cyclic azoalkanes have been undertaken with respect to discovering spin correlation effects,\textsuperscript{2} very little quantitative data on the triplet photoreactivity of these compounds are known. These data are tabulated in Table 15 along with some results from this work.

The triplet sensitized decomposition of 67, previously studied using benzophenone as sensitizer,\textsuperscript{117a} was studied in detail to ascertain whether the reason for its striking seven fold difference in reactivity from the singlet and triplet manifolds was a consequence of inefficient energy transfer from benzophenone ($E_T = 69$ kcal mol$^{-1}$).\textsuperscript{118} This would be the case if the triplet energy of 67 was higher than expected (the triplet energy of a compound similar to 67 has been estimated at 55-65 kcal mol$^{-1}$).\textsuperscript{119} However, use of sensitizers of even higher energy than benzophenone like acetophenone ($E_T = 72$ kcal mol$^{-1}$)\textsuperscript{118} and p-methoxyacetophenone ($E_T = 74$ kcal mol$^{-1}$)\textsuperscript{118} failed to increase the sensitized quantum yield of 67 (Table 15). Thus it appears that energy transfer to 67 is efficient using benzophenone; it is probable that this is also the case for the similar compound 5.

As Table 15 shows, with the exception of 86, decomposition of cyclic azoalkanes from the triplet state is less efficient than than from the singlet. A possible reason for the exceptional behavior of 86 can be gleaned from its absorption spectrum (Fig. 6). Irradiation at
<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Sensitizer&lt;sup&gt;b&lt;/sup&gt;</th>
<th>η&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>86</td>
<td>b</td>
<td></td>
<td>0.52&lt;sup&gt;e,f&lt;/sup&gt;</td>
<td>g</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>BP</td>
<td>0.65&lt;sup&gt;e&lt;/sup&gt;</td>
<td>117</td>
</tr>
<tr>
<td>5</td>
<td>b</td>
<td></td>
<td>0.98</td>
<td>g</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>BP</td>
<td>0.21&lt;sup&gt;117a&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>67</td>
<td>b</td>
<td>BP</td>
<td>0.59</td>
<td>g</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>A</td>
<td>0.08&lt;sup&gt;117a&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>p-MAP</td>
<td>0.043</td>
<td>g</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>T</td>
<td>0.056</td>
<td>g</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>X</td>
<td>0.036</td>
<td>g</td>
</tr>
<tr>
<td>DBH</td>
<td>io</td>
<td></td>
<td>1.0</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>h</td>
<td>BP</td>
<td>0.97&lt;sup&gt;80&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>87</td>
<td>ip</td>
<td></td>
<td>0.91&lt;sup&gt;d&lt;/sup&gt;</td>
<td>121</td>
</tr>
<tr>
<td></td>
<td>ip</td>
<td>BP</td>
<td>0.54&lt;sup&gt;d&lt;/sup&gt;</td>
<td>121</td>
</tr>
<tr>
<td>88</td>
<td>dm</td>
<td></td>
<td>0.98&lt;sup&gt;d&lt;/sup&gt;</td>
<td>121</td>
</tr>
<tr>
<td></td>
<td>dm</td>
<td>BP</td>
<td>0.53&lt;sup&gt;d&lt;/sup&gt;</td>
<td>121</td>
</tr>
<tr>
<td>DB0</td>
<td>io</td>
<td></td>
<td>0.022</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>io</td>
<td>BP</td>
<td>0.014</td>
<td>11</td>
</tr>
<tr>
<td>MV</td>
<td>b</td>
<td></td>
<td>0.9</td>
<td>g</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>BP</td>
<td>0.75&lt;sup&gt;g&lt;/sup&gt;</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> b=benzene, io=isooctane, h=hexane, ip=isopentane, dm=dichloromethane  
<sup>b</sup> BP=benzophenone, A=acetophenone, p-MAP=p-methoxyacetophenone, T=thioxanthone, X=xanthone  
<sup>c</sup> measured by nitrogen evolution unless otherwise noted  
<sup>d</sup> measured by hydrocarbon formation  
<sup>e</sup> see text  
<sup>f</sup> measured by the decrease in the azo absorption  
<sup>g</sup> this work
313 nm occurs in a region far removed from the $n_c \pi^*$ maximum of this compound. It is possible that this irradiation is partially absorbed by either another azo band (note the start of an increase in $\varepsilon$ at $\lambda < 310$ nm, Fig. 6) or an impurity. The $\Phi_r$ of 0.52 in Table 15 was obtained through excitation at 313 nm. Irradiation of 86 at 335 nm, though, at a wavelength nearer its $n_c \pi^*$ maximum ($\lambda_{\text{max}} = 348$ nm) results in a $\Phi_r = 0.65$, which is within experimental error of the triplet sensitized yield of 0.67.117

The reason for the generally lower photoreactivity of the triplet states of the compounds shown in Table 15 when compared to the singlets could be that a higher energy barrier must be surmounted for decomposition to occur from the triplet manifold. This is in accord with a theoretical calculation on cis diimide98 (see Fig. 2, p 45)
which shows a barrier of 22 kcal mol\(^{-1}\) to the crossing point of the \(1\text{n},\pi^*\) state with the dissociative surface. This barrier increases to 38 kcal mol\(^{-1}\) in the case of the \(3\text{n},\pi^*\) state. Note that the singlet barrier calculated theoretically is much higher than those determined in this work (c. f. Table 14, p 67). If this triplet barrier to decomposition exists, the triplet sensitized quantum yields for the compounds in Table 15 should be even more temperature dependent than the direct yields. A further point is that this proposed barrier to triplet photodecomposition should be lowered by radical stabilizing substituents.\(^3\) This latter possibility is shown by comparing the triplet sensitized quantum yields of \textbf{DBO} and \textbf{MV} in Table 15. A dramatic increase in the triplet photoreactivity of \textbf{DBO} is obtained by the replacement of a bridgehead hydrogen with a vinyl group. A similar effect has recently been shown in the triplet sensitized decompositions of certain acyclic azoalkanes.\(^{103}\)

One other factor besides radical stability which also apparently affects the triplet quantum yield of cyclic azoalkanes is molecular flexibility. When the molecule is made more rigid (compare 67 and 5 with \textbf{DBH}, 87, and 88) triplet photoreactivity increases. Additional studies of the triplet photoreactivity of cyclic azoalkanes should be undertaken to lend further support to the above generalizations.
3. Thermolysis of a DBO derivative Possessing an Endo Cyclopropyl Group

Although the DBO derivative with the cyclopropane ring in the exo configuration (Exo-Cp) was synthesized several years ago and its thermal kinetics studied in great detail,45d,76 its corresponding endo isomer (Endo-Cp) remained unknown. The achievement of the synthesis of the latter compound (sec. B.1.) offered the opportunity to assess quantitatively the effect of cyclopropyl group orientation in the thermolysis of DBO derivatives. While Allred and Voorhees51 had measured the activation parameters of CPCA with this idea in mind, their study was somewhat marred by the fact that the compound contained an exo cyclobutyl group in addition to the endo cyclopropyl group. Previous studies of the kinetics of CB have shown that the exo cyclobutyl group increases the reactivity of the DBO system by a factor of almost $10^5$.46

Kinetics of Endo-Cp (0.01 in degassed hexadecane) were obtained by monitoring the decrease in the azo chromophore by uv spectroscopy at four temperatures between 239° and 254° C. The only product produced was 1,4 cycloheptadiene as shown by comparison with an authentic sample.122 The data are presented in Table 16 and yield $\Delta H^+ = 45.9 \pm 2.0 \text{ kcal mol}^{-1}$ and $\Delta S^+ = 10.4 \pm 3.8 \text{ eu}$ (the errors are the standard deviation of the least squares line). Despite the rather high error limits, a comparison of these activation parameters with those of other DBO derivatives (Table 17) reveals that the values so obtained are quite reasonable.

As Table 17 shows, the reactivity rate difference between the
Table 16
Rates of Decomposition of Endo-Cp at Several Temperatures

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Rate x 10^5, sec^-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>239.00</td>
<td>5.213</td>
</tr>
<tr>
<td>244.17</td>
<td>7.958</td>
</tr>
<tr>
<td>248.97</td>
<td>11.82</td>
</tr>
<tr>
<td>253.64</td>
<td>18.97</td>
</tr>
</tbody>
</table>

a) 0.01 M in degassed hexadecane

Table 17
The Effect of Strained Rings on Thermolysis of DBO Derivatives

<table>
<thead>
<tr>
<th>Compound</th>
<th>ΔH^a</th>
<th>ΔS^b</th>
<th>Rel. Rate^c</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exo-Cp</td>
<td>21.5</td>
<td>4.1</td>
<td>1.5 x 10^{16}</td>
<td>76</td>
</tr>
<tr>
<td>CB</td>
<td>38.6</td>
<td>11.0</td>
<td>1.7 x 10^6</td>
<td>46</td>
</tr>
<tr>
<td>CPCB</td>
<td>40.8</td>
<td>10.3</td>
<td>3.0 x 10^3</td>
<td>51</td>
</tr>
<tr>
<td>DBO</td>
<td>45.0</td>
<td>10.6</td>
<td>3.0</td>
<td>10</td>
</tr>
<tr>
<td>Endo-Cp</td>
<td>45.9</td>
<td>10.4</td>
<td>(1.0)</td>
<td>d</td>
</tr>
</tbody>
</table>

a) kcal mol^-1  b) eu  c) at 300^0 K  d) this work

exo and endo cyclopropyl configurations is ca. 10^{16}. Also note that the activation parameters for Endo-Cp are nearly identical with the parent compound DBO. The cyclopropyl group therefore aids thermolysis in the exo orientation but exerts virtually no effect in the endo orientation. The extremely facile thermolysis of Exo-Cp has been explained on the basis that expulsion of nitrogen is aided by disrotation of the cyclopropyl orbitals in a [2s + 4s] cyclorevision
which is allowed by the orbital symmetry rules.\textsuperscript{31} In contrast, the high activation parameters of Endo-Cp indicate that the cyclopropyl group is not properly aligned to assist nitrogen expulsion in this compound (allowed disrotatory ring opening would produce the highly strained trans,trans-1,4-cycloheptadiene) and loss of nitrogen consequently occurs via a higher energy diradical pathway. The amazing dichotomy in the reactivity of Exo-Cp and Endo-Cp ($\Delta\Delta G^\ddagger = 22.5$ kcal mol$^{-1}$ at $300^\circ$ K) can therefore be thought of in a formal sense as the energy difference between an allowed and a forbidden pathway. Most previous estimates of this energy difference, obtained from thermal ring openings of cyclobutanes, fall in the range of 10-15 kcal mol$^{-1}$.\textsuperscript{124}
H. Experimental

General-Materials and Equipment

A Varian EM-390 spectrometer was used to record nmr spectra. CDCl₃ was used as solvent, and with the exception of several cyclopropanated compounds, all spectra were run using TMS lock. The spectra of cyclopropanated compounds were run using CHCl₃ (δ=7.28 ppm) as a lock. Ir's were recorded with either a Perkin-Elmer 727B or a Beckman IR 4230 and uv's were obtained with a Cary 17. Melting points were taken in capillary tubes using a Mel-Temp and are uncorrected. Fluorescence spectra were obtained with a Perkin-Elmer Fluorescence Spectrometer MPF-2A. The geometry of this instrument was such that there was a 90° angle between the excitation and emission beams. A Finnigan 3300 GC/MS and CEC/DuPont 21-110B were used to obtain low resolution and high resolution mass spectral data, respectively. Analytical and preparative vpc was carried out with an HP 700 Laboratory Chromatograph. Relative peak areas were obtained with either a Linear strip chart recorder containing an integrator, or by the cut and weigh method.

For most of this work, purified, thiophene-free reagent benzene (Fisher) was used. Purification was effected by irradiation for several weeks with a 450 W lamp in the presence of chloranil, chromatography through alumina, and distillation from P₂O₅. Ethyl acetate was reagent grade and dried by storage over molecular sieves 4A. Acetonitrile was spectroquality. Azo-tert-butane (ATB) was prepared by the Ohme procedure¹⁴⁰ and was spinning band distilled to >99% purity as determined by gc (10% XE-60, 20' x 0.125", oven 100°). DBH was prepared by the Organic Syntheses procedure¹⁴¹ by R. A. Hayes in our
laboratory and was purified by low temperature recrystallization from pentane and multiple sublimation (uv (benzene): $\lambda_{\text{max}}$ 343 (e=355)). Potassium Ferrioxalate was purified by recrystallization from H$_2$O and stored in the dark in an aluminum foil wrapped bottle. 9,10-diphenyl anthracene (DPA) was used without purification; N,N,N',N'-tetramethyl-phenylenediamine was purified by one recrystallization from ethanol and two from ligroin, mp 47.5-48° C. Biacetyl was purified by Treacy Woods in our laboratory by distillation under nitrogen and stored in degassed and sealed ampules. The sensitizers used in this work had been purified by other workers in this laboratory.142

---

**Nitrogen Quantum Yields**

Direct irradiations were performed in a conventional merry-go-round apparatus using a 450 W medium pressure Hanovia lamp as a light source. The 366 nm line of the lamp was isolated with a solution of 2,7-dimethyl-3,6-diazaocyclohepta-1,6-diene perchlorate (10 mg/ 100 ml H$_2$O) and Corning 7-60 glass filters. Solutions of the azo compounds were prepared such that $A_{366}$ was typically >3.0 and syringed into pyrex tubes. After degassing through five freeze-pump-thaw cycles (p<0.001 mm), the tubes were sealed off with a torch and were ready to be irradiated. Azo-tert-butane ($\phi_r$=0.46) was used as actinometer. Irradiations were typically done to <20% conversion; the nitrogen produced was analysed by means of a Töpler pump. $\phi_{-\text{azo}}$ was determined by using a photolysis tube with an attached 2 mm path length cell. Irradiations at 313 nm were performed using quartz apparatus and employing aqueous solutions of NiSO$_4$ (0.89 M) and K$_2$CrO$_4$ (2.5 x 10$^{-3}$ M)
as lamp filters. DBH \( \phi_r = 1.0 \)^{12} was used as actinometer in this case.

Temperature dependent quantum yields were performed by heating the merry-go-round water bath with a blade heater which was regulated by an RFL 70-115 proportional temperature controller. With this arrangement, the temperature of the water bath did not vary by more than \( \pm 0.1^\circ \) C during the photolysis. The temperature of the run was obtained with a mercury thermometer. At temperatures greater than ambient, the upper part of the photolysis tubes were wrapped with asbestos tape for insulation to prevent refluxing of solvent. Sub ambient runs were performed by cooling the water bath with coils connected to a circulating ethanol refrigerated bath and regulating the temperature as above.

Low temperature \((-78^\circ \) C) photolyses were performed using the apparatus shown in Fig. 7. This apparatus was mounted on a metal plate which enabled it to be inserted into the sample compartment of the Cary 17. Stirring of the azo solution was accomplished by an array of coils driven by an oscillator.\(^{143}\) The coils were attached to the outside of the apparatus (for clarity, these coils are not shown in Fig. 7). A 500 W lamp was mounted in such a way that the light beam could be directed towards a hole cut out of the Cary 17 sample compartment and into the azo solution. The 366 nm line was isolated by using the filters previously described. The following procedure was used to perform photolyses with this apparatus.

1. The light intensity of the lamp was determined by potassium ferrioxalate actinometry \( \phi = 1.21 \) at 366 nm.\(^{78}\) A 6.0 ml aliquot of actinometer solution \((0.02 \text{ M in } 0.1 \text{ N } \text{H}_2\text{SO}_4)\) was typically irradiated for 12 seconds. The solution was gently agitated with a stream of ni-
Fig. 7. Low Temperature Apparatus (1/2 scale)

- To vacuum line
- Inner Section
- Outer Section
- 10/30
- 19/38
- 55/50
- 24/40
- Clamp
- EtOH in here
- Analysing uv
- Azo solution in square cell
- Magnetic stirring bar (glass)
- 10 mm
- 18 mm
- 51 mm
- 58 mm
- 6.5 in
trogen during this period. Two measurements of the light intensity were made along with one blank determination.

2. The inner cell of the low temperature apparatus was then cleaned and cooled to -78°C; 6 ml of the appropriate azo solution was than introduced.

3. The inner cell was connected to the vacuum line and degassed at -78°C with vigorous stirring (about 1 1/2 hours was typically required).

4. Meanwhile in the uv room, a vacuum was pulled on the outer section of the apparatus and with a strong stream of dried air (passed through CaSO₄) being passed into the sample compartment, the absolute ethanol was precooled to ca. -60°C with liquid nitrogen.

5. The degassed inner section was then taken off the vacuum line and united with the outer section in the Cary 17; dry ice was added via the 24/40 joint. A drying tube was then attached to this joint.

6. A uv was taken of the cold azo solution; the solution was irradiated for a period of time and another spectrum recorded.

7. The inner section was removed from the outer section and the nitrogen produced was measured with the Töpler pump.

The quantum yields of MV and DV using various actinometer systems were done by irradiating tubes in the merry-go-round that were contained within metal sleeves with a small window area exposed to the light. A \( \Phi = 0.68 \) was assumed for the benzophenone-benzhydrol actinometer system. The above mentioned metal sleeves were also used to examine the solvent dependent photochemistry of Di-Me.

Triplet sensitized quantum yields of MV were performed on de-
gassed 0.016 M solutions of this azo containing the appropriate sensitizer. The irradiation was performed at 313 nm (the azo does not absorb appreciably at this wavelength) and the concentrations of benzophenone ($\epsilon_{313}=57$) and p-methoxyacetophenone ($\epsilon_{313}=120$) were such that their absorbance was $=3.0$ at this wavelength. Triplet sensitized quantum yields of 67 and 86 were performed on 0.05 M solutions of these azos. Irradiations were performed at 366 nm in this case since these compounds did not absorb at this wavelength. Concentrations of the sensitzers were adjusted such that their absorption was $=3.0$ at 366 nm. The sensitizers and their extinction coefficients at 366 nm were as follows: benzophene, 70; acetophenone, 4.2; p-methoxyacetophenone, 3; thioxanthone, 5150; xanthone, 28.

**Fluorescence Quantum Yields and Lifetimes**

Benzene solutions of the DBQ derivatives with relatively long lifetimes (> 10 nsec) and two standards were prepared such that $A_{337}=0.30 \pm 0.01$; these solutions were degassed and sealed in pyrex cuvettes. The two standards were diphenylanthracene in benzene ($\phi_f=0.96$) and N,N,N',N'-tetramethylphenylenediamine in cyclohexane ($\phi_f=0.18$). Fluorescence spectra (excitation slit = 3.5 nm, emission slit = 4.0 nm) were obtained using $\lambda_{ex}=337$ nm. The spectra were corrected for photomultiplier response and the relative areas of the fluorescence envelopes obtained by the cut and weigh method. The $\phi_f$'s of the two standards were in perfect agreement with one another after making a refractive index correction. Solutions of MV and DV were prepared such that $A_{337}=0.4$. $\phi_f$'s of these two compounds were
obtained relative to TMPD in cyclohexane ($\lambda_{ex}=337$, excitation slit = 8 nm, emission slit = 8 nm). The fluorescence spectrum of Exo-Cp was obtained at 0°C in hexane, $\lambda_{ex}=360$ nm (this solution was not degassed) and the solution was kept cold by blowing cold nitrogen on the cuvette. All the DBO derivatives except MV, DV, Exo-Cp, and DM exhibited excitation spectra that did not change with emission wavelength. Some contribution from impurities cannot therefore be ruled out in the fluorescence spectra of these latter weakly fluorescing compounds.

Fluorescence lifetimes were obtained with the help of M. A. J. Rodgers at CFKR, Austin, Texas. The same samples that were used for fluorescence quantum yields were used for these determinations. The compounds with long lifetimes (>10 nsec) were irradiated with a nitrogen laser ($\lambda_{ex}=337$) while the compounds with short lifetimes (<10 nsec) were irradiated with a picosecond laser ($\lambda_{ex}=353$ nm). The lifetimes are the average of at least three determinations and were obtained by monitoring the emission decay at 440 nm via an interference filter. The compounds with long lifetimes exhibited good single exponential decay. This was not the case for the compounds with short fluorescence lifetimes. The decay curves of these compounds consisted of a short component and a longer lived component.120 At this time, the longer lived component is attributed to an impurity.

The temperature dependence of $\tau_f$ of 67 (0.003 M in spectro-quality benzene) was obtained by using a cell with an outside jacket through which water could be circulated. This water was cooled or heated with a Lauda K-2/RD circulating bath. The temperature of the benzene solution inside the cell was measured with a Digitec 590 TC
Type I thermocouple made by United Systems Corporation. Nitrogen was continuously bubbled through the solution while the determination was being made.

### Quenching of Biacetyl Phosphorescence with DBO and MV

The lifetime of biacetyl was determined by exciting a sample in solution with an air spark flash (flash lifetime = 15 μsec) and monitoring emitted light with a photomultiplier-transient recorder-oscilloscope arrangement. The exciting light was filtered with a solution of CuSO₄·2H₂O (2.2 g/100 ml 2.7 M NH₄OH) of 1 cm path length. A monochromator was used to monitor the decay of biacetyl phosphorescence at 530 nm. A hard copy of the decay curve was obtained with a strip chart recorder. Fig. 8 depicts the apparatus used to acquire the quenching data.

Fig. 8. Apparatus for Biacetyl Quenching Studies
Samples of biacetyl (0.01 M in purified benzene) and the azo quencher solution (≈2 x 10^{-4} M) were degassed in their respective apparatus. Typically after four freeze-pump-thaw cycles, the lifetime of biacetyl had reached its maximum value (≈180 μsec). The contents of both apparatus were then placed under nitrogen and a 100-150 μl aliquot of the azo solution was syringed into the biacetyl solution. After two degassing cycles, the lifetime of the biacetyl solution was remeasured. Nitrogen was added to the biacetyl solution, another aliquot of quencher was introduced, and the above process repeated several times. Control experiments showed that addition of an aliquot of benzene in place of the azo solution had no effect on the lifetime of biacetyl phosphorescence.

**Product Studies of MV, DV, and Di-Me**

Product studies of MV or DV were performed in nmr tubes by irradiating samples in benzene-d_{6} or acetone-d_{6} at 366 nm. The product study of Di-Me was performed by irradiating a solution of this azo (453 mg/110 ml pentane) contained in the outer compartment of a pyrex photochemical well. An inner cell of the well contained a solution of 2,7-dimethyl-3,6-diazacyclohepta-1,6-diene perchlorate which filtered light of λ <350 nm. The entire apparatus was heated to 65° in a water bath until >90% of the azo had decomposed as indicated by uv. A gc analysis of the crude photolysate (15% XE-60, 20' x 0.25", oven 80° C) revealed two major product peaks (retention times 13.3 and 20.0 min). The ratio of these peaks was determined as 73:27 through multiple integrations. After removing most of the solvent by spinning band
distillation, the residual oil was purified by preparative gc. The major product was identified as 2,5-dimethyl-1,5-hexadiene while the minor one was identified as 1,4-dimethylbicyclo[2.2.0]hexane through comparison of their nmr spectra with those reported. Three additional products from the photolysis (retention times 25.8, 33.5, and 37.5 min) which comprised less than 5% of the total product mixture were not identified.

**Attempted Detection of Phosphorescence from Di-Cl and Di-Br**

Solutions of 7.1 mg Di-Cl and 10.2 mg Di-Br in 5 ml methylcyclohexane-isopentane (4:1) were prepared. The isopentane was distilled from Na; methylcyclohexane was reagent grade. In addition to the above solutions, a solution of chrysene in the above solvent mixture and a blank were prepared. Phosphorescence was easily detected from the chrysene sample (-196°C). However, no phosphorescence could be detected from Di-Cl or Di-Br at -196°C ($\lambda_{ex}$=366 nm). At extremely wide slit settings (excitation slit = emission slit = 40 nm) a maximum was detected at 440 nm (Di-Br) and at 490 nm (Di-Cl). These are probably due to impurities. No phosphorescence from these samples was detected when the rotating can was removed, either.

**Kinetics of Endo-Cp**

The kinetics were performed by measuring the decrease in the azo absorption band by uv. A solution of the azo compound (0.003 M) in hexadecane (Aldrich, 99%) was prepared and 2 ml aliquots were syringed into pyrex cuvettes. The samples were degassed by two freeze-pump-
thaw cycles, sealed under vacuum, and a uv spectrum run on each of them. Four cuvettes for each compound at each temperature were preheated to 150° C and plunged into an oil bath that was regulated with a Bayley temperature controller. The temperature of the run was measured by a Minco calibrated platinum resistance thermometer. Samples were removed at regular intervals at up to three half lives, the uv spectrum recorded, and then the tubes were returned to the oil bath for at least 10 half lives to obtain the infinity points. A least squares fit of $\ln[(A_0-A_t)/(A_0-A_{inf})]$ vs. time yielded the rate constants at each temperature. A least squares analysis of $\ln[k/T]$ vs. $1/T$ then gave $\Delta H^\dagger$ and $\Delta S^\dagger$. 
General Procedure for Preparation of Triazolinedione 24a

A solution of 24a of sufficient quantity to react with 0.05 mol diene was prepared in the following manner. Tert-butyl hypochlorite\textsuperscript{125} (9 ml, 0.075 mol) was added to a cooled (0\textdegree) stirred suspension of methylurazole\textsuperscript{42} (8.0 g, 0.07 mol) in 35 ml ethyl acetate. After stirring 20 minutes, the solvent was rotoevaporated to yield red crystals. These crystals were then taken up in 35 ml ethyl acetate and filtered into a dropping funnel for immediate use.

General Procedure for the Preparation of Diazomethane

To a 125 ml Florence flask containing a two phase mixture of 35 ml ether and 15 ml 50% aq. KOH cooled to 0\textdegree was added nitrosomethylurea\textsuperscript{126} (6.0 g, 58 mmol). After stirring for about 10 minutes, all of the solid had decomposed and the flask contents were cooled to -78\textdegree to freeze out the aqueous layer. The yellow ether solution was then dried by decanting onto 15 ml half saturated NaCl solution at 0\textdegree and swirled. After cooling to -78\textdegree, the solution of diazomethane was ready to be decanted and used.

Synthesis of DBO-General Procedures for Preparation of DBO Derivatives by the Triazolinedione Route

Since the syntheses of several of the DBO derivatives used in this work are very similar, only the synthesis of the parent compound, DBO, will be given in detail.\textsuperscript{45}
4-Methyl-2,4,6-triazatricyclo[5.2.2.0^2,6]undec-8-ene-3,5-dione 27a

Ethyl acetate (110 ml) and 1,3-cyclohexadiene (Aldrich, 25.0 g, 0.312 mol) were added to a flask fitted with a dropping funnel, nitrogen inlet, and thermometer adapter. The milky white solution was cooled in an ice bath while 27a in ethyl acetate was added until a slight excess of this reagent was indicated by a persistent pink color in the reaction flask. The red solution of dienophile was added at such a rate that the temperature of the flask contents never exceeded 12\(^\circ\). Rotoevaporation of solvent and high vacuum treatment afforded adduct 27a (60.9 g, 100\%), mp 87-94\(^\circ\). This material, pure by nmr, was used directly in the next step. A sample was recrystallized from ethyl acetate, mp 103-105\(^\circ\).

nmr: 1.42-1.65 (m, 2H), 1.98-2.29 (m, 2H), 2.95 (s, 3H), 4.75-4.91 (m, 2H), 6.38 (t, 2H)

4-Methyl-2,4,6-triazatricyclo[5.2.2.0^2,6]undecane-3,5-dione 28a

A mixture of 27a (15.0 g, 0.077 mol) and 0.15 g 10% palladium on carbon catalyst was added to 300 ml absolute ethanol and hydrogenated at 40 psi using a Paar hydrogenator. Hydrogen uptake was extremely rapid and the bottle had to be recharged with hydrogen several times. After 45 minutes, hydrogen uptake had slowed; after an additional 45 minutes, the reaction mixture was filtered and the solvent rotoevaporated. After high vacuum treatment 28a (14.6 g, 96\%) was isolated as white crystals of sufficient purity to be used in the next step. Recrystallization (EtOAc-hexane) afforded white crystals, mp 80-82\(^\circ\).

nmr: 1.60-2.17 (m, 8H), 3.06 (s, 3H), 4.28 (br s, 2H)
2,3-Diazabicyclo[2.2.2]oct-2-ene DBO (28a → 29a → 30a → DBO)

This procedure is essentially that of Snyder, et al. A flask fitted with a dropping funnel, reflux condenser, and nitrogen inlet was charged with KOH (21 g, 0.38 mol) and isopropanol (135 ml). While this mixture was being heated to reflux, a solution of 28a (14.0 g, 71.7 mmol) in isopropanol was added. After refluxing overnight, the reaction mixture, consisting of an orange solution with a white ppt (K₂CO₃), was filtered and the inorganic solids washed with several portions of methanol. The residue obtained by rotoevaporation of solvent was diluted with 40 ml water and neutralized with concentrated HCl. This latter operation is exothermic and cooling was necessary. This aqueous solution was extracted with methylene chloride (3x50 ml) and the combined organic layers washed with water (20 ml), dried (MgSO₄), and rotoevaporated to yield a brown oil. Last traces of solvent were removed by high vacuum treatment. An NMR revealed a doublet in the N-methyl region (J = 5 Hz) indicating that cleavage of the urazole ring to the methyl urea (29a) had occurred.

The urea compound was taken up in 100 ml water and slowly added to a stirred solution of cupric chloride dihydrate (56 g, 0.33 mol) in 400 ml water. This operation should be conducted in a hood. The brick red copper complex of DBO was soon formed along with copious gas evolution. Stirring was continued for one hour after the addition of 29a was completed. The complex was collected, washed with several portions of water and dried in a dessicator under vacuum. The yield was 14.5 g (93 % from 28a).

The copper complex was decomposed by adding it in several portions
to a two phase system of methylene chloride (50 ml) and aq. con. NH₄OH (300 ml). After stirring 10 minutes, the layers were separated and the deep blue aqueous phase extracted with methylene chloride (3x50 ml). The combined organic layers were washed with water, dried (K₂CO₃), and most of the solvent removed by distillation through a glass packed column. The residual dark brown oil remaining was transferred to a sublimation apparatus and the last traces of solvent removed under reduced pressure (or alternatively with a nitrogen stream). Sublimation (60-85⁰, 0.1 mm) afforded DBQ (4.55 g, 66% from 28a) as white crystals. Low temperature recrystallization from pentane followed by three sublimations and drying in a dessicator over drierite afforded material of mp 148-150⁰.

nmr: 1.00-1.75 (distorted q, 8H), 5.04 (br s, 2H)

uv (benzene): \( \lambda_{\text{max}} \) 379 (ε=264), 369 (s) (ε=151)

1,4,7-Trimethyl-2,4,6-triazatricyclo[5.2.2.0²,6]undec-8-ene-3,5-dione 27b

Following the procedure for o-xylene, p-xylene was Birch reduced to 1,4-dimethyl-1,4-cyclohexadiene (bp 64-65⁰, 52 mm; the diene contained about 10% of aromatic material). A 100 ml flask fitted with a reflux condenser and nitrogen inlet was then charged with 20 g of the above mixture, 4.5 g potassium tert-butoxide, and 55 ml dry DMSO (dried by distillation from CaH₂). This reaction mixture was heated to 55⁰ C and monitored periodically by gc (10% XE-60, 20' x 0.125", oven 120⁰ C; retention times were, p-xylene, 6.7 min; 1,4 diene, 8.7 min; 1,3 diene, 9.7 min). After 5 hours, the peak attributable to 1,3 diene had reached its maximum value (ca. 50% of the total mix-
ture) and the reaction was quenched by pouring over 250 ml ice. Extraction with ether (3x80 ml), drying (MgSO₄), and rotoevaporation afforded 16.4 g of diene mixture.

Some of this mixture (10 g, containing ca. 0.046 mol of 1,3 diene) was placed into a 250 ml flask along with 40 ml EtOAc. The flask contents were cooled to 0°C and a solution of 24a in EtOAc was slowly added until all of the 1,3 diene had been reacted as indicated by gc. Rotoevaporation of solvent and high vacuum treatment yielded a yellow oil which crystallized upon standing in the refrigerator. Recrystallization from EtOAc-hexane afforded 27b as white crystals, mp 112-118°C. The yield was 6.87 g (67%).

nmr: 1.25-1.50 (m, 2H), 1.83 (s, 6H), 1.89-2.16 (m, 2H), 2.86 (s, 3H), 6.11 (s, 2H)

1,4,7-Trimethyl-2,4,6-triazatricyclo[5.2.2.0²,6]undecane-3,5-dione 28b

Adduct 27b (6.87 g, 0.0310 mol) was hydrogenated at atmospheric pressure in ethanol using palladium on carbon catalyst. A pale yellow oil was obtained which solidified upon pumping under vaccum. One recrystallization (EtOAc-hexane) afforded 28b (4.73 g, 68%) as white needles, mp 106-107°C.

nmr: 1.67-2.21 (m, 8H), 1.78 (s, 3H), 3.19 (s, 3H)

1,4-Diazabicyclo[2.2.2]oct-2-ene Di-Me

Into a 50 ml flask fitted with a reflux condenser and nitrogen inlet was added 10 ml methanol (dried over K₂CO₃). Sodium (1.8 g, 78 mmol) was added in several large chunks. After the ensuing exother-
mic reaction had subsided and all the sodium had reacted, the methanol was pumped off at reduced pressure. The remaining sodium methoxide was heated to 100°C for 25 minutes under vacuum and then cooled to room temperature. Dry DMSO was introduced (25 ml) and the orange colored mixture was heated to 100°C for 10 minutes. After cooling again to room temperature, 28b (3.00 g, 13.4 mmol) was added and the reaction mixture heated to 104°C overnight. The reaction mixture was poured onto 200 g of ice water and neutralized with con. HCl. Addition of several ml of 1M CuCl₂·2H₂O furnished the brick red complex 30b. This was collected by Buchner filtration. The filtrate was neutralized with more con. HCl and the above process repeated until no more complex was obtained (note: if too much CuCl₂ solution is added at any one time, a blue greasy material can form which makes filtration difficult). After washing with water, the complex was pumped dry in a vacuum dessicator. The yield was 1.65 g (52%).

The brick red cuprous chloride complex (1.65 g, 6.96 mmol) was decomposed in a manner analogous to the DBQ precursor 30a. One sublimation (100-110°C, 0.4 mm) yielded the azo compound (0.50 g, 52%) as white crystals, mp 70-73°C; lit.¹¹⁴ mp 70.5-71.5.

nmr: 0.99-1.68 (m, 8H), 1.74 (s, 6H)

uv (benzene): λ_max 384 (ε=254)

Exo-4-methyl-2,4,6-triazaquadricyclo[5.3.2.0²,6⁰,10]dodec-11-ene-3,5-dione 27c

Cycloheptatriene (4.0 g, 0.043 mol) was reacted with triazoline-dione 24a. Tan crystals (8.77 g) were obtained which were triturated
with absolute ethanol to afford adduct 27c (6.75 g, 75%) as white crystals. A sample was recrystallized (EtOAc) to yield transparent platelets, mp 143-144°; lit. 56 mp 178-180°, 129

nmr: 0.15-0.35 (m, 1H), 0.46-0.73 (distorted q, 1H), 1.37-1.64 (m, 2H), 2.94 (s, 3H), 4.90-5.14 (m, 2H), 5.92 (t, 2H)

Exo-4-methyl-2,4,6-triazaquadricyclo[5.3.2.0.2,6,8,10]dodecane-3,5-dione 28c

Adduct 27c (5.78 g, 28.2 mmol) was hydrogenated at one atmosphere to yield 28c (5.56 g, 96%). A sample recrystallized from EtOAc-hexane as white platelets, mp 123-124°; lit. 56 mp 115-116°.

nmr: 0.56-0.80 (t, 2H), 1.34-1.97 (m, 6H), 3.04 (s, 3H), 4.42-4.62 (br s, 2H)

Exo-6,7-diazatricyclo[3.2.2.0.2,4]non-6-ene Exo-Cp (28c → 30c → Exo-Cp)

This reaction was run in a manner analogous to the bridgehead dimethyl adduct 28b. The hydrolysis was carried out by heating to 73° overnight; the cuprous bromide complex 30c 76 was made by neutralization with 48% HBr and addition of cupric bromide solution. From 2.0 g (11 mmol) of 28c, 2.32 g (82%) of brick red complex 30c was produced.

Since Exo-Cp is unstable at ambient temperatures, special precautions had to be taken when liberating this compound from 30c. The following procedure produced a solution of Exo-Cp that was suitable for low temperature photolysis work. The copper complex 30c was decomposed by stirring 200 mg of it with 5 ml con. NH₄OH at 0° C, extraction of the
resulting deep blue solution with cold ether (3x3 ml), and drying the ether layers over CaCl₂. All of these operations were performed in a walk-in freezer. The ether solution was decanted into a flask and solvent was removed at -40⁰C to yield white azo crystals. After dissolving these in 6 ml cold EtOAc, the solution of azo was filtered through a K₂CO₃ pad at -78⁰C using a low temperature recrystallization apparatus. The filtrate was fed directly into the low temperature photolysis apparatus previously described. The solution of azo thus obtained had A₃₆₆ > 3.0.

uv (EtOAc): λₚₐₓ 378 (ε=190), 368 (s) (ε=100); lit. 76 (isoctane) 377 (180), 366 (80)

Exp-4-methyl-2,4,6-triazaquadracyclo[5.4.2.0^2,6.8,11]tridec-12-ene-3,5-dione 27d

Into a 100 ml flask fitted with a reflux condenser, nitrogen inlet, and dropping funnel was added 50 ml ethyl propionate (bp 99⁰, distilled from CaH₂) and cyclooctatriene 130 (5.98 g, 56.5 mmol). The solution was brought to reflux and a solution of triazolinedione 24a in ethyl propionate was added. Rotoevaporation yielded tan crystals (11.8 g, 95%) which were purified by rapid chromatography through silica gel (EtOAc eluent) and recrystallization (EtOAc). Adduct 27d (6.98 g, 56%) was obtained as dense white crystals, mp 118.5-120⁰; lit. 54 mp 120-121⁰.

nmr: 1.20-1.70 (m, 2H), 1.88-2.33 (m, 2H), 2.88-3.16 (m, 2H), 2.97 (s, 3H), 4.73-4.94 (m, 2H), 6.56 (t, 2H)

If this Diels-Alder reaction was performed in refluxing ethyl
acetate, the reaction was much slower than above and an oil was obtained which consisted of two components in a 69:31 ratio. These were readily separated by prep tlc (EtOAc, 2x). The minor component \( (R_f = 0.41) \) was identified as 27d while the major product \( (R_f = 0.28) \) was identified as isomer 31 on the basis of nmr evidence.

nmr (31): 1.83-2.50 (m, 4H), 3.04 (s, 3H), 4.85-5.17 (t with overlapping m, 2H), 5.57-6.51 (m, 4H)

Exo-4-methyl-2,4,6-triazaquadricyclo[5.4.2.0^2,6.0^8,11]triadecane-3,5-dione 28d

Adduct 27d (2.10 g, 9.58 mmol) was hydrogenated to afford an oil which solidified upon high vacuum treatment. The yield of 28d was 2.15 g (100%). A sample crystallized from EtOAc-hexane as white needles, mp 65-66\(^\circ\); lit. 56 mp 70-71\(^\circ\).

nmr: 1.78-2.52 (m, 8H), 2.73-2.97 (m, 2H), 3.05 (s, 3H), 4.22 (br s, 2H)

Exo-7,8-diazatricyclo[4.2.2.0^2,5]dec-7-ene CB (28d + 29d + 30d + CB)

The cuprous chloride complex 30d was produced in a manner analogous to that of 30a. By starting with 3.5 g (15.8 mmol) of 28d, 3.08 g (83%) of 30d was obtained. This complex was decomposed in the manner described previously to afford CB (1.38 g, 77%) after purification by two sublimations (60-90\(^\circ\), 0.001 mm), mp 144-145\(^\circ\); lit. 19,46,131 mp 142-143; 142-144.100

nmr: 0.97-1.39 (m, 2H), 1.71-2.44 (m, 8H), 5.04 (br s, 2H)

uv (benzene): \( \lambda_{\text{max}} \) 385 (e=226), 372 (s) (e=122)
Exo-7,8-dicarbomethoxy-7,8-diazatricyclo[4.2.2.0\textsuperscript{2,5}]dec-9-ene 32

1,3,5-cyclooctatriene\textsuperscript{130} (1.98 g, 18.7 mmol) and ethyl propionate (10 ml) were added to a 25 ml flask fitted with a reflux condenser, nitrogen inlet, and dropping funnel. This solution was heated to reflux and dimethylazodicarboxylate\textsuperscript{132} (2.73 g, 18.7 mmol) in 5 ml ethyl propionate was added over a 20 min period. The resulting orange solution was refluxed overnight. Rotoevaporation of solvent yielded and orange oil which was pumped under full vacuum. This compound, pure by nmr, was used without further purification.

nmr: 1.30-1.63 (m, 2H), 1.83-2.35 (m, 2H), 2.63-3.10 (m, 2H), 3.72 (s, 6H), 4.68-5.00 (m, 2H), 6.40-6.95 (m, 2H)

Reaction of 32 with diazomethane to produce 33

An ethereal solution of diazomethane was generated by decomposing 0.6 g (6 mmol) nitrosomethyl urea according to the general procedure. The diazomethane was added to adduct 32 (1.18 g, 4.68 mmol) which was dissolved in 30 ml ether and contained in a pressure bottle (capacity of the bottle: 100 ml). After capping the bottle, the yellow solution was stirred overnight at 80-85\textdegree. A white insoluble solid formed on the sides of the bottle and the yellow diazomethane color was discharged. Filtration followed by rotoevaporation yielded an oil containing about 50% starting material (nmr analysis). The oil was dissolved in ether and reacted with additional diazomethane as above. After rotoevaporation and pumping under full vacuum, crude adduct 33 (1.06 g, 78%) was isolated as a yellow, foamy oil.

Combined crude adduct from several bottle reactions (4.08 g) was
purified by chromatography on florisil (EtOAc eluent). The fractions of $R_f = 0.20$ by tlc (EtOAc development) were combined and rotoevaporated to yield 33 (1.30 g) as a colorless, foamy oil.

$\text{uv (CH}_3\text{CN): } \lambda_{\text{max}} 324 (\varepsilon=376)$

**Photolysis of 33 to yield 34**

Diazomethane adduct 33 (1.27 g, 4.70 mmol) was dissolved in 100 ml acetonitrile. Photolysis for eleven hours in a pyrex photochemical apparatus resulted in complete destruction of the pyrazoline absorption. Rotoevaporation of solvent and pumping under full vacuum yielded crude 34 (1.01 g, 87%) as an off-white semisolid of suitable purity for the next reaction. A sample was purified by prep tlc (EtOAc). Several minor low $R_f$ components were thus removed from 34 ($R_f = 0.40$).

$\text{nmr: } 0.34-0.77 (m, 2H), 1.36-1.72 (m, 2H), 1.83-2.30 (m, 4H), 2.56-2.97 (m, 2H), 3.62 (s, 6H), 4.20-4.49 (m, 2H)$

$\text{ms: } m/e 266 (m^+), 207 (m^+ \text{ minus CO}_2\text{Me}), 153 (m^+ \text{ minus CO}_2\text{Me and C}_2\text{H}_4), 59 (\text{CO}_2\text{Me}^+)$

**CPCB (34 → 35 → CPCB)**

The copper complex precursor to this azo compound was prepared by the NaOMe-DMSO method in a manner analogous to that of 30b. By reacting 101 mg (0.378 mmol) of 34 (70°, overnight), complex 35 was obtained and was decomposed with conc. NH$_4$OH to afford the azo compound (11.7 mg, 21% from 34) as white crystals after purification by sublimation (30-60°, 0.2 mm). A second sublimation yielded material of mp 59-60°; lit.$^{51}$ mp 59.5-60.5.
nmr: 0.39-0.17 (m, 1H), 0.07-0.43 (m, 1H), 1.36-1.86 (m, 2H), 2.20 br s, 6H), 5.20-5.49 (m, 2H)

uv (benzene): $\lambda_{\text{max}}$ 383 ($\varepsilon=289$), 372 (s) ($\varepsilon=150$); lit. $\lambda_{\text{max}}$ 383 ($\varepsilon=294$), 372 (s) ($\varepsilon=112$)

2,3-Diazabicyclo[2.2.2]oct-2,5-diene N-oxide 36

A modification of the published procedure was devised which enabled convenient preparation of this azoxy compound in multigram quantities (attempts to scale up the literature procedure invariably led to a vigorous exotherm). A 1 l flask equipped with a mechanical stirrer and two dropping funnels was charged with adduct 27a (6.00 g, 31.0 mmol) and 100 ml water. The aqueous mixture was cooled in an ice bath and 210 ml of 30% $\text{H}_2\text{O}_2$ was added over a 45 minute period. Simultaneously, a solution of 120 g KOH in 120 ml water was added at a slightly slower rate than the peroxide solution (addition took 55 min). The ice bath was then removed, the pale yellow solution allowed to warm slowly to room temperature, and the solution heated to 75-85° for one hour while 180 ml 30% $\text{H}_2\text{O}_2$ was added. After cooling to room temperature, the solution was extracted with chloroform (5x100 ml), dried ($\text{K}_2\text{CO}_3$), and rotoevaporated to yield a pale yellow oil. By pumping under full vacuum and cooling in the freezer, the oil solidified to afford azoxy compound 36 (3.4 g, 88%) as a white, low melting solid (mp 41-44°) which was pure by nmr. One recrystallization (Et$_2$O) yielded white crystals, mp 47-49°; lit. mp 48-49°.

nmr: 1.40-2.08 (m, 4H), 5.28 (br s, 2H), 6.46 (t, 2H)
Endo-2,3,6,7-tetraazatricyclo[5.2.2.05,9]undec-2,6-diene 2-N-Oxide and 3-N-Oxide 37

A solution of diazomethane was generated from 9.3 g nitrosomethylurea (see general procedure). The diazomethane solution was partitioned among three pressure bottles (100 ml capacity), each of which contained 2.0 g (16 mmol) of 36 in 20 ml ether. The bottles were capped and the contents stirred. Soon the heterogeneous mixture became homogeneous and then turned cloudy with the separation of a pale yellow oil. Stirring was continued overnight. The bottles were then cooled to −78°C, and the ether layer decanted from the oil or semisolid product at the bottom of the bottle. Since the decanted ether layers consisted of mainly unreacted starting material, nitrogen could be bubbled through to remove the excess diazomethane and the solvent rtoevaporated to afford a yellow oil which was treated with diazomethane as above. Purification of the combined crude product (9.05 g) was accomplished by chromatography on 300 g fluorisil (EtOAc eluent). Compounds 37a and 37b were obtained as a white powder, mp 85-94°C (5.7 g, 71% yield).
nmr: 1.58-2.06 (m, 3H), 2.06-2.67 (m, 1H), 4.23-4.77 (m, 3H), 5.05 (d, 1H), 5.25-5.45 (m, 1H)
ir (KBr): 1495 (NNO)
uv (EtOH): λmax 322 (ε=413), 230 (ε=6.79 x 10³)
cmr: 89.25 (d, J=2.52), 88.77 (d, J=2.62), 81.34 (t, J=2.30), 79.56 (t, J=2.30), 73.31 (d, J=2.87), 71.47 (d, J=2.55), 58.35 (d, J=2.42), 57.40 (d, J=2.77), 33.70 (d, J=2.72), 30.93 (d, J=2.80), 22.66, 21.79, 21.11, 20.32 (these last four resonances exhibit complex splitting)
anal (C<sub>7</sub>H<sub>10</sub>N<sub>4</sub>O): calcd 166.0854, found 166.0855

**Endo-2,3-diazatricyclo[3.2.2.0<sup>5,7</sup>]non-2-ene N-oxide 38**

Into a 500 ml pyrex photochemical reactor with a gas inlet was added 37 (2.54 g, 15.3 mmol) and 550 ml acetonitrile. After purging, irradiation of the solution for six hours resulted in complete destruction of the azo chromophore. Rotoevaporation of solvent afforded 2.9 g of a pungent orange oil. This oil was purified by chromatography (silica gel, EtOAc eluent) to yield 38 (1.28 g, 61%) as an orange oil.

This material was not pure by nmr (it contained several extra resonances in the olefinic region) but attempts to purify the compound by inducing crystallization from various solvents and also short path distillation failed.

nmr: "0.10-0.18 (m, 1H), 0.27-0.59 (qu, 1H), 1.17-1.50 (m, 2H), 1.54-2.07 (m, 4H), 4.50 (br s, 1H), 4.72 (br s, 1H)

**Endo-2,3-diazatricyclo[3.2.2.0<sup>5,7</sup>]non-2-ene Endo-Cp**

Azoxy compound 38 (1.00 g, 7.24 mmol), lithium aluminum hydride (750 mg, 20 mmol), and 110 ml dry ether were added to a 250 ml flask fitted with a reflux condenser and nitrogen inlet. A mildly exothermic reaction ensued and the resulting brown heterogeneous mixture was stirred for two hours at reflux. Excess LAH was then decomposed by adding successive portions of 0.75 ml water, 0.75 ml 15% aq. NaOH, and 2.25 ml water and stirring for one hour. The white inorganic salts were removed by filtration. Separation of layers, drying (K<sub>2</sub>CO<sub>3</sub>), and removal of ether by distillation under nitrogen yielded a yellow oil
which was purified further by preparative gc (5% SE-30, 5" x 0.375", oven 128°C) to furnish Endo-Cp (118 mg, 13%) as a colorless oil, mp -2-0°C.

nmr: -0.27 to 0.11 (m, 1H), 0.11-0.36 (q, 1H), 1.03-1.93 (m, 6H), 5.22 (br s, 2H)

uv (benzene): λ_{max} 379 (ε=214), 368 (s) (ε=114)

anal (C_{7}H_{10}): calcd 94.0783, found 94.0786 (m-N_{2}, no m^{+} peak seen)

**Addition of Diazomethane to 27a to Afford 41a and 41b**

A pressure bottle (100 ml capacity) was charged with 27a (2.0 g, 10 mmol) and 20 ml ether. A solution of diazomethane generated from 2.0 g (20 mmol) nitrosomethylurea (see general procedure) was then added, the bottle capped, and the contents stirred at 60°C overnight. The bottle was then cooled to -78°C and uncapped. An nmr spectrum revealed the presence of substantial amounts of starting material in the oil obtained from rotoevaporation of solvent so this oil was treated with an additional batch of diazomethane as above. After rotoevaporation of solvent and pumping under full vacuum, 2.12 g of a white semisolid was obtained. An nmr of the N-Me region revealed two products were produced in a 60:32 ratio along with 8% starting material. These products could be separated by prep tlc (EtOAc eluent). The slowest band (R_f = 0.05) had an absorption in the region expected for a pyrazoline (λ_{max}=323 nm in CH_{2}Cl_{2}) and was assigned the endo structure 41a. The next band (R_f = 0.14) had a similar absorption (λ_{max}=325 nm in CH_{2}Cl_{2}) and was assigned the exo configuration 41b. Adduct 41a was an oil while 41b was crystalline, mp 153-155°C.
nmr (41a): 1.75-2.55 (m, 5H), 2.97 (s, 3H), 4.13-4.26 (m, 1H), 4.40-5.08 (m, 3H), 5.14-5.30 (m, 1H)
nmr (41b): 1.32-1.90 (m, 4H), 2.23-2.64 (m, 1H), 3.07 (s, 3H), 4.08-4.21 (m, 1H), 4.27-5.10 (m, 3H), 5.10-5.26 (m, 1H)

uv (41b, EtOH): \( \lambda_{max} \) 324 (\( e = 408 \))

1,4-Dichloro-2,3-diazabicyclo[2.2.2]oct-2-ene N,N'-dioxide 42a

The procedure of Pilgoty and Steinbock\(^{58} \) was followed. Chlorination of 10 g 1,4-cyclohexanedione dioxime\(^{135} \) yielded 1.43 g (10\%) of 42a, mp 175° (dec) along with 12.3 g (83\%) of trans-1,4-dichloro-1,4-dinitrosocyclohexane, mp 108-110°.

nmr (HOAc-d\(_4\)): 2.68 (m)

ir (KBr): 1444, 1398, 1350 (cis diazox)\(^{57} \)

uv (MeOH): \( \lambda_{max} \) 271 (\( e = 6500 \))

1,4-Dichloro-2,3-diazabicyclo[2.2.2]oct-2-ene N-oxide 43a

A 50 ml flask fitted with a nitrogen inlet and rubber septum was heated with a heat gun under a strong nitrogen flow. When the flask had cooled, it was charged with 42a (0.90 g, 4.3 mmol) and 40 ml chloroform (freshly distilled from \( \text{P}_2\text{O}_5 \)). Hexachlorodisilane (0.80 ml, 4.8 mmol) was then added via disposable syringe. The heterogeneous mixture was stirred for two hours. After one hour, the reaction mixture had turned homogeneous. The reaction was quenched with 15 ml 1 M NaOH (caution- the reaction of this reagent with hexachlorodisilane is very exothermic), the inorganics filtered off, and the layers separated. The organic layer was washed with water, dried (\( \text{K}_2\text{CO}_3 \)), and the solvent
rotoevaporated to yield 43a (0.84 g, 100%) as a white solid, mp 184-185⁰. One recrystallization from methanol yielded white needles, mp 188-189⁰; lit.²⁷ mp 186⁰.

nmr: 2.45 (m)

ir (CHCl₃): 1498 (N=N), 1335 (N-O)

uv (EtOH): λ_max 230 (ε=6.85 x 10³)

1,4-Dichloro-2,3-diazabicyclo[2.2.2]oct-2-ene Di-Cl

The procedure of Luttke and Schabacker²⁷ was used. From 0.84 g (4.3 mmol) 43a, 0.62 g (81%) of Di-Cl was obtained after recrystallization from methanol. A second recrystallization afforded long, white needles, mp 184-185⁰; lit.²⁷ mp 182⁰.

nmr: 2.06 (m)

uv (benzene): λ_max 366 (ε=128)

ms: m/e 154 (m⁺ + 4 minus N₂), 152 (m⁺ + 2 minus N₂), 150 (m⁺ minus N₂), 80 (m⁺ minus N₂ and Cl₂)

1,4-Dibromo-2,3-diazabicyclo[2.2.2]oct-2-ene N,N'-dioxide 42b

Bromination of 1,4-cyclohexane dione dioxime (10 g, 0.070 mol) by the procedure of Piloty and Steinbock⁵⁸ yielded 42b (0.71 g, 2.6%) as a white powder along with trans-1,4-dibromo-1,4-dinitrosocyclohexane (9.6 g, 36%) as deep blue crystals. The diazoxy compound was pure enough for use in the next step. A sample crystallized from methanol as white needles, mp 129-130⁰ (dec).

ir (KBr): 1442, 1398, 1345 (cis diazoxy)

uv (MeOH): λ_max 272 (ε=7.02 x 10³)
1,4-Dibromo-2,3-diazabicyclo[2.2.2]oct-2-ene N-oxide 43b

This procedure was the same as that for the corresponding 1,4-
dichloro compound 43a, except that the reaction mixture was stirred
overnight. From 554 mg (1.85 mmol) of 42b, 530 mg (100%) of 43b
was obtained as a white solid. A sample crystallized from methanol as
small, dense crystals, mp 213-215° (dec).
nmr: 2.53 (m)
ir (KBr): 1478, 1445 (N=N), 1330 (d), 1275 (d) (N-O)
uv (benzene): λmax 232 (ε=6.74 x 10³)
anal (C₆H₈NBr₂, m⁺ - NO): calcd 251.90227, found 251.9020

1,4-Dibromo-2,3-diazabicyclo[2.2.2]oct-2-ene Di-Br

The procedure of Luttke and Schabacker27 was used. To a 25 ml
flask was added 43b (390 mg, 1.37 mmol) and 8 ml triethyl phosphite.
A reflux condenser and nitrogen inlet were attached and the mixture
heated to reflux one hour. After cooling to room temperature, the
phosphorus compounds were removed under vacuum yielding a semisolid
residue. This was taken up in hot methanol. The azo compound (264 mg,
72%) was isolated as long needles. A second recrystallization furn-
nished material of mp 210-211°. During a study of the fluorescence pro-
erties of this compound, the presence of an impurity was revealed in
the excitation spectrum. Sublimation (105-130°, 0.05 mm) removed this
impurity.
nmr: 2.21 (AB q )
uv (benzene): λmax 366 (ε=129)
ms: m/e 242 (m⁺ + 4 minus N₂), 240 (m⁺ + 2 minus N₂), 238 (m⁺ minus N₂)
anal (C₆H₈Br₂, m⁺ – N₂): calcd 237.8992, found 237.8990

Preparation of the bis-hydrazone of 1,4-cyclohexanedione³³⁶

Into a 100 ml flask fitted with a reflux condenser and drying tube was added diketone (1.50 g, 0.013 mol), 30 ml EtOH, 30 ml (0.42 mol) Et₃N, and 3.3 g (0.10 mol) 97% hydrazine. The resulting yellow, homogeneous mixture was stirred at reflux overnight. Ethanol was then distilled off and the higher boiling components removed under vacuum. A brownish oil was obtained which slowly crystallized upon standing. One recrystallization afforded light tan crystals (1.25 g, 68%) mp 120-122⁰.

nmr: 2.20-2.76 (m, 8H), 4.80 (br s, 4H)

ir (KBr): 1630 (d) (C=N)

1,4-Diiodo-1,3-cyclohexadiene³³⁵,³³⁶

A 1 l flask equipped with an addition funnel and nitrogen inlet was charged with the above bis-hydrazone (5.0 g, 0.036 mol), 300 ml benzene (over Na), and 150 ml Et₃N (dried by passage through alumina). While this mixture was stirred, iodine (48 g, 0.19 mol) in 400 ml benzene was added over a period of one hour. During the addition, a white ppt formed (Et₃NH⁺ I⁻) and gas evolution was observed. When all of the iodine solution had been added, the reaction mixture (which was at this point black) was stirred for 15 minutes and filtered. The filtrate was washed with 4% HCl until the washings were acidic (4x100 ml), and then washed with 100 ml portions of water, aq Na₂SO₃, water again, and aq NaHCO₃. The black solution was dried over MgSO₄ and filtered.
The benzene solution was then placed into a 1 l flask fitted with a dropping funnel and a nitrogen inlet. A solution of DBU (10.8 g, 0.071 mol) in 40 ml benzene was added, the reaction mixture refluxed (3 hrs), and then filtered. The filtrate was washed with 100 ml portions of 4% HCl, water, and aq NaHCO₃. After drying (MgSO₄), the solvent was rotoevaporated to yield a dark residue which was dissolved in a minimum of methylene chloride, placed onto a 100 g silica gel column, and eluted with 10% EtOAc-hexane. A mixture of 1,3 and 1,4 dienes (3:1) was obtained as light orange crystals, mp 91-92°. The yield of the diene mixture was 3.75 g (31%).

nMr (45): 2.69 (s, 4H), 6.20 (s, 2H)
nMr (1,4-diiodo-1,4-cyclohexadiene): 3.13 (s, 4H), 6.08 (s, 2H)

4-Methyl-1,7-diiodo-1,2,4-triazatricyclo[5.2.0.0²,⁶]undec-8-ene-3,5-dione 46

The above diene mixture (2.70 g, contains 6.1 mmol 1,3 diene) was placed in a 50 ml flask equipped with a dropping funnel. Ethyl acetate (20 ml) was added and the mixture was cooled in an ice bath. A solution of triazolinedione 24a was added in 10-20 drop increments to the diene mixture and progress of the reaction was monitored by gc (10% XE-60, 20' x 0.125", oven 160°; retention times were, 1,4 diene, 14.4 min; 1,3 diene, 18.0 min). When greater than 95% of the 1,3 diene had been reacted, the white crystals that had precipitated out of the reaction mixture were collected by Buchner filtration, washed with several portions of hexane, and air dried. The yield of 46 so obtained was 1.94 g (76%), mp 79-80° (dec).
nmr: 2.22-2.52 (m, 2H), 2.70-3.12 (m, 2H), 2.97 (s, 3H), 6.45 (s, 2H)
Since this adduct decomposed rather quickly to a black oil which was acidic, it was quickly hydrogenated to 47. This latter compound was stable indefinitely.

4-Methyl-1,7-diiodo-2,4,6-triazatricyclo[5.2.0.0^2,6]undecane-3,5-dione 47

A 250 ml flask fitted with a mechanical stirrer, dropping funnel and nitrogen inlet was charged with dipotassium azodicarboxylate,\(^{137}\) 46 (1.94 g, 4.34 mmol), and 75 ml methanol. The flask contents were stirred to a paste and cooled in an ice bath. Acetic acid (24 ml, 0.38 mol) was added over a 45 minute period and the ice bath was removed. An additional 12 ml acetic acid was added to the reaction mixture and stirring was continued overnight. The reaction mixture was worked up by pouring it onto 100 ml water, extracting with CH\(_2\)Cl\(_2\) (6x50 ml), and washing the organic layer with saturated NaHCO\(_3\) solution (2x100 ml, the second wash was basic). After drying over MgSO\(_4\), rotoevaporation of solvent yielded tan crystals. An nmr revealed that these crystals consisted of about 75% 47 with the remainder starting material. A sample of this mixture could be hydrogenated completely at one atmosphere using Adam's catalyst (an attempt to hydrogenate pure 46 using Adam's catalyst led to extensive decomposition of this material and little hydrogen uptake). Adduct 47 crystallized from methanol as white needles, mp 170-171 (dec).

nmr: 2.51-3.01 (distorted q, 8H), 3.10 (s, 3H)
1,4-dicyano-1,4-hydroxylaminocyclohexane 52

This procedure is after Porter and Hellermañ61 who ran this reaction on the oxime of cyclohexanone. A 100 ml Morton flask, equipped with a mechanical stirrer and addition funnel, was charged with 1,4-cyclohexanedione dioxime\(^{135}\) (2.84 g, 0.0200 mol), \(\text{KH}_2\text{PO}_4\) (19.1 g), and 100 ml water. The dioxime had been pulverized to a fine powder with a mortar and pestle. The reaction mixture was then cooled in an ice bath and a solution of 3.62 g (0.10 mol) \(\text{NaCN}\) in 10 ml water was introduced over a 20 minute period. Stirring of the reaction mixture was continued for 10 days at room temperature. The tan crystals were collected by Buchner filtration, washed with several portions of water, and air dried. Compound 52, mp 169-170\(^0\) (dec), was not soluble in the common organic solvents. The yield of the reaction was 3.64 g (97%).

\(\text{ir (KBr): 3320} \text{ (broad envelope, O-H), 2265 (C\equiv N)}\)

\(\text{ms: m/e 169 (m}^+\text{ minus HCN)}\)

**Attempted Formation of Di-Cyano Di-Azoxy Compound 53**

Into a 25 ml flask fitted with a mechanical stirrer, gas inlet, and gas outlet to an oil bubbler was added 52 (1.25 g, 6.4 mmol) and 15 ml 5% HCl. This slurry was stirred and cooled to 0\(^0\) at which time chlorine gas was introduced into it. After about one hour, an excess of chlorine had been added as evidenced by gas escaping through the bubbler. The light blue crystals were isolated by collection with a Buchner funnel. The melting point behavior of this blue substance was most interesting. At 105-107, the crystals changed from blue to white
and at 138° they melted to a colorless oil. An ir (KBr) revealed no evidence for the cis azoxy functionality and the synthesis was dropped at this point.

**Attempted Formation of Adduct 57**

Into an nmr tube was placed 30 mg (0.15 mmol) of diene $^{56}_{64}$ and 45 mg (0.22 mmol) of benzyl azodicarboxylate.$^{138}$ Benzene-$d_6$ was then introduced and the reaction mixture was irradiated with light from a 450 W mercury lamp using a pyrex filter. After 7 hours irradiation time, a complex mixture was produced as shown by both nmr and tlc (at least 5 components). This synthesis was not pursued further.

**Attempted Halogen-Lithium Exchange Reactions with Di-Cl and Di-Br**

Several attempts were made to exchange the halogens of both Di-Cl and Di-Br with lithium. The attempt recounted here is fairly typical. A 25 ml flask was dried in the oven and and equipped with a mechanical stirrer, rubber septum, and nitrogen inlet (the nitrogen was dried by bubbling through $H_2SO_4$ and passage through $CaCl_2$). About 10 ml reagent hexane (dried by distillation from sodium immediately before use) was added to the flask along with 102 mg (0.57 mmol) of Di-Cl. This heterogeneous mixture was stirred while 1.0 ml (1.3 mmol) of a 1.3 M solution of t-butyllithium in pentane was added via syringe. The two phase mixture turned from light yellow immediately after the addition of the lithium reagent to a light brown after stirring over a weekend (69 hours). An aliquot of the reaction mixture was worked up by adding 1 ml EtOH, diluting it with water, and extrac-
ting with CH₂Cl₂. The organic layers were then washed with water and dried (K₂CO₃). The solution was then placed in a molecular still, the solvent removed at atmospheric pressure, and the azo compound sublimed (40⁰, 0.1 mm). A uv of the sublimed material revealed an absorption maximum at 366 nm (A=0.7) which corresponds to that of Di-Cl. No absorption corresponding to that of DB0 (λ_max=379 nm), which is the product expected from hydrolysis of the bridgehead dilithiated compound, was found. After refluxing the rest of the reaction mixture overnight, a similar result was obtained. The above procedure was tried on Di-Br with analogous results.

3,3,6,6-Tetramethyl-1,2-diazacylohexene 6

This azo was made in 15% yield by the procedure of Greene and Gilbert⁵⁷ and purified by distillation, bp 49⁰, 3.8 mm; lit. bp 48-50⁰, 4.2 mm, ⁵⁷ 62⁰, 12 mm;¹⁰ 48⁰, 4 mm.¹³⁹

nmr: 1.29 (s, 12H), 1.49 (s, 4H)

uv (hexane): λ_max 380 (ε=144); lit.¹⁰ (hexane) 380 (138)

N-N'-Dicarboxyethoxy-1,2-diazacyclohex-4-ene 64

Methyl azodicarboxylate (13.1 g, 90 mmol) and butadiene (42 ml, 26g, 0.48 mol) were reacted according to the procedure of Bishop.⁶¹ Compound 64 (15.50 g, 86%) was obtained as a clear oil, bp 122⁰, 1.3 mm. This oil eventually solidified to a white solid, mp 40-43⁰.

nmr: 3.65-4.03 (m, 2H), 3.75 (s, 6H), 4.25-4.60 (m, 2H), 5.76-5.85 (m, 2H)
**N,N'-Dicarbomethoxy-1,2-diazacyclohexane 65**

Adduct 64 (3.0 g, 0.015 mol) was hydrogenated at atmospheric pressure using 0.03 g Pd/C catalyst and 120 ml absolute ethanol. Rotoevaporation of solvent and molecular distillation (90-110°, 1.8 mm) yielded 65 (2.43 g, 81%) as an oil which eventually crystallized upon storage in the freezer, mp 40-41.5°.

**nmmr:** 1.53-1.83 (m, 4H), 2.74-3.15 (m, 2H), 3.72(s, 6H), 3.97-4.30 (m, 2H)

**N,N'-Dicarbomethoxy-3,4-diazabicyclo[4.1.0]heptane 66**

This compound was prepared by carbene addition to 64 by the procedure of Bishop. Separation of 66 from unreacted starting material (64) was accomplished by prep gc (15% SE-30, 6' x 0.375", oven 185°, retention times, 64, 12.6 min, 66, 19.2 min). Compound 66 was obtained as a white solid, mp 66-70°.

**nmmr:** 0.05-0.40 (m, 1H), 0.60-1.44 (m, 3H), 3.05-3.53 (m, 2H), 3.72 (s, 6H), 4.00-4.56 (m, 2H)

**3,4-Diazabicyclo[4.1.0]hept-3-ene 61**

A solution of 113 mg (0.53 mmol) of 66 in 590 mg of a 25% solution of KOH in methanol was refluxed for 3 hours under nitrogen. The reaction mixture was then allowed to cool and the methanol was removed under reduced pressure. The semisolid residue was triturated with ether and the ether extracts were filtered through a short Na₂SO₄ column into a graduated centrifuge tube. Ether was added to bring the volume of the extracts to 5 ml. HCl gas, dried by passage through H₂SO₄ and
CaSO₄, was then passed into the ether solution until the solution was acidic to litmus. The solution was very turbid at this point. Crystals of the hydrochloride salt precursor to 61 were obtained by centrifuging the cloudy solution and carefully decanting off the ether. The hydrochloride was quickly placed into a dessicator and dried under full vacuum. The yield was 69.6 mg (98%).

The hydrochloride salt (30 mg, 0.22 mmol) was then treated with enough 10% KOH in methanol to turn the solution basic to litmus. The methanol was removed under vacuum and the resulting residue was taken up in ether. After filtering the ether solution through a short Na₂SO₄ column, most of the ether was removed in vacuo and two drops of Et₃N and two drops hexadecane chaser were added along with 2 ml EtOAc to the residue. This solution of the hydrazine precursor to 61 was then distilled through a short path column.

A solution of 61 suitable for low temperature photolysis work was prepared in the following manner. A solution of 48 mg t-BuOCl in 3 ml EtOAc was freshly made and 1 ml of this solution was added to the above solution of hydrazine at -78⁰ contained in a low temperature recrystallization apparatus. The amount of t-BuOCl added (0.15 mmol) was enough to insure an A₃₆₅>2.0. After stirring for several minutes, the solution was filtered directly into the low temperature photolysis apparatus. Compound 61 had an absorption maximum at 373 nm.

1,2-Diazacyclohexene 60

This compound was prepared in a manner analogous to that above. A solution of this azo in EtOAc had an absorption maximum at 370 nm.
3,5-Dicyano-3,6-dimethyl-1,2-diazacycloclohexane 63

This compound was prepared in two steps by the procedure of Overberger, et al.;\(^67\) mp 109-111°; lit.\(^67\) mp 99-100°.

3,6-Dicyano-3,6-dimethyl-1,2-diazacyclohexene 62

A solution of this thermally labile azo was prepared by adding 2.0 ml of a solution of t-BuOCl (16.2 mg/3 ml EtOAc) to 4.0 ml of a solution of hydrazine 63 (68.0 mg/10 ml EtOAc) at -78° C. The amount of t-BuOCl added represented a 15% deficiency of this reagent relative to the hydrazine. The solution of azo thus obtained had an absorption maximum at ca. 383 nm.
I. Spectra
J. Appendix I-Computer plots of absorption and emission of DBO derivatives in benzene (unless otherwise noted)
RELATIVE INTENSITY

--- CB

--- CPCB

(ex. slit=3.5 mm; em. slit=4.0 mm)

EXTINCTION COEFFICIENT
RELATIVE INTENSITY

--- Endo-Cp
(ex. slit=3.5 mm; em. slit=4.0 mm)

--- Exo-Cp
(in hexane at ca. 0°C; ex. slit=6.0 mm; em. slit=3.0 mm; λ = 360 nm)

EXTINCTION COEFFICIENT
Appendix II—Actual output of the lamp and filter system used for photolyses at 366 nm as monitored by a monochromator-phototube arrangement. Monochromator slit settings: entrance=1 nm; exit=2 nm.

<table>
<thead>
<tr>
<th>$\lambda$, nm</th>
<th>voltage</th>
<th>$\lambda$, nm</th>
<th>voltage</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>0.011</td>
<td>370</td>
<td>6.6</td>
</tr>
<tr>
<td>440</td>
<td>0.011</td>
<td>366</td>
<td>6.6</td>
</tr>
<tr>
<td>430</td>
<td>0.010</td>
<td>360</td>
<td>6.4</td>
</tr>
<tr>
<td>420</td>
<td>0.011</td>
<td>355</td>
<td>2.4</td>
</tr>
<tr>
<td>410</td>
<td>0.011</td>
<td>350</td>
<td>0.34</td>
</tr>
<tr>
<td>405</td>
<td>0.011</td>
<td>340</td>
<td>0.12</td>
</tr>
<tr>
<td>400</td>
<td>0.013</td>
<td>335</td>
<td>0.10</td>
</tr>
<tr>
<td>395</td>
<td>0.022</td>
<td>330</td>
<td>0.080</td>
</tr>
<tr>
<td>390</td>
<td>0.027</td>
<td>320</td>
<td>0.009</td>
</tr>
<tr>
<td>385</td>
<td>0.092</td>
<td>310</td>
<td>0.008</td>
</tr>
<tr>
<td>380</td>
<td>0.13</td>
<td>300</td>
<td>0.006</td>
</tr>
<tr>
<td>375</td>
<td>0.27</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
K. References and Notes

1. For reviews of cyclic azo photochemistry, see refs. 2 and 3; for a table of biradicals synthesized from azo compounds, see ref. 2, p 143.


4. Certain 3,4 cyclopropanated and cyclobutanated pyrazolines (below) upon photolysis yield products not only formally derived from biradicals but also from diazo compounds:

\[
\text{(CH}_2)_n\text{H} \xrightarrow{\text{h}v} \text{N}^+\text{N}^-
\]

n=1,2


9. A photo-inert pyrazoline is shown below.

```
\text{N=O}
```


90, 2249 (1968).


21. The convention of Allred (ref. 46) will be used in describing rings anti to the azo moiety as exo and rings syn as endo. Pacquette and Epstein (ref. 24) refer to syn rings as exo.


28. This scheme is taken from ref. 2.


32. B. Jacobson, personal communication.


38. For a study of the effect of temperature on some cyclicazoalkanes and ketones, see:


39. For recent studies regarding the effect of temperature on the product distribution from photolysis of cyclicazoalkanes, see:


40. Recently, a study of the photochemistry of many cyclicazoalkanes in different solvents has been published:


43. R. C. Cookson, S. S. H. Galani, and I. D. R. Stevens, J. Chem. Soc. C., 1905 (1967); see also ref. 56.


45a. For syntheses of DBO, see ref. 41; ref. 44.

b. For syntheses of Di-Me, see ref. 44; ref. 80.

c. For syntheses of CB, see ref. 20; ref. 46.


47. An adduct similar to 31 has recently been reported from the reaction of 24a with cyclooctatetraene:


50. This gift from professor W. R. Roth (via professor J. P. Snyder) is gratefully acknowledged.


53. It is known that increased pressure (5000 atm.) can aid the 1,3 dipolar cycloadition of diazomethane to an unactivated double bond (H. de Suray, G. Leroy, and J. Weiler, Tetrahedron Lett., 2209 (1974)) but apparently the effect of temperature on the rate of this cycloadition has not been studied.


55. For references establishing the desheilding effect of the azo moiety, see:


60. The effective van der Waals radius of the methyl group is 2.0 Å while that of iodine is 2.15 Å:


69. Professor J. P. Snyder (personal communication) reports that diazomethane seems to have no effect on the N-oxide moiety; some theoretical calculations on the charge distribution of this group revealed that it was much more like a nitro group than a nitrene.

70. For a description of the syntheses of these compounds, see:

71. For reviews of the spectroscopy of azoalkanes, see ref. 72 and ref. 40.


79. Ibid., p 125.


82. It is known that in the presence of hydrogen donors, photolysis of benzophenone can produce light absorbing transients (LAT's):


83. For a discussion, see:


84. The diffusion controlled rate in benzene for quenching of biacetyl phosphorescence is $1 \times 10^{10}$ m$^{-1}$sec$^{-1}$:


87. Actually, in the case of acceptors with extremely short lifetimes like DBQ (τ<10⁻⁹ sec),11 back energy transfer from acceptor to donor should not be possible. It thus appears that quenching will become inefficient when ET(donor)-ET(acceptor)<0 kcal/mol in this case and not when this difference is <3 kcal/mol. This fact does not alter the arguments in section C.4., however.

88. For a diagram illustrating this point, see ref. 78, p 63.

89. For an equation relating the energy separation between the triplet energy of donor and acceptor and the rate of energy transfer (i.e. kQ) see:


90. O. L. Chapman and R. A. Hayes, unpublished results at UCLA.


92. A supply of 72 from professor J. W. Timberlake is gratefully acknowledged.

93. Authentic 74 was made according to the procedure of G. B. Butler and M. A. Raymond, J. Org. Chem., 30, 2414 (1965). A generous supply of the sulfone below, used to initiate the synthesis of 74, was kindly provided by professor Timberlake.

\[
\begin{align*}
\text{CH}_2\text{Br} & \\
\text{SO}_2 & \\
\end{align*}
\]

94. These compounds were identified by nmr comparison with the known spectra:


96. The sensitized quantum yields were carried out using benzophenone and also p-methoxyacetophenone as sensitizers and irradiating at 313 nm (a wavelength at which MV does not absorb appreciably).


99. An nmr spectrum of the crude reaction mixture from photolysis of Endo-Cp (gas phase, 70°C) revealed a compound which had resonances in the cyclopentyl region. Since these resonances did not correspond to those reported for anti-tricyclo[4.1.0.0²⁵]heptane (11a), it is probable that this product is the syn isomer. An attempt to purify this compound from other components in the crude photolysate and to secure its identity was unsuccessful, however.


109. This model and the resulting mathematical treatment are similar to those used to explain temperature effects in other systems.
110. This discussion is essentially that of ref. 38.


114a. α-Methylation of ketones and ring strain has been shown to decrease $k_{ISC}$ in ketones, see:


b. Addition of methyl groups to the benzene ring enhances $\Phi_f$, see ref. 97 ($\tau_f$ is unaffected, however).

115. Ref. 102, p 256.

116. To obtain an idea of how quickly the triplet state of azoalkanes can deactivate, Clark and Stee11 have estimated the triplet lifetime of DBO as $<10^{-10}$ sec.


b. This number was determined by irradiating 86 in benzene solution at 335 nm using a high intensity monochromator, measuring the rate of azoalkane disappearance by uv, and comparing this rate to that of a solution of DBH ($\Phi_f = 1.0$) under identical conditions.


120. The compounds with short fluorescence lifetimes also exhibited a relatively long lived fluorescence component. The lifetime of this component for each of the azos is as follows: MV, 9.4 nsec; DV, 8.0 nsec; Exo-Cp, 11 nsec; DM, 5.9 nsec.


122. An authentic sample of 1,4-cycloheptadiene was prepared by thermal
decomposition of Exo-Cp. 20


b. For an excellent discussion of the $[4_5+2_2]$ cycloreversion in azo systems, see:


127. N-methyl adducts were prepared in this work. For properties of the corresponding N-phenyl adducts, see ref. 43.


129. While the melting point does not agree with that of the literature, the nmr spectrum of 27c agrees perfectly with the one described in ref. 76.

130. This compound was made in two steps starting from 1,5 cyclooctadiene; see ref. 48.


133. I would like to thank professor E. L. Allred for sending an nmr spectrum of this material.

134. This procedure makes work-up easier, see:


137. This was prepared from azodicarbonamide according to the procedure of J. A. Berson, M. S. Poonian, and W. J. Libbey, J. Am.

138. This material was a gift from Professor J. W. Timberlake.


145. The question of the ring strain in DBO and Di-Me is currently under investigation in this laboratory. A lower ring strain of Di-Me relative to DBO has been advanced as one explanation for the surprisingly small difference in the thermal activa-parameters of these two compounds (see ref. 10).
Part II

The Synthesis and Thermal Rearrangement of 1-Vinylbicyclo[2.2.0]hexane
A. Introduction

An amazing result from the azo work recounted in Part I was the complete absence of ring closed product 1-vinylbicyclo[2.2.0]hexane (1) from the photolysis of MV. Since 1 was an unknown compound, it was decided to synthesize it by an independent route to assess its stability.

\[
\text{MV} \xrightarrow{\text{hv}} \text{[no]} \quad \text{100%}
\]

The bicyclo[2.2.0]hexane moiety is one of the rarer structures in organic chemistry, a situation that apparently reflects the difficulties encountered in gaining entry into this system.\(^1\) Photochemical reactions are generally required to gain access to bicyclo[2.2.0]hexanes and therefore special conditions and quartz apparatus are often required. The syntheses of these compounds fall into three main categories.\(^2\)

1. Photochemical or thermal extrusion of CO, N\(_2\), or some other stable molecule from a suitable precursor.


3. Electrocylic ring closure of a constrained 1,3 cyclohexadiene system.

Many examples of synthesis via category 1 can be found with respect to the parent compound 2. Photolysis of the bicyclic heptanone
3 in the gas phase furnishes 2, albeit in low yield (ca. 5%). Actually, the major product from this reaction is 1,5 cyclohexadiene 5. The primary fate of the 1,4 biradical 4 is thus 2,3 bond rupture to yield 5 at the expense of 2. This problem occurs to a lesser extent in the photolysis of DBO. In this case, the initially formed diradical 6 undergoes ring closure to the extent of 42%. Pyrolysis of oxazine 7 offers perhaps the best synthesis of 2. A 60% yield of the bicyclic compound is obtained along with only a 35% yield of 5. Compound 2 has additionally been obtained in low yield from thermolysis of 1,1-diazene 8 and photolysis of ketone 9. Compound 5 is an additional product in these cases also.

Synthesis of bicyclo[2.2.0]hexanes by the intermolecular [2+2] cycloaddition route has been explored by Owsley and Bloomfield. These workers have shown that the low temperature addition of ethylene to dimethylcyclobutene dicarboxylate 10 occurs quite readily to afford 11.
In fact, 11 is obtained in quantitative yield. An interesting extension of this reaction is the discovery by these same workers\(^9\) that 11 could be made in good yield from dimethyl acetylenedicarboxylate by low temperature photoaddition of two equivalents of ethylene. Although the product was contaminated with 10% dimethyl bicyclopropyl-1,1'-dicarboxylate 12, a convenient one step entry into the bicyclo[2.2.0]hexane system from readily obtainable starting material was achieved.

An example of the third method of synthesis of bicyclo[2.2.0] hexanes is the valence isomerization of cyclohexadiene 13 to 14.\(^10\) Treatment of 14 with lead tetraacetate then furnished dewar benzene 15 in good yield. Note that in 13 photoisomerization to hexatriene 16, the typical photochemical reaction of 1,3-cyclohexadienes,\(^11\) is precluded due to the steric crowding that would develop between the hydrogens.
on carbons 3 and 8 in the transition state leading to 16.

Of the methods outlined above, the one that seemed to offer the most promise for gaining entry into the 1-substituted bicyclo[2.2.0]hexane system and of therefore furnishing a suitable precursor for 1-vinylbicyclo[2.2.0]hexane was that of intermolecular [2+2] cycloaddition of ethylene with a cyclobutene. In the past several years, there has been considerable interest in the use of cyclobutene carboxylates as isoprene equivalents in the synthesis of germacrandienes, a sesqui-terpene family characterized by the presence of a ten membered ring. The strategy is outlined below. Addition of a cyclobutene carboxylate
17 to cyclohexene yields the bicyclohexane adduct 18 which through thermally induced ring opening affords the germacradiene derivative 19 or its Cope rearrangement product 20. Wender and Lechleiter[^14] have recently extended this cycloaddition to the synthesis of 1-carbomethoxybicyclo[2.2.0]hexane 21.

![Chemical structure](image)

While 21 would appear to be an ideal precursor for 1 via a synthetic route involving reduction to alcohol, oxidation to aldehyde, and Wittig reaction, trouble was anticipated at the oxidation step. Collins oxidation of diol 22 in this laboratory, for example, yielded only dialdehyde 23, even at 0 °C. This result, coupled

![Chemical structure](image)

with a previous failure in this laboratory at obtaining the extremely sensitive cyclobutene carboxylate 17a,[^14] made an alternative route to 1 based upon a [2+2] cycloaddition reaction attractive. The results of this alternative route and the eventual synthesis of 1 will be now be recounted.
B. Attempted Synthesis of 1-Vinylbicyclo[2.2.0]hexane via a Tosylhydrazone Decomposition

Since α,β cyclohexenones and cyclopentenones are known to react efficiently with olefins under the influence of uv light,\textsuperscript{15} attention was directed to the synthesis of methylcyclobutanyl ketone \textsuperscript{26}, a compound first synthesized in this laboratory several years ago.\textsuperscript{16} Photoaddition of \textsuperscript{26} with ethylene would then furnish a 1-substituted bicyclo-

\[
\text{CO}_2\text{Me} \quad \text{Br} \quad \xrightarrow{\text{KOH, toluene, } \Delta} \quad \text{CO}_2\text{H} \quad \xrightarrow{1) \text{2eq MeLi}} \quad \text{O} \quad \xrightarrow{2) \text{aq NH}_4\text{Cl}} \quad \text{OH}
\]

\textbf{24} \quad \textbf{25} \quad \textbf{26} \quad \textbf{27}

hexane which could be transformed through known chemistry to \textsuperscript{1}. It was thought that the use of \textsuperscript{26} would offer a distinct advantage over the cyclobutene ester \textsuperscript{17a} in the cycloaddition step because it possessed a long wavelength chromophore (λ\text{max} = 324 nm in CH\textsubscript{2}Cl\textsubscript{2}). The reaction could therefore be carried out using common pyrex photochemical equipment.

Synthesis of \textsuperscript{26} was achieved by reaction of unsaturated acid \textsuperscript{25} (which was not isolated) with two equivalents of methyllithium and subsequent hydrolysis with aqueous ammonium chloride.\textsuperscript{17} The acid in turn was readily obtained in 64% yield by the procedure of Dauben and Wiseman.\textsuperscript{18} Invariably, \textsuperscript{26} synthesized in this manner was contaminated with small amounts of carbinol \textsuperscript{27} (ca. 10%),\textsuperscript{19} but this impurity was readily removed in a subsequent step. In view of the tendency of \textsuperscript{26}
to polymerize, it was stored as a dilute solution (0.03 M) with a small amount of t-butyl catechol inhibitor.

As expected, irradiation of 26 in the presence of ethylene afforded the bicyclic ketone 28. This major product, however, was contaminated with a small amount of an isomeric substance, which was identified as 2-acetyl-1,5-hexadiene 29 on the basis of spectral evidence (below). Further study of the photoreaction revealed that the formation of 29 was favored by long irradiation time (Table 1).

Table 1

<table>
<thead>
<tr>
<th>Reaction Time</th>
<th>28:29</th>
</tr>
</thead>
<tbody>
<tr>
<td>45 minutes</td>
<td>87:5 (+ 8% 26)</td>
</tr>
<tr>
<td>120 minutes</td>
<td>72:28</td>
</tr>
</tbody>
</table>

It is apparent from Table 1 that the primary photoproduction is 28 with longer irradiation times leading to decomposition of this substance to 29. This photodecomposition of 28 is reminiscent of the β-cleavage reaction of cyclopropyl ketones. A particularly relevant example of this latter reaction is the irradiation of 30 by Winter
and Landauer\textsuperscript{21} to yield \textbf{31}. By analogy to the mechanism for \(\beta\)-cleavage of cyclopropyl ketones,\textsuperscript{20} it is proposed that electronic excitation of \textbf{28} results in the rupture of the strained 1,4 bond and production of the diradical \textbf{32}. This diradical then either reverts back to \textbf{28} or undergoes \(\beta\)-scission to \textbf{29}. This mild photochemical cleavage could find eventual use in the synthesis of germacranediene derivatives.\textsuperscript{13}

Structure \textbf{28} was assigned primarily on the basis of the lack of olefinic resonances in the nmr. Furthermore, interaction of the strained central bond with the keto function was indicated in both the ir \((v_{CO} = 1685 \text{ cm}^{-1} \text{ in CHCl}_3)\) and uv \((\lambda_{max} = 295 \text{ nm}, e = 30.6 \text{ in hexane})\) of this compound. Structure \textbf{29} was assigned on the basis of spectral data and the known chemistry of 1,4 diradicals produced from rupture of the central bond in bicyclo[2.2.0]hexanes.\textsuperscript{23}

Upon reaction of \textbf{28} with tosylhydrazine in pentane (room temperature, overnight),\textsuperscript{24} an intractable orange oil was obtained. Reaction with tosylhydrazine in methanol (1 hour, reflux),\textsuperscript{25} however, yielded the crystalline tosylhydrazone \textbf{33} in 34\% yield along with some
orange oil.

The decomposition of 33 with two equivalents of methyllithium to produce 1 was anticipated to proceed smoothly. Indeed, this reaction has been used to synthesize a variety of sensitive and strained olefins. Reaction of an ether slurry of 33 with methyllithium (room temperature, 30 min) followed by removal of ether by distillation and preparative gas chromatography (oven temp. 80°C) of the olefin-smelling residue yielded three components. The major component was identified as 3-methylene-1,6-heptadiene 34 on the basis of spectral data and comparison to authentic material. The second component was shown to be ethenylidene cyclohexane 34 by spectral data. Identification of the third component was not possible due to insufficient quantities of material. Particularly noteworthy is the complete absence of the expected product, 1-vinylbicyclo[2.2.0]hexane 1.

Formation of 35 was quite unexpected and appears to be an unprecedented tosylhydrazone fragmentation reaction. These fragmenta-
tions typically occur only when a leaving group is situated α to the tosylhydrazone moiety. Foster and Agosta, for example, have noted formation of allenes via decomposition of α-alkoxy tosylhydrazones using n-butyllithium. An attempt to fragment the tosylhydrazone of a cyclopropyl ketone (36) by these same workers, however, led exclusively to formation of 37; no other products were detected. Formation of 35 can be rationalized by invoking the known mechanism of decomposition of tosylhydrazones bearing primary α hydrogens and the supposition that the extra 26 kcal mol⁻¹ of strain in 33 relative to 36 provides the driving force necessary for rupture of the central bond (40 → 41 in the scheme below).

The formation of triene 34 could be explained by protonation of vinyl anion 40 upon workup to afford 1 and thermal decomposition of
the latter compound under the conditions used for its isolation. To test this possibility, the decomposition of 33 and the subsequent workup were run under as mild conditions as possible. Treatment of an ether slurry of 33 with two equivalents of methyllithium (0 °C, 1.5 hours) followed by cold workup, removal of solvent at 0 °C, and low temperature (ca. -30° C) nmr analysis of the residue revealed only the presence of triene 34 and allene 35 along with some residual ether. No evidence for 1 was found. This result, coupled with the eventual synthesis of 1 in the following section, proves that had 1 been produced in the above reaction, its presence would have been detected by nmr. Since 34 does not arise from thermal decomposition of 1, further work concerning the formation of 34 via decomposition of 33 is clearly warranted.
C. Synthesis of 1-Vinylbicyclo[2.2.0]hexane via the Wittig Reaction

Since the synthesis of 1 by the tosylhydrazone route failed, an alternative route employing 1-carbomethoxybicyclo[2.2.0]hexane 21 as the key intermediate was explored. Note that a previous attempt in this laboratory at synthesizing 21 by photoaddition of ethylene to cyclobutene ester 17a was thwarted by an inability to obtain this latter compound. Difficulties associated with the synthesis of 17a have been noted by other workers. For these reasons, a route to 21 which avoided isolation of 17a was tried.

By analogy with the work of Owsley and Bloomfield, it was decided to try irradiating methyl propiolate 42 in the presence of ethylene. In addition to offering a one step synthesis of 21, this reaction had the further advantage that the potentially troublesome 17a would be generated in situ at -78°C and therefore problems associated with it would be minimized. Not surprisingly, irradiation of 42 (0.015 M

\[ \begin{align*}
42 & \xrightarrow{\text{hv}} \text{CO}_2\text{Me} \quad 17a \quad 21
\end{align*} \]

in CH₂Cl₂) at -78°C in the presence of ethylene did lead to production of 21 along with a considerable amount of polymer and several minor unidentified products. These impurities could be conveniently removed by distillation, affording essentially pure 21 although the yield (10%) was very low. An attempt to run the reaction on a larger scale
with a more concentrated solution of 42 (0.06M) and correspondingly longer irradiation time led to an even lower yield of 21.

Due to the low yield of 21 from the preceding reaction, the synthesis of this compound by the route of Wender and Lechleiter\textsuperscript{13a} was reinvestigated. The overall yield (24 \rightarrow 21) using their sequence

\[
\begin{array}{c}
\text{CO}_2\text{Me} \\
\text{Br}
\end{array} \xrightarrow{\text{KOH, toluene, } \Delta} \begin{array}{c}
\text{CO}_2\text{H} \\
\text{CH}_2\text{N}_2
\end{array} \xrightarrow{64\%} \begin{array}{c}
\text{CO}_2\text{Me} \\
\text{25}
\end{array} \xrightarrow{84\%} \begin{array}{c}
\text{CO}_2\text{Me} \ \ | \\
\text{17a}
\end{array} \xrightarrow{\text{hv, } -78^\circ} \begin{array}{c}
\text{21}
\end{array} \xrightarrow{38\%}
\]

in our hands was only 20\% and in view of the additional steps involved, only marginally better than the one step route from 42. While it was clear that much further work needed to be done to improve upon the yields to 21, a sufficient quantity of this material had been obtained by this time and the synthesis of 1 by a different route was begun.

Reduction of 21 proceeded smoothly to afford alcohol 43\textsuperscript{2} in good yield (86\%). Oxidation using pyridinium dichromate (PDC),\textsuperscript{32} although it

\[
\begin{array}{c}
\text{21} \\
\text{LAH}
\end{array} \xrightarrow{\text{PDC, } \text{CH}_2\text{Cl}_2, \text{3\% days}} \begin{array}{c}
\text{43}
\end{array} \xrightarrow{\text{Ph}_3=\text{CH}_2, \text{DMSO-pentane, 15\%, 5 min.}} \begin{array}{c}
\text{44}
\end{array} \xrightarrow{\text{49\% yield}} \begin{array}{c}
\text{1}
\end{array}
\]

occurred at a rate slower than expected, furnished the bicyclic aldehyde 44 (49\% yield) contaminated with a small amount of pyridine. The
pyridine could be removed under conditions of neutral pH by washing with an aqueous solution of nickel chloride, but this treatment created several small peaks in the olefinic region of the nmr spectrum of 44. The nmr spectrum of 44 was very similar to that of ketone 28 and in addition, the ir revealed interaction between the carbonyl and the strained bond ($\nu_{CO} = 1702 \text{ cm}^{-1}$ in CHCl$_3$). Conversion of 44 to 1 was achieved by running the Wittig reaction using methyl sulfinyl carbon in DMSO as the base and employing virtually the same conditions used by Brown, et al. to synthesize the extremely thermally labile compound cis-divinylcyclopropane. The yield of 1 from this reaction was 30-40% after trap to trap distillation.

Assignment of structure 1 was based upon both spectral and chemical evidence. The nmr of 1 reveals saturated and olefinic protons in the ratio of 9:3 respectively. In addition, the olefinic region could be analysed in detail as an ABX system yielding the following coupling constants characteristic of the vinylic structure:

\begin{align*}
J_{AX} &= 17.2 \text{ Hz}, \quad J_{BX} = 9.8 \text{ Hz}, \quad J_{AB} = 1.9 \text{ Hz}.
\end{align*}

Further evidence for structure 1 lies in its facile rearrangement to triene 34 upon heating ($t_\text{ess} = \text{ca. 8 hours @ 33.7}^\circ \text{ C}$). This is the product expected from initial cleavage of the strained 1,4 bond in 1 followed by 2,3 bond
rupture of diradical 43. 23,13
D. Thermal Isomerization of 1-Vinylbicyclo[2.2.0]hexane 1

Thermal decompositions of 1-substituted and 1,4-disubstituted bicyclo[2.2.0]hexanes have attracted a great deal of attention recently with respect to the assessment of the radical stabilizing ability of various functional groups.\textsuperscript{37,38} Since these thermal decompositions are postulated to proceed through a diradical intermediate,\textsuperscript{23} substituents which lower the energy of the diradical should also lower the energy of the transition state leading to it. Comparison of the activation parameters of substituted bicyclo[2.2.0]hexanes should therefore be a measure of the relative stabilizing ability of the substituents. Solly and Cain, for example, have compared the activation parameters of 45 and 46 and determined that the carbomethoxy moiety stabilizes the adjacent radical center by 6.0 kcal mol\textsuperscript{-1}.\textsuperscript{37} A similar comparison of 47 and 2 led to the assessment of the radical stabilizing ability of the cyano group as 7.3 kcal mol\textsuperscript{-1}.\textsuperscript{38} The synthesis of 1 offered the chance to assess the stabilizing ability of the vinyl group in the bicyclo[2.2.0]hexane system.

Kinetics of 1 in degassed deuterochloroform solution were obtained by nmr integration of the olefinic region versus an internal
standard (p-dioxane). The decomposition of 1 was strictly first order; no other products besides 34 could be detected. Rates of isomerization at various temperatures were obtained using standard procedures (see experimental). These rates are presented in Table 2 while in Table 3, the derived activation parameters of 1 are compared to a closely related system.

Table 2
Solution Phase Decomposition of 1a

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Rate x 10^5, sec^-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>44.7</td>
<td>7.18</td>
</tr>
<tr>
<td>53.2</td>
<td>14.5</td>
</tr>
<tr>
<td>61.4</td>
<td>32.7</td>
</tr>
</tbody>
</table>

a) in degassed CDCl₃ solution.

Table 3
Activation Parameters for Thermolysis of Small Ring Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>ΔH°(±)</th>
<th>ΔS°(±)</th>
<th>ΔG°(±)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethylcyclobutane</td>
<td>61.4</td>
<td>10.3</td>
<td>57.6</td>
<td>39</td>
</tr>
<tr>
<td>vinylcyclobutane</td>
<td>48.6</td>
<td>5.4</td>
<td>46.6</td>
<td>40</td>
</tr>
<tr>
<td>bicyclo[2.2.0]hexane 2</td>
<td>35.4d</td>
<td>0.5e</td>
<td>35.2</td>
<td>41</td>
</tr>
<tr>
<td>1</td>
<td>18.5d</td>
<td>-19.5e</td>
<td>25.8</td>
<td>f</td>
</tr>
</tbody>
</table>

a) kcal mol⁻¹  b) eu  c) at 100° C  d) ± 1.4 kcal mol⁻¹; this uncertainty is the standard deviation  e) ± 3.8 eu  f) this work

As Table 3 indicates, addition of a vinyl group to the bicyclo[2.2.0]hexane system lowers ΔG° by 9.4 kcal mol⁻¹. While
this decrease is slightly less than in the corresponding cyclobutane system, it is in good agreement with the effect expected on the basis of iodine atom abstraction reactions which place the stabilization energy of the allyl radical at 10 ± 1.5 kcal mol\(^{-1}\).\(^{42}\)

Since alkyl groups (and presumably the vinyl group) have been found to stabilize the ground state of bicyclo[2.2.0]hexanes,\(^{37}\) perhaps the activation parameters of 1-ethylbicyclo[2.2.0]hexane 48 would be more suited for comparison with those of 1. Although 48 is an unknown compound, work by Solly and Cain\(^{37}\) allows the estimation of its activation parameters. They found that replacement of the bridge-

![Diagram of compounds 48 and 49](image)

head hydrogen in 49 by an ethyl group raised the activation energy by 1.5 kcal mol\(^{-1}\). Assuming the addition of an ethyl group to 2 will have the same effect, the \(\Delta G^+\) of 48 can be estimated as 36.7 kcal mol\(^{-1}\). The difference in \(\Delta G^+\) between 48 and 1 would then become 10.9 kcal mol\(^{-1}\), in excellent agreement with the results from the cyclobutane system.

The extremely negative activation entropy of 1 (-19.5 eu) is of some interest. Generally, isomerizations of bicyclo[2.2.0]hexanes yield entropy terms close to zero.\(^{43}\) While entropy terms this negative can indicate the occurrence of a concerted process,\(^{45}\) the decrease in the \(\Delta G^+\) of 1 relative to 2 is exactly that expected on the basis of
a diradical mechanism. The decrease in the $\Delta S^+$ of 1 is too great to be explained on the basis of hindered rotation about the single bond of the vinyl group due to orbital overlap of the vinyl pi system with the developing radical center.\textsuperscript{44} This effect should only produce a decrease in $\Delta S^+$ of about 4 eu's.\textsuperscript{45} In conclusion, while the origin of the extremely negative entropy term of 1 is uncertain, it should be noted that entropy terms of similar magnitude have been found in the decompositions of bicyclohexanes \textsuperscript{50}\textsuperscript{46} and \textsuperscript{51}.\textsuperscript{47}

\[\Delta S^+ = -22.7 \text{ eu}\]

\[\Delta S^+ = -9.3 \text{ eu}\]
E. Experimental

Methyl 1-Bromocyclobutanecarboxylate 24

To a 500 ml flask fitted with a mechanical stirrer, N₂ inlet, reflux condenser, and dropping funnel was added cyclobutane carboxylic acid (Aldrich 98%-34.0 g, 0.340 mol) and thionyl chloride (44.5 g, 0.374 mol). After the mixture had refluxed for one hour, phosphorus tribromide (0.7 g) and bromine (59.7 g, 0.374 mol) were added and the mixture refluxed for 22 hours. Several additional grams of bromine were added after 1½ hours of reflux as some of this reagent had escaped through the reflux condenser. The dark reaction mixture was cooled to room temperature and poured onto 70 ml methanol. This step should be conducted with caution as the methanolysis of the acid chloride is extremely exothermic. After stirring 15 minutes, the methanol solution was diluted with 100 ml water, extracted with ether (3x50 ml), and the ether layers dried (K₂CO₃). Filtration, removal of ether, and distillation through a four inch glass packed column afforded the bromo ester (58.2 g, 96% yield), bp 51-54° (3.5 mm).

nmr: 1.60-2.38 (br m, 2H), 2.38-3.13 (br m, 4H), 3.78 (s, 3H)

1-Cyclobutene-carboxylic Acid 25

Potassium hydroxide (8.0 g, 0.14 mol) and 110 ml toluene were added to a 250 ml Morton flask equipped with a dropping funnel, mechanical stirrer, reflux condenser, and N₂ inlet. Heating this mixture to reflux caused the KOH to become "molten". The bromo ester 25 (8.00 g, 0.0446 mol) was added at such a rate as to maintain a gentle reflux with little external heating. The reaction mixture turned
cloudy during the addition and a precipitate (K₂CO₃, KBr) formed. Re-
fluxing was continued one hour after the addition of ester was complete;
the reaction mixture was cooled to room temperature and extracted with
water (2x50 ml). The aqueous layer was then washed with 25 ml hexane
and acidified to pH 1 with 1 M HCl. After extraction with ether (4x25
ml) and washing with brine, the ether layers were dried dried over
stirred MgSO₄. Due to the sensitive nature of this acid,¹⁴a it was not
isolated but handled as a dilute solution. Analysis of the dried ether
solution by nmr indicated that it still contained a large amount of
water which could not be removed by adding fresh MgSO₄ and storing the
solution in the freezer overnight. Efficient drying was accomplished,
however, by storing the ether solution over molecular sieves 4A over-
night. A crude yield of the reaction was obtained by evaporation of an
aliquot of the ether solution, dissolution of the residue in water,
and titration of the resulting solution with standardized sodium hy-
droxide. The yield thus obtained was 64%.
nmr: 2.46 (m, 2H), 2.70 (m, 2H), 6.85 (s, 1H), 10.43 (s, 1H, exchange-
able with D₂O)

**Acetylcyclobutene ²⁶¹⁶**

To a 250 ml Morton flask fitted with a mechanical stirrer, N₂
inlet, and dropping funnel was added the above solution of acid in
ether (ca. 28.5 mmol). This solution was cooled to 8⁰ with an ethylene
glycol bath which contained coils connected to a refrigerated ethanol
bath. A 2.16 M solution of methylthium in ether (26.5 ml, 57 mmol)
was added over a half hour period and the resulting heterogeneous reac-
tion mixture was stirred overnight. After decomposing the lithium salts by pouring the reaction mixture into a well stirred, cold solution of ammonium chloride (100 ml), the layers were separated and the aqueous layer extracted with with ether (2x50 ml). The combined organic layers were washed with brine (30 ml), dried (MgSO₄), and concentrated by distillation through a short column. Distillation at reduced pressure (0.5 mm) using the molecular still yielded the ketone as a clear oil contaminated with about 10% carbinol 27 (singlet in the nmr at 1.29 ppm). Yield: 1.4 g, 51% (corrected for the presence of carbinol).

nmr: 1.13 (s, 3H), 2.38-2.54 (m, 2H), 2.61-2.73 (m, 2H), 6.68 (s, 1H)

Due to the sensitive nature of this compound, it was immediately taken up in 500 ml methylene chloride and stored in the freezer. The solution had a uv absorption, λ_max=324 nm (ε=40).

1-Acetyl bicyclo[2.2.0]hexane 28

Into a 150 ml capacity pyrex photolysis apparatus containing an air space between the lamp cooling water and the sample jacket was added 150 ml of the enone solution. Ethylene was passed into the solution via a syringe needle while cooling was effected with a dry ice-acetone bath. Irradiation for 45 minutes led to efficient take up of ethylene. Rotoevaporation of solvent and nmr analysis of the crude pale yellow oil revealed it to contain bicyclic ketone 28, ring opened ketone 29 and starting material 26 in the ratio 87:5:8, respectively. Longer irradiation times led to higher conversions of ring opened ketone at the expense of bicyclic ketone. Irradiation for two hours, for example, led to a 74:26 ratio of 28 to 29. Analytical samples of the
two product ketones were obtained by prep tlc (20% Et$_2$O-pentane) of the reaction mixture that had been irradiated for two hours. The fastest moving band (R$_f$ = 0.47) contained 29 while the next band (R$_f$ = 0.32) consisted of 28. This latter band was further purified by molecular distillation.

**Bicyclic Ketone 28**

nmr: 1.72-2.78 (br m, 8H), 2.07 (s, 3H), 2.78-3.07 (m, 1H)
ir (CHCl$_3$): 1689 (C=O)
uv (hexane): $\lambda_{max}$ 295 ($\epsilon$=30.6)
ms: m/e 124 (m$^+$), 109 (m$^+$ minus CH$_3$), 81 (m$^+$ minus CH$_3$CO), 43 (CH$_3$CO$^+$, base peak)

**5-Methylenehepten-6-one 29**

nmr: 1.97-2.49 (m, 4H), 2.21 (s, 3H), 4.86-5.10 (m, 2H), 5.50-6.07 (m, 3H)
ir (CHCl$_3$): 1678 (C=O)
ms: m/e 124 (m$^+$), 109 (m$^+$ minus CH$_3$), 81 (m$^+$ minus CH$_3$CO), 43 (CH$_3$CO$^+$, base peak)

**1-Acetyl bicyclo[2.2.0]hexane Tosylhydrazone 33**

A mixture of ketone 28 (793 mg, 6.38 mmol) and tosylhydrazone (1.19 g, 6.38 mmol) in 2 ml methanol was refluxed 2 hours under nitrogen. The reaction mixture was then placed in a refrigerator overnight. The resulting white crystals were isolated by Buchner filtration, washed with several portions of cold methanol, and dried under full vacuum to yield 473 mg of tosylhydrazone (mp 127-129$^\circ$). Rotoevaporation of the filtrate and chromatography of the orange oil on 50 g silica gel elu-
ting with 33% EtOAc-hexane furnished an additional 73 mg of 33. The combined yield of 33 was 34%.

nmr: 1.05-2.45 (br m, 8H), 1.58 (s, 3H), 2.59-2.90 (m, 1H), 7.16 (d, 2H, J=8 Hz), 7.76 (d, 2H, J=8 Hz)

ir (CHCl₃): 1601 (C=N)

ms: m/e 292 (m⁺), 137 (m⁺ minus Ts)

anal (C₁₅H₂₀N₂O₂S): calcd 292.1245, found 292.1263

**Attempted Formation of 1-Vinylbicyclo[2.2.0]hexane 1**

Into a 10 ml flask with a serum stoppered side arm and N₂ inlet was added 33 (200 mg, 0.68 mmol) and 1ml dry ether. To this slurry was added 1.4 ml (3 mmol) of 2.16 M methyllithium in ether via syringe over a five minute period. Gas was evolved and the pale orange solution was stirred for 30 minutes. The reaction mixture was then carefully quenched with water (3 ml), the layers separated, and the aqueous phase extracted with ether (3X2 ml). Drying (Na₂SO₄) and concentration by distillation through a short path apparatus (conducted under N₂) yielded a yellow, olefin-smelling oil which contained three components by gc (15% SE-30, 6' x 0.375", oven temp 80⁰). The first peak (53% of the product mixture, retention time 8.2 min) was identified as 3-methylene-1,6-heptadiene 34 by its identity to authentic material (gc retention time and nmr).²⁷ The second peak (37%, 17.7 min) was identified as ethenylidenecyclohexane²⁸ (spectral data below). The third peak (10%, 27.7 min) was not identified.

Ethenylidenecyclohexane

nmr: 1.50 (m, 6H), 2.10 (m, 4H), 4.48 (br s, 2H)
ir (CHCl₃): 1960 (C=C=C)
ms: m/e 108 (m⁺)

Methyl bicyclo[2.2.0]hexane-1-carboxylate ²¹¹⁴ - Method 1

A large (3.25 l capacity) quartz photochemical well containing a gas inlet tube was charged with freshly distilled methyl propiolate (3.52 g, 41.9 mmol) and 3.25 l methylene chloride. Ethylene was bubbled into the solution as it was cooled to -78⁰ with a dry ice-acetone bath. Irradiation at this temperature with a 450 watt mercury lamp resulted in 75% reaction of starting material (determined by integration of the methyl ester region in the nmr). Further irradiation (6.5 hours) did not effect more reaction. A gc analysis of the crude photolysate (XE-60, 20' x 0.125", oven 135⁰) revealed that the bicyclic ester (retention time 7.5 min) comprised greater than 89% of the volatile components (retention times 4.4, 5.1, and 5.6 min). Rotoevaporation of solvent afforded an orange oil which was distilled through a four inch glass-packed column fitted with an efficient reflux head. Fractions were analysed by gc. The bicyclic ester (0.58 g, 10% yield) was obtained as a colorless oil, bp 35⁰ (2 mm). Lit.¹⁴ bp 47-54⁰ (3.7 mm). A major amount of material was left in the distilling pot.
nmr: 1.72-3.10 (m, 9H), 3.61 (s, 3H)
ir (film): 1722 (C=O)
ms: m/e 140 (m⁺), 109 (m⁺ minus OCH₃)
**Methyl bicyclo[2.2.0]hexane-1-carboxylate 21** - Method 2

This route to 21 was developed by Wender and Lechleiter. A solution of diazomethane in ether was generated from the base-induced decomposition of 22 g (0.21 mol) nitrosomethyl urea (see experimental, part I). This solution was slowly added to a cooled ether solution of cyclobutene-carboxylic acid 25 (produced from 16 g of bromo ester precursor 24) until gas evolution ceased and a slight excess of diazomethane was evident by a slight pale yellow color in the reaction flask. After stirring an additional several minutes, the excess diazomethane was decomposed with several drops of acetic acid. The ether solution was transferred to a separatory funnel, washed with dilute aq. NaOH until the washings were basic, and then washed with water. After drying (Na$_2$SO$_4$) and removal of ether under N$_2$, the yellow liquid was distilled through a short path distillation apparatus. Methyl cyclobutene-1-carboxylate 17a (5.03 g) was collected as a clear oil, bp 42-50° (12 mm); lit. bp 43-46° (12 mm);$^{14}$ 42-43° (25 mm);$^{52a}$ 46-48° (12 mm).$^{52b}$

nmr: 2.38-2.55 (m, 2H), 2.65-2.80 (m, 2H), 3.68 (s, 3H), 6.70 (br s, 1H)

This ester was immediately diluted with 3 l methylene chloride and reacted at -78° in the presence of ethylene as in method 1. After 17 hours irradiation, the reaction was essentially complete. After rotoevaporation of solvent, distillation through a 4" glass packed column afforded 21 as a clear oil in two fractions: 1, bp 49-50° (5mm) and 2, bp 52-55° (3mm). Fraction 1 (1.99 g) contained ca. 5% 17a impurity while fraction 2 (0.42 g) was essentially pure 21. Combined yield was 2.41 g (38%).
1-Hydroxymethylbicyclo[2.2.0]hexane 43

A 100 ml flask fitted with an N₂ inlet and Claisen adapter was charged with ester 21 (314 mg, 2.24 mmol) and 30 ml dry ether. Lithium aluminum hydride (150 mg, 3.94 mmol) was added to the adapter. After the flask contents had been cooled to 0°, the reducing agent was added over a five minute period. The resulting heterogeneous mixture was stirred for 2.5 hours at which time gc analysis (XE-60 column, 20' x 0.125", oven 135°) indicated the absence of starting material. Successive portions of 150 μl water, 150 μl 15% aq. NaOH, and 450 μl water followed by stirring for several hours yielded a fine white precipitate which was easily removed by filtration. The filtrate was dried (K₂CO₃), filtered, and rotoevaporated to afford an oil which was purified by molecular distillation (65-85°, 15 mm). The alcohol was obtained as a colorless oil (214 mg, 86%).

nmr: 1.80-2.38 (m, 9H), 2.38-2.66 (br s, 1H), 3.38 (s, 2H)

ir (film): 3325 (broad envelope, O-H)

ms: m/e 112 (m⁺)

Bicyclo[2.2.0]hexane-1-carboxaldehyde 44

Into a 100 ml flask (dried with a heat gun under nitrogen) was added alcohol 43 (1.88 g, 16.7 mmol) and 40 ml methylene chloride (dried over molecular sieves 4A). Pyridinium dichromate 32 (9.42 g, 25.0 mmol) which had been ground to a powder, washed with several portions of ether and dried under vacuum was added and the reaction mixture stirred for 3½ days under nitrogen. The reaction mixture was then diluted with 10 volumes of ether and the chromium salts allowed to settle. After
filtration, the yellow solution was washed with dilute aqueous NiCl₂. Careful rotoevaporation of solvent afforded a brown oil which was diluted with ether and filtered through K₂CO₃ to remove the last traces of chromium salts. Rotoevaporation of ether at 0°C followed by bulb to bulb distillation afforded 44 as a colorless, musty smelling, volatile oil (0.90 g, 49%) in 95% purity. This material was sufficiently pure for use in the next step.
nmr: 1.76-3.20 (m, 9H), 9.61 (s, 1H)
ir (CHCl₃): 1702 (C=O)
anal (C₇H₁₀O): calcd 110.07316, found 110.0729

1-Vinylbicyclo[2.2.0]hexane 1

A 10 ml pear-shaped flask with a side arm was dried in the oven and assembled hot under nitrogen. NaH (90 mg, 3.8 mmol, 50% dispersion in oil) was added to the flask and washed with several portions of dry pentane. Residual pentane was removed by pumping under vacuum. Dry DMSO (1 ml, distilled from CaH₂ and stored over molecular sieves 4A) was added via syringe and the flask was heated to 80-90°C until hydrogen evolution ceased and a greenish-grey solution was obtained. After cooling the solution to room temperature, methyl triphenylphosphonium bromide (670 mg, 1.88 mmol) in 1 ml DMSO was then added to the flask. A homogeneous orange solution resulted which was stirred for 10 minutes. Isopentane (2 ml, over Na) was introduced, the resulting biphasic mixture cooled to 15°C, and then aldehyde 44 (150 mg, 1.36 mmol) was added. After stirring 5 minutes, the reaction mixture was quenched with cold brine and extracted with cold pentane (3x10 ml).
The pentane layers in turn were washed with two portions of cold brine, dried \((K_2CO_3)\), and rotoevaporated at 0° C. The residue was distilled (5 mm) into a dry ice-acetone cooled trap. Compound 1 was isolated as a colorless oil (40 mg, 27%).

**nmr**: 1.20-2.50 (m, 8H), 2.50-2.79 (m, 1H), 4.73-6.20 (ABX pattern:

\[ \nu_A = 4.86, \ \nu_B = 4.84, \ \nu_X = 5.97; \ \nu_{AX} = 17.2 \text{ Hz}, \ \nu_{BX} = 9.8 \text{ Hz}, \ \nu_{AB} = 1.9 \text{ Hz.} \]

**anal \((C_{12}H_8)\)**: calcd 108.0939, found 108.0936

**Kinetics of 1**

Samples of 1 were prepared in CDCl₃, placed into nmr tubes, and degassed and sealed under vacuum. A run was performed by plunging one of the tubes into a hot water bath that was regulated with an RFL 70-115 proportional temperature controller (±0.1° C). Points were obtained by periodically pulling the tube from the hot water bath and measuring the ratio of the vinyl region to p-dioxane internal standard through multiple integrations (3 to 4 were typically done). Temperature was measured with a mercury thermometer and the run was continued to about 3 half lives. When the run was completed, the tube was returned to the bath for >10 half lives to obtain the infinity point. A conventional first order treatment yielded the rate constants at each temperature and a plot of In k/T vs. 1/T yielded \(\Delta H^\ddagger\) and \(\Delta S^\ddagger\).
F. Spectra
G. References and Notes

1. For reviews of bicyclo[2.2.0]hexane chemistry, see:

2. For a relatively lengthy synthesis of bicyclo[2.2.0]hexanes based upon the ring contraction of a bicyclo[2.2.1]heptanone, see:


   For problems associated with this synthesis, see:


12. Recently, an additional method of synthesis of bicyclo[2.2.0]hexanes has appeared based upon the ring contraction of bicyclo[3.2.0]heptanones. see:

b. S. R. Wilson, L. R. Phillips, Y. Pelister, and J. C. Huffman, 

14a. Professor P. A. Wender, private communication.

b. A procedure for the synthesis of 21 was kindly supplied by 
Professor Wender along with its nmr spectrum.

15. For a review, see:


(1975).


(1967).

19. This is a common by product in the reaction of methyllithium with 
carboxylic acids; see ref. 17.


22. The carbonyl stretch is in the region expected of an α,β un-
saturated ketone, see:

R. M. Silverstein, G. C. Bassler, T. C. Morrill, "Spectrometric 
and Sons, New York, 1974.


27. A sample of 34 from professor J. W. Timberlake is gratefully 
acknowledged.


30. The strain energy of bicyclo[2.2.0]hexane is about 51 kcal mol⁻¹:


31. Since the acid was not isolated, this yield was determined by titration of an aliquot of ether solution.


34. A "normal" C=O stretch in α,β unsaturated aldehydes occurs in this region, see ref. 22, p 99.


39. Calculated from data in:


41. Calculated from data in ref. 23a.


43. For an excellent discussion of this point, see ref. 37.


48. I would like to thank Dr. Saul C. Cherkofsky at E. I. DuPont de Nemours and Company for this procedure.

49. The corresponding ethyl ester is available from Aldrich.

50. This material was obtained from Farchan Chem. Co. and distilled at 101°C at 760 mm.


