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PART I. EVIDENCE FOR THE DISCRETE EXISTENCE
OF BICYCLO[4.1.0]-HEPTATRIENES. PART II.
REACTIONS OF SOME STRAINED RING SYSTEMS WITH
DIIRON NONACARBONYL.

Rice University, Ph.D., 1975
Chemistry, organic

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PART I. EVIDENCE FOR THE DISCRETE EXISTENCE OF BICYCLO[4.1.0]-HEPTATRIENES

PART II. REACTIONS OF SOME STRAINED RING SYSTEMS WITH DIIRON NONACARBONYL

BY

LEE PHONE LIN

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

DOCTOR OF PHILOSOPHY

Thesis Director's signature

W. E. Billups

Houston, Texas
May, 1975
DEDICATION

To My Dearest Parents
ACKNOWLEDGEMENTS

I wish to express my deepest thanks to Dr. W. E. Billups for the conception and guidance of the projects presented in this dissertation. I would also like to express my sincere appreciation to the students and professors who were invaluable in my graduate education.

The financial support provided by Rice University in the form of a Rice Fellowship is gratefully acknowledged.

Finally, I wish to express my gratitude to my parents for their continuous encouragement and help throughout these years.
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PART I

EVIDENCE FOR THE DISCRETE EXISTENCE OF BICYCLO[4.1.0]HEPTATRIENES
INTRODUCTION

In contrast to the impressive number of carbonium ion, carbanion, and free radical rearrangements, the first nontrivial carbene-carbene rearrangement—differing from the other rearrangements in that more than one bond had to be broken and remade—was recorded less than ten years ago with the report from Schechter's group in 1965 that the pyrolysis of o-methylphenyldiazomethane gave, as one product, styrene. To explain this surprising result, a double carbene-carbene rearrangement was proposed.

In 1968 the next report of a carbene-carbene rearrangement appeared in the first of a series of elegant studies by Strausz and co-workers on the migration of oxygen to a carbene site. Carbonyl carbenes were found to undergo two fundamentally different types of reaction. In one, ring closure to an oxirene was believed to occur. The oxirene, an anti-aromatic ring system, was then thought to open to give a new carbene. The other was the well-known Wolff rearrangement which involved
formation of a ketene.

\[
\text{R-C-C=O} \quad \overset{\text{Wolff rearrangement}}{\leftrightarrow} \quad \text{R-C=C=O}
\]

In the same year, both Crow and Wentup, as well as Sumberg and his co-workers published initial reports on the chemistry of pyridyl carbene and phenyl nitrene in which both carbene-carbene and carbene-nitrene rearrangements were postulated.\(^3\),\(^4\)
These were followed by a report of the base-induced contraction of ferrocenyl cycloheptatrienyl fluoroborate, and a number of examples of the conversion of phenyl carbene and its derivatives to cycloheptatrienyldenes in the gas phase, and of benzo[cycloheptatrienyldene] to naphthyl carbene in solution.
Besides detailed studies in the field of the heterocyclic and benzenoid systems, a growing number of reports describing nonbenzenoid systems are now appearing.\textsuperscript{8}
Nevertheless, the mechanisms of these reorganizations remain a subject of considerable conjecture, although several mechanistic alternatives have been put forward. The first possibility involves a bicycloheptatriene intermediate (or transition state) and certainly has ample precedent in the well known formation of cyclopropene from vinylcarbene and pyrolysis of cyclopropene to give vinylcarbene derived products.\textsuperscript{9,10}

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For these reasons, it is not surprising that it has been the preferred choice of many workers in this field. Furthermore, Coburn and Jones failed to detect the ring contracted product 1-methylacenaphthylene\textsuperscript{23} in the pyrolysis of the sodium salt of phenalen-1-one tosylhydrazone\textsuperscript{19}. That rearrangement occurs less readily in systems in which more highly strained cyclopropenes must be postulated gives additional indirect evidence to support this mechanism.
The second possibility which is intuitively less attractive for carbocyclic systems than for heterocyclic analogs takes the form of the Wolff rearrangement in which the vacant orbital of the carbene is presumably orthogonal to the π system and therefore properly oriented for migration of σ bond. This mechanism, which is limited to cyclic conjugative systems would lead to, or take place from, an intermediate zwitterion as shown below. Drawing from acyclic systems, the Wolff mechanism would be expected to be favored by appropriately positioned electronegative elements with nonbonded electrons. The electronegativity
favors a conformation with the filled orbital conjugated with the π-system leaving the vacant orbital aligned with the σ framework, and the nonbonded pair of electrons can stabilize the resulting zwitterion. On the other hand, the instability of the bent vinyl cation makes the Wolff mechanism an intuitively unattractive alternative, especially for the non-heterocyclic systems. Furthermore, anellation should retard the Wolff type mechanism (which would require a pseudo-aromatic system), while it should favor a cyclopropene mechanism since less aromaticity would be lost in forming the small ring. Thus, the cyclopropene mechanism is further
supported by the facile contraction of benzocycloheptatrienyldene as compared with the non-annelated form.\textsuperscript{6,7}

\[ \text{Scheme 1} \]

The third possibility involves diradical formation (or charge separated species) followed by closure to a cyclic allene which can give the carbene.\textsuperscript{6,12} The allene as a possibility is probably trivial

\[ \text{Scheme 2} \]

since ring strain would be expected to bend the allene moiety and twist its terminal carbons to such an extent that it would probably become tantamount to resonance form of cycloheptatrienyldene. However, this

\[ \text{Scheme 3} \]
possibility appears unlikely in many systems, primarily due to the low temperatures at which some rearrangements occur and the absence of hydrogen abstraction or other radical products when the rearrangement is carried out in ether solvents.\textsuperscript{6,7,8}

Another interesting mechanism that can be written for the contraction of cycloheptatrienyldiene is essentially the Skattabøl vinylcyclopropyldiene -cyclopentenyldiene rearrangement with cleavage of different bonds. The

\[
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\end{align*}
\]

effect of annelation again argues against this possibility since it should retard norcaradiene formation and hence the rate of contraction.\textsuperscript{6,7}

\[
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\end{align*}
\]
My goal in this area was to develop simple routes to members of the bicyclo[4.1.0]heptatriene family, thereby providing the first direct evidence for the discrete existence of these hypothetical species. The synthetic approach described here had its origin in the work of Chow on the synthesis of benzocyclopropene (25) from 7,7-dichlorobicyclo[4.1.0]hept-4-ene (24). In fact, some evidence for a bicycloheptatriene derivative is found in the synthesis of naptho[b]cyclopropene (27) from 7,7-

dichloro-4,5-benzobicyclo[4.1.0]hept-4-ene (26). The cyclopropene 27 is accompanied by the ether 28, which might arise from the bicycloheptatriene 29, especially since blank experiments showed that 28 probably

did not arise from 27. Although evidence which clearly implicates 29 is still missing, adaptation of this synthetic method to the generation of certain bicycloheptatriene derivatives seemed to have considerable merit.
RESULTS AND DISCUSSION

7,7-Dichlorodibenzo[a;c]bicyclo[4.1.0]heptane (30) was prepared in 45% yield by addition of dichlorocarbene to phenanthrene using a slightly modified version of the phase transfer method of Joshi, Singh and Pande. TEBA = triethylbenzylammonium chloride.

Treatment of 30 with a suspension of KOt-Bu (2 equiv.) in THF at 0°C for 18 hrs gave a yellow viscous oil identified as 31 (mixture of diastereomers in about a 3 to 1 ratio) in 72% yield. Compound 31 was identified by its spectral properties: nmr (CCl₄) δ 1.17-2.20 (m, 4H), 3.65-4.10 (m, 2H), 4.40-4.80 (m, 1H), 5.50-5.71 (the major diastereomer exhibits a doublet at 5.53, 1H, J=5 Hz; the remaining diastereomer has
a doublet at 5.63, 1H, J=5 Hz and 7.30-8.80 (m, 9H); ir (neat) 1690 (s), 1498 (m), 1450 (s), 1060 (s) and 745 (s) cm⁻¹; elemental composition was provided by high resolution mass spectroscopy m/e 296.0984 (M⁺), cal. 296.0964. Using nmr as a limit of detection, insertion into the β position in THF was not observed. This observation is readily understood in terms of the dibenzocycloheptatriene 32. The observed product 31 could then arise by rearrangement of the cyclopropene to the chlorophenan-thrylcarbene 33 followed by insertion into the solvent. However, a

![Chemical structure](image)

second rational mechanism that bypasses the cyclopropene in which carbon serves as the leaving group is shown below. In this scheme, the carbene

![Chemical structure](image)
would be formed by loss of chloride from the anion 34. Formation of the solvent insertion product can, of course, be taken as strong evidence for formation of the carbene 33. In order to distinguish between these two mechanisms, an attempt was made to trap the cyclopropene before it rearranged to the carbene. The result of this study is shown in the equation. Compound 35, identified by its spectral properties, nmr (CCl₄)  

![Chemical structure](image)

δ 1.21 and 1.80 (AB, J_AB = 5.5 Hz, 2 H, cyclopropyl), 2.1 (s, 6 H, -SCH₃), 7.1–7.6 (m, 4 H, aromatic) and 7.9–8.7 (m, 2 H, aromatic); ir (CHCl₃) 3085 (m, broad), 3010 (s), 2940 (m), 1480 (s) and 1430 (s); mass spectrum, m/e 284.0688 (M⁺), cal. 284.0692.

Compound 35 almost certainly arises by addition of the mercaptide to the cyclopropene intermediates 32 and 37 as illustrated below. The
addition of nucleophiles such as mercaptide and alkoxide to the cyclopropene double bond is well preceded in the work of Shields and Gardner\textsuperscript{15} who have shown these reactions to be general.

Attempts to trap the cyclopropene intermediate in the presence of furan or cyclopentadiene as the Diels-Alder adducts \textbf{38} and \textbf{39} respectively were unsuccessful. Similarly, attempts to trap the carbene as \textbf{40} in the presence of benzene failed.
It is interesting that the cyclopropene 32 must be so unstable that it rearranges even at temperature as low as 0°C to give the arylcarbene 33, a species normally considered to be a high energy one. On the other hand, it must be sufficiently long-lived to experience addition of the nucleophile. The strain associated with 32 and the increase in resonance energy upon ring opening is probably sufficient to place the carbene 33 at a lower energy than the cyclopropene 32. This is consistent with other examples of low temperature bicycloheptatriene → arylcarbene rearrangements.7

We did not observe insertion products arising from the bicycloheptatrienylidene44, but this is not surprising since bicycloheptatriene → cycloheptatrienyldiene rearrangements normally occur at much higher temperatures (250–600°C). Another fate of 32 would be base-catalyzed isomerization to the cyclopropene 42; however, this requires cyclopropene anion intermediate which is probably too energetic to be formed under these conditions.16

A second example illustrating this new bicycloheptatriene entry is provided below for the naphthalene system. Thus 1,2-dihydronaphthalene (43) was prepared in 95% yield by treating 1,4-dihydronaphthalene with a catalytic amount of KOt-Bu in DMSO. Compound 43 was converted to 7,7-dichloro-3,4-benzonorcarane 44, b.p. 108°C/1.2 mm Hg, by the phase
transfer method of Makosza\textsuperscript{17} (NaOH-\(\text{H}_2\text{O}\), CHCl\(_3\), triethylbenzyl ammonium chloride) in 44% yield. When the dichlorocarbene was generated from CHCl\(_3\)-KOt-Bu in pentane a 32% yield of \(\text{44}\) was obtained. Bromination of \(\text{44}\) with NBS in refluxing CCl\(_4\) with benzoyl peroxide initiator gave \(\text{45}\), m.p. 97°C, in 73% yield.

Treatment of \(\text{45}\) with the KOt-Bu-THF system described earlier (0°C, 18 hrs) gave the THF insertion product \(\text{46}\) (mixture of diastereomers in a 5:4 ratio) in 47% yield. Compound \(\text{46}\) is a yellow viscous liquid identified from its spectral properties: nmr (CCl\(_4\)) \(\delta\) 1.60-2.10 (m, 4 H), 3.65-3.97 (m, 2 H), 4.30-4.68 (m, 1 H), 5.47-5.70 (the major diastereomer has a doublet at 5.53, 1 H, \(J = 5\) Hz; the remaining diastereomer has the doublet at 5.63, 1 H, \(J = 5\) Hz) and 7.30-8.32 (m, 7 H); ir (neat) 3060 (s), 2900 (s), 2870 (s), 1595 (s), 1510 (s), 1060 (s, broad) and 745 (s) cm\(^{-1}\).
The formation of 46 is rationalized in terms of the scheme shown below, although the immediate precursor of 49, i.e. 47 or 48 or both, is not known. It should be noted, however, that attempts to selectively dehydrobrominate 45 to give 48 failed. Attempts to trap the bicycloheptatriene 49 with nucleophile (CH$_3$S$^-$) in strict analogy to the result described earlier for the phenanthrene system failed. Curiously, when metoxide was used as nucleophile an addition product identified as 52 was observed. The mechanism of formation of 52 is puzzling, and
rationalization in terms of a bicycloheptatriene intermediate is difficult. When 44 was treated with KOt-Bu in THF decomposition products (or polymers) were formed. This is presumably a consequence of initial formation of cyclopropene 53, in which the double bond has no avenue of escape to
give ultimately naphtho[a]cyclopropene (55) or the bicycloheptatriene 56 without destroying aromaticity of the benzene ring. The initial formation of 53 rather than 58 is expected, since it results from abstraction of the more labile benzylic proton.

Attempts to generate non-annelated members of the bicyclohepta[4.1.0]-triene family were largely unsuccessful. 7,7-Dibromo-1-methylbicyclo-[4.1.0]hept-4-ene (60), 4,5,7,7-tetrabromo-1-methylbicyclo[4.1.0]heptane (61) and 4,5,7-tribromo-1-methylbicyclo[4.1.0]heptane (63) were synthesized as follows. Birch reduction of toluene by sodium in liquid ammonia using
isopropyl alcohol as proton source gave 1-methylcyclohexa-1,4-diene (59) (b.p. 105-108°C, yield 92%). Addition of dibromocarbene (t-BuOK, CHBr₃, pentane) to 59 gave the desired addition product 60 (colorless solid, m.p. 32-33°C) in 42% yield. Compound 61 was obtained as a brown viscous liquid in 92% yield from bromination of 60 (Br₂-CCl₄ at 0°C). Reaction of 60 with methyl magnesium bromide in THF for 48 hours at room temperature according to the method of Seyferth and Proskai gave a colorless liquid, b.p. 94°C/2.8 mm Hg, identified as 62 in 70% yield. Bromination of 62 in CCl₄ system at 0°C gave 63 (yellow viscous liquid) in 90% yield.

Compounds 60, 61 and 63 were treated with alkali under a variety of conditions and in the presence of cyclohexene. Mainly polymers, but several unidentified products were isolated. In some cases very offensive odors were associated with derivatives of benzocyclopropene. Attempts to isolate a derivative of benzocyclopropene by preparative glpc and tlc were unsuccessful probably due to the very low yield. Furthermore, we failed to detect any of the expected products 64-73 shown in the scheme.

\[ \text{X = H or Br} \]
When compound 61 was reacted with [t-BuOK in DMF a yellow liquid (turned black on standing) identified as 2-formyl-3-methyl-N,N-dimethyl-aniline (74), or an isomer, was isolated in 12% yield. Elemental analysis was provided by high resolution mass spectroscopy, parent molecular ion M⁺, m/e 163.0995, cal. 163.0997 along with m/e 148, 134, 119, 104, 90 and 75 corresponding to the loss of methyl, formyl and N,N-dimethyl amino groups; nmr (CCl₄) showed 6 2.31 (s, 3H, benzylic methyl), 2.93 (s, 6H, N,N-dimethyl), 6.47-6.59 (m, 1H, aromatic), 6.72-6.83 (m, 2H, aromatic) and 9.62 (s, 1H, aldehyde); ir (neat) 2950 (m), 2830 (m), 1695 (s), 1600 (s), 1495 (s), 1365 (s), 1250 (m), 1145 (m), 835 (m), 705 (m) and 685 (m) cm⁻¹.

In conclusion, although this study does not provide any evidence which implicates bicycloheptatrienes in the many arylicarbene → cycloheptatrienyldiene rearrangements that have been reported, the evidence provided for the discrete exisistence of such species is rather compelling.
EXPERIMENTAL

General. All melting points and boiling points were uncorrected. The infrared spectra were recorded on a Beckman IR 8 spectrometer as either neat films, chloroform solutions or KBr plates. Proton nmr spectra were obtained with a Varian A-56/60A or a Perkin-Elmer R-12 spectrometer in CCl₄ or CDCl₃ solution and results were expressed in parts per million downfield from internal TMS. GLPC analysis were carried out on a Hewlett Packard model 700 gas chromatograph and preparative work was done on an Autoprep Model A-700 gas chromatograph with a thermal conductivity detector. Specific columns and conditions were noted with the individual experiments. Mass spectra were obtained with a double focusing C.E.C. 21-110B mass spectrometer (Mattauch-Herzog design).

Materials. All reactions were run in a atmosphere of purified nitrogen. Tetrahydrofuran was distilled from sodium-benzophenone ketyl immediately before use. DMSO was distilled from calcium hydride under reduced pressure and stored over 4A molecular sieves prior to use. DMF was dried over 4A molecular sieves several days before use. All other chemicals were reagent grade and used as received.

7,7-Dichlorodibenzo[a,e]bicyclo[4.1.0]heptane (39). A modified procedure of Joshi, Singh and Pande was employed. To a stirred mixture of phenanthrene (89 gm, 0.50 mole), triethylbenzylammonium chloride (TBAC) (1.1375 gm, 5 mmole) and chloroform (800 ml, 10 mole) maintained at 50°C was added saturated aqueous sodium hydroxide (100 gm, 2.5 mole) over two hours. The reaction mixture was refluxed an additional 5 hours followed
by the addition of water. The organic layer was separated and neutralized with dilute hydrochloric acid. The crude product was dried over sodium sulfate and decolorized with charcoal. Purification by repeated recrystallization in acetone gave 58.7 gm (45% yield, m.p. 142°C) of compound 30 as colorless long silky needles.

nmr (CDCl₃): δ 3.27 (s, 2H, cyclopropyl), 7.3 (m, 6H) and 7.9 (m, 2H, aromatic).

ir (KBr): 1430 (s), 830 (s), 750 (s) and 720 (s) cm⁻¹.

**Dehydrochlorination of Compound 30 in t-BuOK-THF.** Compound 30 (2.61 gm, 0.01 mole in 20 ml THF) was added under nitrogen to a suspension of potassium t-butoxide (2.26 gm, 0.02 mole) in THF (50 ml) at 0°C. The mixture was stirred at 0°C for 18 hours followed by addition of 500 ml of water and 50 ml of chloroform. The organic layer was separated and washed several times with water. After drying over sodium sulfate and removal of solvent in vacuo, purification by column chromatography (silica gel with chloroform) eluent) gave 31 (3:1 mixture of diastereomers by nmr), a yellow liquid, 2.36 gm, yield 72 %. Further purification was achieved by using preparative thin layer chromatography (silica gel-CHCl₃).

nmr (CCl₄): δ 1.70-2.20 (m, 4H), 3.50-4.10 (m, 2H), 4.40-4.80 (m, 1H), 5.50-5.70 (the major diastereomer had doublet at 5.53, 1H, J=5 Hz and the remaining diastereomer had the doublet at 5.63, 1H, J=5 Hz) and 7.30-8.80 (m, 9H).

ir (neat): 1690 (s), 1498 (m), 1450 (s), 1060 (s) and 745 (s) cm⁻¹.

mass spectrum: m/e 296.0984 (M⁺), calculated, 296.0967.

**Reaction of compound 30 with t-BuOK-MeSK-DMSO.** To a cooled solution of t-BuOK (10 gm, 0.08 mole) in 50 ml of purified DMSO was added methanethiol
(1.92 gm, 0.04 mole). The mixture was stirred for 30 min then 2.61 gm
(0.01 mole) of compound 30 in 50 ml of DMSO was added dropwise. The mixture
was stirred at room temperature for 3 hours followed by addition of excess
water. The resulting solution was extracted with chloroform, washed with
water and dried over sodium sulfate. After removal of solvent, 35 was
isolated as a yellow solid. Discoloration by charcoal and recrystallization
from pentane gave 2.36 gm (84%) of colorless material, m.p. 149-149.5 °C.

{\text{nmr} (\text{CCl}_4)}: \delta 1.21 and 1.80 (\text{AB}_q, J_{AB}=5.50 \text{ Hz}, 2H, cyclopropyl), 2.1 (s,
6H, -SCH}_3), 7.1-7.6 (m, 4H, aromatic) and 7.9-8.7 (m, 4H, aromatic).

{\text{ir} (\text{CHCl}_3)}: 3085 (m, broad), 3010 (s), 2940 (m), 1480 (s), 1430 (s, broad).

mass spectrum: m/e 284.0688, calculated, 284.0692.

1,2-Dihydronaphthalene (43). 65.0 gm of 1,4-dihydronaphthalene (0.50
mole) was added dropwise with cooling to a mixture of \text{BuOK} (5.65 gm,
0.05 mole) in 200 ml of DMSO. After stirring at room temperature for 30 min,
500 ml of water was added and the resulting solution was extracted with
pentane and dried over sodium sulfate. Vacuum distillation gave
62.4 gm of 43 (96%) yield) as a colorless liquid, b.p. 78°C/9 mm Hg.

7,7-Dichloro-3,4-benzobicyclo[4.1.0]hepta-3-ene (44). Method A: To a
stirred mixture of 1,2-dihydronaphthalene (58.5 gm, 0.45 mole), \text{BuOK}
(56.5 gm, 0.50 mole) and pentane (500 ml) maintained at 0 °C was added
chloroform (0.50 mole, 60 gm) over a period of one hour. After an additional
four hours, water was added and the organic layer separated, washed and dried
over sodium sulfate. Distillation under reduced pressure gave 44 as a
colorless oil like liquid, 30.5 gm, 32% yield.

Method B: To a stirred mixture of 1,2-dihydronaphthalene (58.5 gm, 0.45
mole), triethylbenzylammonium chloride (TBAC) (1.14 gm, 5 mmole) and
chloroform (80 ml, 1.0 mole) maintained at 50 °C was added saturated aqueous sodium hydroxide (20 gm, 0.50 mole) dropwise. The reaction mixture was refluxed an additional five hours. The organic layer was then separated and washed several times with water and dried over sodium sulfate. Distillation under reduced pressure (1.2 mm Hg) gave compound 44 (42 gm, 44% yield). nmr (CCl₄): δ 1.55-2.20 (m, 3H), 2.20-2.80 (m, 3H) and 6.70-7.30 (m, 4H, aromatic).

ir (neat): 3080 (m), 3040 (m), 2950 (s), 2870 (m), 1490 (s), 1450 (m), 1430 (m), 740 (m, broad) cm⁻¹.

7,7-Dichloro-5-bromo-3,4-benzobicyclo[4.1.0]hept-3-ene (45). A mixture of 44 (42.5 gm, 0.20 mole) and N-bromosuccinimide (35.6 gm, 0.20 mole) in CCl₄ was refluxed under nitrogen with a trace of benzoyl peroxide for five hours. The reaction mixture was then washed with water and dried over sodium sulfate. 45, m.p. 97°C, was obtained in 73% yield (42.6 gm) after recrystallization from pentane.

nmr (CCl₄): δ 2.00-3.00 (m, 6H), 5.01 (t, J=3.0 Hz, 1H) and 7.00-7.50 (m, 4H, aromatic).

ir (KBr): 3080 (m), 3040 (m), 2980 (s), 2930 (m), 1715 (m), 1615 (m), 1600 (m), 1490 (s), 1430 (s), 1375 (m), 1205 (s), 1160 (s), 1085 (s), 1010 (s), 930 (s) and 750 (s, broad) cm⁻¹.

1-Methylcyclohexa-1,4-diene. To a stirred mixture of 92 gm (1.0 mole) of toluene in 1000 ml of liquid ammonia was added small pieces of sodium (57.5 gm, 2.5 mole) under nitrogen at -78°C. The reaction mixture was stirred for four hours and then 180 gm of isopropyl alcohol (3 mole) was added dropwise over a two hour period. The ammonia was then allowed to evaporate overnight. 500 ml of saturated aqueous ammonium chloride solution
was then added slowly and the resulting solution extracted by four 200 ml portions of pentane. The organic layers were combined, washed and dried over sodium sulfate. Distillation gave 86.5 gm (92% yield) of a colorless liquid, b.p. 114-116°C, identified as 1-methylocyclohexa-1,4-diene.

nmr (CCl₄): δ 1.65 (s, 3H, methyl), 2.55 (broad s, 4H), 5.20-5.40 (m, 1H) and 5.60 (broad s, 2H).

7,7-Dibromo-1-methyl-bicyclo[4.1.0]hept-4-ene (60). Bromoform (1.10 mole, 278 gm) was added slowly to a stirred mixture of t-BuOK (1.25 mole, 142 gm), 1-methylocyclohexa-1,4-diene (1.00 mole, 94 gm) and pentane (800 ml) under nitrogen at 0°C. The mixture was then stirred for 18 hours and water was added. The organic layer was separated, washed and dried over sodium sulfate. Removal of the solvent gave 60 as a brown oil which was purified by recrystallization from pentane to give 112 gm (42% yield) of colorless solid, m.p. 32-33°C.

nmr (CCl₄): δ 1.43 (s, 3H, methyl), 1.57 (m, 1H, cyclopropyl), 2.00-2.50 (m, 4H, allylic) and 5.35-5.65 (m, 2H, olefinic).

ir (neat): 3050 (s), 3005 (s), 2980 (s), 2905 (s), 2860 (s), 1665 (m), 1625 (w), 1425 (s), 1025 (s), 995 (s), 755 (s) and 655 (s) cm⁻¹.

4,5,7,7-Tetrabromo-1-methyl-bicyclo[4.1.0]heptane (61). Bromine (16 gm in 200 ml CCl₄) was added slowly at 0°C to a stirred solution of 60 (0.10 mole, 26.6 gm) in 150 ml of CCl₄. After the color of bromine had disappeared, the solvent was removed in vacuo. The crude product was purified by column chromatography (silica gel- CHCl₃) giving 39 gm (92% yield) of 61 as a yellow-brown liquid.

nmr (CCl₄): δ 1.52 (s, 3H, methyl), 1.52-3.30 (m, 5H) and 3.70-5.20 (m, 2H).

ir (neat): 3010 (m), 2970 (m), 2940 (s), 2890 (m), 1615 (w), 1430 (s),
1160 (m) and 755 (m) cm$^{-1}$.

7-Bromo-1-methyl-bicyclo[4.1.0]cyclohept-4-ene (62). Methyl magnesium bromide was prepared from 0.20 mole of \( \text{CHBr}_3 \) and 0.20 mole of magnesium in THF at -15°C. A solution of \( \text{61} \) (0.20 mole, 53.2 gm) in THF (200 ml) was then added slowly to the Grignard. After a few hours a white precipitate was formed. The mixture was then stirred at room temperature for 48 hours and the solid was filtered. The filtrate was then washed with water, extracted with pentane and the combined organic layers dried over sodium sulfate. After removal of solvent, distillation afforded 26.2 gm (70.5% yield) of \( \text{62} \), b.p. 94°C/2.8 mm Hg, as a colorless liquid.

nmr (CCl$_4$): $\delta$ 1.49 (s, 3H, methyl), 1.00-1.65 (m, 2H, cyclopropyl) and 5.35-6.65 (m, 2H, olefinic).

ir (neat): 3010 (s), 2970 (s), 2900 (s), 2855 (s), 1665 (s), 1615 (w), 1450 (s), 1425 (s), 1020 (s), 750 (s) and 650 (s) cm$^{-1}$.

4,5,7-Tribromo-1-methyl-bicyclo[4.1.0]heptane (63). Bromination of 14.1 gm of \( \text{62} \) (0.75 mole) was carried out according to the procedure described earlier for the bromination of \( \text{60} \). Compound \( \text{63} \) was obtained in 90% yield 23.5 gm).

nmr (CCl$_4$): $\delta$ 1.10-1.80 (m, 2H, cyclopropyl), 1.52 (s, 3H, methyl), 1.80-1.34 (m, 4H) and 3.70-4.60 (m, 2H).

ir (neat): 3010 (m), 2980 (s), 2940 (s), 2890 (m), 1430 (s), 1160 (s) and 755 (s) cm$^{-1}$.

2-Formyl-3-N,N-dimethylaniline (64) or Its Isomer. Compound \( \text{60} \) (5.32 gm, 0.02 mole) was treated with a suspension of \( t-\text{BuOK} \) (0.24 mole, 27.12 gm) in DMF (70 ml) under nitrogen at room temperature for 24 hours.
Work-up as described for 30 gave 0.39 gm of a yellow liquid, identified as 64 or an isomer.

nmr (C\textsubscript{6}H\textsubscript{4}): δ 2.31 (s, 3H, benzylic methyl), 2.93 (s, 6H, N,N-dimethyl), 6.47-6.59 (m, 1H, aromatic), 6.72-6.83 (m, 2H, aromatic) and 9.62 (s, 1H, aldehyde).

ir (neat): 2950 (m), 2830 (m), 1695 (s), 1600 (s), 1495 (s), 1365 (s), 1250 (m), 1145 (m), 835 (m), 705 (m) and 685 (m) cm\textsuperscript{-1}.

**Reaction of Compound 45 with t-BuOK-MeOK-DMSO.** Compound 45 (2.92 gm, 0.01 mole) was treated with a mixture of t-BuOK (9.04 gm, 0.08 mole) and MeOH (0.96 gm, 0.03 mole) in DMSO (70 ml) under nitrogen at room temperature for 18 hours. Work up as described for 45 gave a colorless liquid, identified as 52, in 41% yield (0.89 gm).

nmr (C\textsubscript{6}H\textsubscript{4}): δ 3.04 (s, 2H), 3.36 (s, 3H, -O\textsubscript{Me}), 3.60 (s, 3H, -O\textsubscript{Me}), 4.77 (AB\textsubscript{q}, J\textsubscript{AB}=6.6 Hz, 1H), 5.43 (AB\textsubscript{q}, J\textsubscript{AB}=6.6 Hz, 1H) and 6.70-7.70 (m, 4H, aromatic).

ir (neat): 3055 (s), 3000 (s), 2940 (s), 2900 (s), 2830 (s, sharp), 1730 (m), 1635 (s), 1600 (s), 1485 (s), 1440 (s), 1355 (s), 1250 (s), 1135 (s), 1080 (s) and 1015 (s) cm\textsuperscript{-1}.

mass spectrum: m/e 202.998, calculated, 202.993.
REFERENCES


PART II

REACTIONS OF SOME STRAINED RING SYSTEMS WITH DIIRON NONACARBONYL
Reactions of carbonyl iron complexes with compounds whose structural features incorporate the vinylcyclopropane or methylenecyclopropane carbon skeleton have received considerable attention recently.\textsuperscript{1-10} Vinylcyclopropanes, when properly activated, afford a novel source of four $\pi$-electrons suitable for complexing with iron tricarbonyl. Thus compound 2 probably results from an initial complexing at the vinyl group, followed by cyclopropane ring opening, to yield a four-electron-donor complex intermediate, in which the organic moiety is bound to the metal by both a $\sigma$-component and a $\pi$-allylic component. The formation of the final product involves a hydrogen shift to the terminal carbon atom, $\sigma$-bound to the metal to obtain the more stable trans-diene $\pi$-complex.\textsuperscript{1}

Reaction of 1,1-dicyclopropylethane(3) with Fe(CO)$_5$ gives the diene
complex 4, accompanied by 5, a product resulting from carbon monoxide insertion coupled with a double cyclopropane ring-opening.²

\[ \text{3} \xrightarrow{\text{4}} \text{Fe} \quad \text{(CO)}_3 \quad \text{5} \]

Spiro[2.4]hepta-4,6-diene(6) gives the expected diene complex 7 and (6-methylfulvene)diiron hexacarbonyl(8). The mechanism proposed¹ for the reaction of activated cyclopropanes with Fe(CO)₅ which involves the formation of an iron-carbon bond is sterically impossible in this case.³

\[ \text{6} \xrightarrow{\text{7}} \text{Fe} \quad \text{(CO)}_3 \quad \text{8} \]

Bullvalene(9), isobullvalene(11) and semibullvalene(12) give complexes resulting from cleavage of the cyclopropane rings with formation of both a π-allyl and a σ component bound to the Fe(CO)₃ unit.⁴,⁵

\[ \text{9} \xrightarrow{\text{10a}, \text{10b}} \text{Fe} \quad \text{(CO)}_3 \]
In contrast to semibullvalene (13), the reaction of dibenzobullvalene (15) with \( \text{Fe}_2(\text{CO})_9 \) gives the very stable and unique \( \sigma \)-bonded compound (16), formed by a simple oxidative cleavage of the cyclopropane ring.\(^6\) The stability of (16) is probably kinetic in origin, that is, there are no normal metal-alkyl decomposition pathways available such as \( \beta \)-elimination or carbon-carbon \( \sigma \) bond rearrangement for its decomposition.\(^7\)

Benzvalene (17) reacts with \( \text{Fe}_2(\text{CO})_9 \) by a complicated mechanism of fragmentation, rearrangement and hydrogen transfer to give (18), (19), (20) and (21).\(^8\)
Vinylcyclopropane (22) itself reacts with Fe$_2$(CO)$_9$ at -50°C to give 4,5-η-vinylcyclopropane iron tetracarbonyl (23) and 3,4,5,6-η-hex-4-en-3,6-yl-6-one iron tricarbonyl (24). Compound 23 is converted to the diene complexes 25a and 25b on warming to 50°C. Compound 24 decomposes at 25°C losing carbon monoxide to give 26. This reaction is reversible and when carbon monoxide is bubbled through a hexane solution of 26 for a few seconds, compound 24 is formed.
Methylene cyclopropane (27) gives a low yield (2%) of butadiene tricarbonyliron (28) upon reaction with Fe$_2$(CO)$_9$; however methylenecyclopropanes bearing either phenyl or methyl substituent on C-2, 29a-c, give the trimethylenemethane-coordinated products 30a-c.
Very recently an interesting report has appeared on the reaction of Feist's ester (dimethyl methylenecyclopropane-2,3-carboxylate) (31) with diiron nonacarbonyl. The reaction of Fe₂(CO)₉ with cis and trans 31 leads first to the corresponding iron tetracarbonyl olefin complexes, and then predominately to the cleavage of the sp²-sp³ bond of the methylenecyclopropane ring followed by a series of stereospecific

\[
\begin{align*}
\text{CO}_2\text{CH}_3 & \quad \rightarrow \quad \text{CO}_2\text{CH}_3 \\
\text{CO}_2\text{CH}_3 & \quad \rightarrow \quad \text{CO}_2\text{CH}_3 \text{Fe} \quad (\text{CO})_4
\end{align*}
\]

31-trans

\[
\begin{align*}
\text{CO}_2\text{CH}_3 & \quad \text{Fe}(\text{CO})_4 + \quad \text{CO}_2\text{CH}_3 \\
\text{CO}_2\text{CH}_3 & \quad \text{Fe}(\text{CO})_4 \quad \rightarrow \quad \text{CO}_2\text{CH}_3 \text{Fe}(\text{CO})_4 \\
\text{CO}_2\text{CH}_3 & \quad \text{CH}_3\text{O}_2\text{C} \quad \rightarrow \quad \text{CH}_3\text{O}_2\text{C}
\end{align*}
\]

32-trans
reactions leading eventually to diene iron tricarbonyl complexes of cis and trans dimethyl 1,3-butadiene-1,2-dicarboxylate (32). A minor pathway involves cleavage of the sp\(^3\)-sp\(^3\) ring bond, and leads to the diiron species 33. Curiously, trimethylenemethane complexes 34 and 35 were not observed.

Vinylmethyleneacylpropene (37) and its derivatives offer interesting substrates for reaction with iron carbonyls since their structural features incorporate both the vinylcyclopropane and methylenecyclopropane carbon skeleton. Part II of this thesis involves such a study.
RESULTS AND DISCUSSION

Vinylmethylene cyclopropane (37) was synthesized from 1,1-dichloro-
2-ethyl-3-methylcyclopropane (36) according to the method of Shields,
Billups and Lepley.11

\[
\begin{align*}
\text{Cl} & \quad \text{KOT-Bu} \\
\text{Cl} & \quad \text{DMSO} \\
\text{36} & \quad \text{37}
\end{align*}
\]

An equimolar mixture of 37 and Fe\textsubscript{2}(CO)\textsubscript{9} was stirred in benzene at
35-40°C for two hours under nitrogen and then filtered through celite.
Bulb-to-bulb distillation (92°C/2.5 mm Hg) gave a green oil, identified
as 38, vinyltrimethylenemethane tricarbonyliron, in 43% yield. It’s

\[
\begin{align*}
\text{H}^4 & \quad \text{H}^5 \\
\text{H}^3 & \quad \text{H}^6 \\
\text{H}^7 \text{H}^8 & \quad \text{H}^1 \\
\text{Fe}^2 & \quad \text{Fe}^3
\end{align*}
\]

molecular composition was shown to be C\textsubscript{6}H\textsubscript{8}Fe(CO)\textsubscript{3} by its mass spectrum
(parent molecular ion m/e 220 together with fragments at 192, 164 and
136 from successive loss of three carbonyl groups and at m/e 80 due
to the C\textsubscript{6}H\textsubscript{8} ion). The infrared spectrum showed carbonyl absorptions
at 2048, 1984 cm\textsuperscript{-1} and C=C absorption at 1615 cm\textsuperscript{-1}. The \textsuperscript{1}H nmr spectrum
(Table 1) of 38 provides convincing evidence for the proposed structure.
Table 1. $^1$H-NMR parameters of (38) determined at 60 MHz and relative to TMS=0

<table>
<thead>
<tr>
<th></th>
<th>δ (ppm)</th>
<th>J (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-1</td>
<td>3.67 (d, d)</td>
<td>$J_{1,6} = 9.7; J_{1,4} = 2.1$</td>
</tr>
<tr>
<td>H-2</td>
<td>1.80 (d)</td>
<td>$J_{2,5} = 4.3$</td>
</tr>
<tr>
<td>H-3</td>
<td>1.79 (s)</td>
<td></td>
</tr>
<tr>
<td>H-4</td>
<td>2.18 (m)</td>
<td></td>
</tr>
<tr>
<td>H-5</td>
<td>2.66 (d)</td>
<td>$J_{2,5} = 4.3$</td>
</tr>
<tr>
<td>H-6 to H-8</td>
<td>4.83-6.03 (m)</td>
<td></td>
</tr>
</tbody>
</table>

In addition, the decoupled $^{13}$C-NMR spectrum of 38 at ambient probe temperature shows seven distinct signals. Two $^{13}$C resonances may be immediately identified as due to the carbonyl carbon (~214.8 ppm) and the central carbon of the trimethylenemethane ligand (~105.2 ppm) by simple chemical and signal consideration. The two methylene resonances at -51.9 and -52.5 ppm are quite near those observed for trimethylenemethane tricarbonyliron, while those at -137.6 and -118.7 ppm are near the resonances of the vinyl group of compound 37. The nonequivalence of the signals at -51.9 and
and -52.2 ppm indicates, not surprisingly, that there is restriction to rotation of the carbon-carbon bond adjoining the vinyl group and the central carbon of the trimethylenemethane moiety. Similarly, the observation of a singlet for the three carbonyls implies free rotation of the Fe(CO)$_3$ group, consistent with observation made by others for related systems.\textsuperscript{13}

An X-ray diffraction study for the interestingly related compound, phenyltrimethylenemethane tricarbonyliron (30a), has been reported.\textsuperscript{14}

The iron atom is located directly beneath the central carbon atom of the trimethylenemethane skeleton (the Fe-C$_1$ distance being 1.929 Å) and is $\pi$ bonded to all four carbon atoms of the ligand. The carbon skeleton of the ligand forms a tetrahedron, with C$_1$ displaced away from the iron atom relative to the C$_2$-C$_3$-C$_4$ plane by 0.31 Å. The trimethylenemethane ligand and the Fe(CO)$_3$ moiety adopt a mutually staggered conformation,
forming a trigonal antiprism. It also appears that the phenyl ring makes an angle of ca. 59° with the plane defined by C₂–C₃–C₄ which seems to indicate that there is little conjugation between the phenyl and trimethylenemethane systems. Introduction of phenyl groups into the trimethylenemethane portion of the complex does not greatly effect the principal carbonyl frequencies (Table 2). This might imply that, in agreement with the result of the X-ray diffraction study, the phenyl ring is not coplanar with the plane of the adjacent sp² carbon atom even in solution.¹⁰ The spectral properties of compound 38 do not support extensive conjugation between the vinyl and trimethylenemethane functions of this compound.

Table 2. The principal carbonyl absorptions of compounds 39, 30α and 38

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>NARROW BAND</th>
<th>BROAD BAND νCO cm⁻¹ in CCl₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>39</td>
<td>2061 (m)</td>
<td>1995 (s)</td>
</tr>
<tr>
<td>30α</td>
<td>2058 (m)</td>
<td>1996 (s)</td>
</tr>
<tr>
<td>38</td>
<td>2048 (m)</td>
<td>1984 (s)</td>
</tr>
</tbody>
</table>

trimethylenemethane tricarbonyliron (39)
2,2-Dimethyl-1-allylidencyclopropane (43)\textsuperscript{16} is an interesting substrate for reaction with Fe\textsubscript{2}(CO)\textsubscript{9}. This compound incorporates both the conjugated diene and allylidencyclopropane functionalities. It was synthesized as a mixture of syn and anti isomers as illustrated below. Purification was accomplished by bulb-to-bulb distillation.

\[ \text{HO} \xrightarrow{1. \text{NaHSO}_3} \xrightarrow{2. \text{KOT-Bu}} \text{DMSO} \]

GLpc and nmr analyses showed that the two isomers were present in a ratio of 56:44, although stereochemical assignments were not made.

Reaction of 50 m mole of 43 with 50 m mole of Fe\textsubscript{2}(CO)\textsubscript{9} in refluxing benzene (70 ml) for 50 min, followed by filtration through celite and bulb-to-bulb distillation gave a mixture of C\textsubscript{6}H\textsubscript{12}Fe(CO)\textsubscript{3} complexes (3.96 gm, 32% yield). Gas chromatography (10 ft.×1/4 in. 10% UCON W-98 on chromosorb P operated at 130°C using He, 30 ml/min, as carrier gas) showed two major products in a ratio of 41:59 in order of their retention times. These two products were isolated by column chromatography (silica gel-
CCl₄) under nitrogen and identified as 44 and 45. Traces of a third compound were found and characterized as 46. Compound 44 was found in early fractions. The mass spectrum showed a parent molecular ion m/e 248 with other fragments at m/e 220, 192 and 164 from successive loss of CO. The infrared spectrum showed carbonyl absorptions at 2045 and 1975 cm⁻¹. ¹H nmr spectral parameters are shown in Table 3. Pure 45

Table 3. ¹H-NMR data (60 MHz) for compounds 44, 45 and 46

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>δ(ppm)</th>
<th>ASSIGN</th>
<th>J(Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.27(ABq)</td>
<td>cyclopropyl</td>
<td>J_AB = 4.66</td>
<td></td>
</tr>
<tr>
<td>0.68(ABq)</td>
<td>cyclopropyl</td>
<td>J_AB = 4.66</td>
<td></td>
</tr>
<tr>
<td>0.92(m)</td>
<td>H-1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.15(s)</td>
<td>methyl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.22(s)</td>
<td>methyl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.92(m)</td>
<td>H-2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.00-5.70(m)</td>
<td>H-3,4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

44

|          |        |        |       |
| 1.53(s)  | methyl |        |       |
| 1.60(s)  | methyl |        |       |
| 2.46(d)  | H-1    |       | J = J₁₃ = 2.43 |
| 2.53(s)  | H-2    |       |       |
| 4.11(d, d) | H-3   |       | J₃₄ = 9.43 |
| 4.75-6.00(m) | vinyl |       |       |

45

TMS = 0.
was isolated from later fractions. The following spectral properties were obtained for this compound: mass spectrum, parent molecular ion m/e 248; ir, 2045 and 1975 cm⁻¹ (C≡O) and 1610 cm⁻¹ (C=O). The H-nmr data are listed in Table 3. Compound 46 was isolated in sufficient purity from intermediate cuts (mixed with 44) for characterization by nmr (Table 3).

The H-nmr provides convincing evidence for the proposed stereochemistry. The nmr spectrum of trimethylenemethane tricarbonyliron (39) appears a sharp singlet at δ 2.00 indicating the equivalency of all hydrogens, whereas substitution causes all the ligand protons to become nonequivalent. Further, only trans coupling (W coupling) of the ligand protons are observed. Thus for compound 45, the proton H-1, couples with H-3 by long range trans or W coupling (J₁,₃ = 2.43 Hz), whereas H-2 appears as a singlet since it is located over a W configuration from the methyl substituent. With this in mind, it is easy to distinguish compound 46 (syn) from its anti-isomer 45.

There is no indication that these products interconvert during purification. In fact, attempts to thermally interconvert the isomers by heating 44 or 45 in refluxing benzene or CCl₄ resulted in decomposition,
but not isomerization. In addition, when the pure isomers were passed through the silica gel column no isomerization but some decomposition was observed.

It was of interesting to determine whether the syn and anti stereoisomers behaved differently in the reactions with Fe₂(CO)₉. The pure isomers are readily available by preparative glpc (15 ft. x 1/4 in. 15% β, β'-oxydipropionitrile on chromosorb P operated at 45°C using He as carrier gas). Both isomers exhibit near identical nmr spectra as shown in Table 4. The isomer with the shorter retention time is called isomer A and the remaining one isomer B.

Table 4. ¹H-NMR parameters of stereoisomers of 43 determined at 60 MHz and relative to TMS

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>δ(ppm)</th>
<th>ASSIGN</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISOMER A</td>
<td>0.94(broad s, 2 H)</td>
<td>cyclopropyl</td>
</tr>
<tr>
<td></td>
<td>1.19(s, 6 H)</td>
<td>methyl</td>
</tr>
<tr>
<td></td>
<td>4.64-5.40(m, 2 H)</td>
<td>olefinic</td>
</tr>
<tr>
<td></td>
<td>6.04-6.74(m, 2 H)</td>
<td>olefinic</td>
</tr>
<tr>
<td>ISOMER B</td>
<td>1.01(broad s, 2 H)</td>
<td>cyclopropyl</td>
</tr>
<tr>
<td></td>
<td>1.23(s, 6 H)</td>
<td>methyl</td>
</tr>
<tr>
<td></td>
<td>4.68-5.43(m, 2 H)</td>
<td>olefinic</td>
</tr>
<tr>
<td></td>
<td>6.00-6.75(m, 2 H)</td>
<td>olefinic</td>
</tr>
</tbody>
</table>

TMS = 0.

Upon reaction with Fe₂(CO)₉, isomer A gave 67% of the diene complex 44 and 33% trimethylenemethane complex 45 (total yield 46%), whereas
the remaining isomer, isomer B, gave 45 (21% yield) and a trace of 46. Formation of the diene complex from the syn isomer would be difficult since the gem-dimethyl group would be expected to impose a severe steric restraint for diene coordination. On this basis, isomer A is identified with the anti stereoisomer and B with the syn stereoisomer.

Additional evidence for this stereochemical assignment is provided by the nuclear Overhauser effect (nOe).\textsuperscript{20,21,22} Thus, when the terminal diene protons of isomer A (δ 4.64-5.40) were irradiated the relative intensity ratio of methyl and cyclopropyl protons did not change. However, when isomer B was irradiated (δ 4.68-5.43) this ratio increased from 3.00 to 3.11. The results of several such experiments are shown in Tables 5 and 6.

Finally, the reaction mechanism shown below accounts for these observations. In this mechanism the 5-bond is opened by the Fe(CO)\textsubscript{4} group to form the intermediates 47 and 48 from the syn- and anti-stereoisomers of 43 respectively. For steric reasons, 47 is probably unstable relative to 48, and would isomerize to 48. Loss of CO from these supposed intermediates would then lead directly to products.
Table 5. The Intramolecular nOe Study of the syn- and anti-Stereoisomers of Compound (43)

<table>
<thead>
<tr>
<th>Molecule</th>
<th>δ(ppm)</th>
<th>δ(ppm)</th>
<th>% Area Increase(+ or Decrease(-)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Protons</td>
<td>Protons</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Irradiated</td>
<td>Observed</td>
<td></td>
</tr>
<tr>
<td>ISOMER A</td>
<td>6.04-8.74(olefinic)</td>
<td>6.64-5.40(olefinic)</td>
<td>-33</td>
</tr>
<tr>
<td></td>
<td>6.64-5.40(olefinic)</td>
<td>6.04-6.74(olefinic)</td>
<td>-14</td>
</tr>
<tr>
<td></td>
<td>1.19(methyl)</td>
<td>1.19(methyl)</td>
<td>+7</td>
</tr>
<tr>
<td></td>
<td>0.94(cyclopropyl)</td>
<td>0.94(cyclopropyl)</td>
<td>+7</td>
</tr>
<tr>
<td>1.19(methyl)</td>
<td>6.04-6.74(olefinic)</td>
<td>4.64-5.40(olefinic)</td>
<td>+13</td>
</tr>
<tr>
<td></td>
<td>0.94(cyclopropyl)</td>
<td>0.94(cyclopropyl)</td>
<td>-13</td>
</tr>
<tr>
<td>0.94(cyclopropyl)</td>
<td>6.04-6.74(olefinic)</td>
<td>4.64-5.40(olefinic)</td>
<td>+20</td>
</tr>
<tr>
<td></td>
<td>1.19(methyl)</td>
<td>1.19(methyl)</td>
<td>-13</td>
</tr>
<tr>
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<td>6.00-6.75(olefinic)</td>
<td>4.68-5.43(olefinic)</td>
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</tr>
<tr>
<td></td>
<td>1.23(methyl)</td>
<td>1.23(methyl)</td>
<td>+11</td>
</tr>
<tr>
<td></td>
<td>1.01(cyclopropyl)</td>
<td>1.01(cyclopropyl)</td>
<td>+12</td>
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<tr>
<td></td>
<td>1.01(cyclopropyl)</td>
<td>1.01(cyclopropyl)</td>
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</tr>
<tr>
<td>1.23(methyl)</td>
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<td>4.68-5.43(olefinic)</td>
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<tr>
<td></td>
<td>1.01(cyclopropyl)</td>
<td>1.01(cyclopropyl)</td>
<td>+18</td>
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<tr>
<td>1.01(cyclopropyl)</td>
<td>6.00-6.75(olefinic)</td>
<td>4.68-5.43(olefinic)</td>
<td>+18</td>
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<tr>
<td></td>
<td>1.23(methyl)</td>
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Relative to TMS internal standard.
Table 6. Relative Intensity Calculated from the Intramolecular nOe Study of the syn- and anti-Stereoisomers of Compound (43)

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<tr>
<th>ISOMER A</th>
<th>6.04-6.74</th>
<th>4.64-5.40</th>
<th>1.19</th>
<th>0.94 δ (ppm)</th>
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<tr>
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<td>1.60</td>
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<td>0.63</td>
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<tr>
<td>0.75</td>
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<td>1.14</td>
<td>1.29</td>
<td>3.00</td>
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</table>

<table>
<thead>
<tr>
<th>ISOMER B</th>
<th>6.00-6.75</th>
<th>4.68-5.43</th>
<th>1.23</th>
<th>1.01</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>1.00</td>
<td>3.00</td>
<td>1.00</td>
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</tr>
<tr>
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<td>1.00</td>
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<td>1.46</td>
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<tr>
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<td>0.68</td>
<td>3.17</td>
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<tr>
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<td>8.21</td>
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<tr>
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<td>3.11</td>
<td>1.00</td>
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<td>1.25</td>
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<tr>
<td>1.00</td>
<td>1.11</td>
<td>3.00</td>
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</tbody>
</table>
In another study the reaction of naphtho[b]cyclopropene (51) with Fe₂(CO)₉ was investigated with the expectation that the high strain energy and resulting π-bond distortion associated with this ring system might lead to compounds such as 52 and 53.

![Chemical structures](image)

Naphtho[b]cyclopropene (51) was synthesized according to the method of Billups and Chow²⁴ and reacted with Fe₂(CO)₉ by stirring in benzene or methylenechloride under nitrogen. Some typical reaction conditions are listed in the Table 7. After the reaction was complete (TLC), the

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>Fe₂(CO)₉</th>
<th>SOLVENT</th>
<th>TEMPERATURE</th>
<th>YIELD: C₁₂H₈Fe(CO)₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.005 mole</td>
<td>0.010 mole</td>
<td>benzene</td>
<td>25°C</td>
<td>no reaction</td>
</tr>
<tr>
<td>0.005 mole</td>
<td>0.010 mole</td>
<td>benzene</td>
<td>40-45°C</td>
<td>24-27%</td>
</tr>
<tr>
<td>0.005 mole</td>
<td>0.010 mole CH₂Cl₂</td>
<td>40-41°C</td>
<td>28%</td>
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</tr>
<tr>
<td>0.005 mole</td>
<td>0.005 mole CH₂Cl₂</td>
<td>25°C</td>
<td>30%</td>
<td></td>
</tr>
<tr>
<td>0.005 mole</td>
<td>0.010 mole CCl₄</td>
<td>40-45°C</td>
<td>polymerization</td>
<td></td>
</tr>
</tbody>
</table>

mixture was filtered through celite and discolored with charcoal. The
solvent was then removed leaving a residue of yellow needle-like crystals.

Purification of products proved to be difficult, even though a variety of techniques including fractional crystallization and column and thin layer chromatography were tried. As a last resort, the mixture was refluxed in benzene (80°C) until the minor product was destroyed. In this manner a pure compound was isolated. This compound was insoluble in \( \text{CCl}_4 \) and pentane, but soluble in \( \text{CH}_2\text{Cl}_2 \) and \( \text{CHCl}_3 \). It was stable at room temperature even under air. Decomposition occurred above 140°C.

Provisional identification of this wholly novel compound as \( \text{54} \) was provided by spectroscopic data: nmr (CDCl\(_3\)) \( \delta 3.57 \) (s, 2H) and 7.25-8.25 (m, 6H, aromatic); ir (KBr) carbonyl absorptions at 2115, 2070, 2020 and 1660 cm\(^{-1}\). Elemental composition was provided by high resolution mass spectroscopy: parent molecular ion m/e 335.9731, cal. 335.9719. Other fragments at m/e 308, 280, 252, 224 and 196 correspond to the successive loss of CO. The major impurity \( \text{55} \) has a singlet at \( \delta 1.56 \) (spectra shown in Appendix). Attempts to purify this material failed. Complete structural confirmation of \( \text{54} \) was provided by X-ray crystal analysis at Texas A & M University by professor F. A. Cotton.

![Diagram](image.png)

\( \text{54} \)

An nmr singlet at \( \delta 1.22 \) was frequently observed in the spectrum of the crude reaction mixture of \( \text{51} \) and \( \text{Fe}_2\text{(CO)}_9 \), but disappeared after work-up by column chromatography. When the reaction was run for a short time and the crude products passed through a column (silica gel, \( \text{CHCl}_3 \)) at a rapid
rate, a green oil was isolated whose nmr (CDCl$_3$) spectrum showed in addition to the singlet at $\Delta$ 1.22 a multiplet in the aromatic region at 6.80-7.80 (6H). The instability of this material prevented further characterization.

In addition to the organoiron compound 54, a trace of the organic dimer 57 was isolated. Compound 57 was identified from its spectral properties. Nmr (CDCl$_3$) showed signals at $\Delta$ 4.56 (s, 4H), 7.10-7.90 (m, 10H, aromatic) and 8.17 (s, 2H, aromatic); ir carbonyl absorption at 1672 cm$^{-1}$; mass spectrum, parent molecular ion m/e 536 and fragments at 310, 296, 268. The fragmentation of 57 in the mass spectrum excluded the alternative structure 58. The origin of diketone 57 is not clear; however, the thermal stability of 54 would seem to preclude it as a precursor of 57.

Finally, structures very similar to compound 54 have been proposed in several reports by Collman and his co-workers as intermediates in their synthesis of aldehydes and ketones$^{25,26}$ from Na$_2$Fe(CO)$_4$ and alkyl halides (illustrated below). A similar decomposition of 54 would give naphtho[b]-cyclobutenone (59), but this compound was not observed. In fact, 54 might own its stability to the difficulty in forming the four membered ring since other normal decomposition pathways such as $\beta$-elimination or carbon-carbon $\sigma$ bond rearrangement are not available.
General. All melting points and boiling points were uncorrected. The infrared spectra were recorded on a Beckman IR 8 spectrometer as either neat films, chloroform solution or KBr plates. Proton nmr spectra were obtained with a Varian A-56/60A or a Perkin-Elmer R-12 spectrometer in CCl₄ or CDCl₃ solution and results were expressed in parts per million downfield from internal TMS. GLpc analysis were carried out on a Hewlett Packard Model 700 gas chromatograph and preparative work was done on a Autoprep Model A-700 gas chromatograph with a thermal conductivity detector. Specific columns and conditions were noted in individual experiments. Mass spectra were obtained with a double focusing C.E.C. 21-110B mass spectrometer (Mattauch-Herzog design).

Materials. Benzene and methylene chloride used in the organoiron carbonyl reactions were spectroquality and were degassed by continuous nitrogen purging before use. All reactions were run in an atmosphere of purified nitrogen. Tetrahydrofuran was distilled from sodium-benzophenone ketyl immediately before use. DMSO was distilled from calcium hydride under reduced pressure and stored over 4A molecular sieves prior to use. DMF was dried over 4A molecular sieves several days before use. All other chemicals were reagent grade and used as received.

Diiron Nonacarbonyl. A stirred solution of iron pentacarbonyl (39.2 gm, 0.20 mole) in 150 ml of glacial acetic acid was irradiated at 0°C under nitrogen with a sunlight lamp. After ten hours, the precipitate of red-orange diiron nonacarbonyl was collected and washed several times with benzene. Irradiation of the mother liquid produced additional Fe₂(CO)₉
for an overall yield of about 80%.

**Vinyltrimethylenemethane tricarbonyliron (38).** 4.00 gm of vinylmethylene cyclopropane (37) (0.05 mole) and 70 ml of benzene were placed in a three necked flask equipped with nitrogen flushing system, a condenser, a stirrer and a thermometer. 18.20 gm (0.05 mole) of Fe₂(CO)₉ was then added under nitrogen and the mixture was stirred at 35-40°C for two hours. The reaction mixture was then cooled and filtered through celite. After removal of benzene, bulb to bulb distillation gave 4.73 gm (43% yield) of 38, b.p. 92°C/2.5 mm Hg, as a deep green oil.

nmr (CDCl₃): $\delta$ 3.67 (d, d, J=9.7 Hz, 2.1 Hz, 1H), 1.80 (d, J=4.3 Hz, 1H), 1.79 (s, 1H), 2.18 (m, 1H), 2.66 (d, J=4.3 Hz, 1H) and 4.83-6.03 (m, 3H).

ir (CHCl₃): 2048 (s) and 1984 (s) cm⁻¹.

mass spectrum: m/e 220 (M⁺), 192 (-CO), 164 (-2CO), 136 (-3CO) and 80 (-Fe(CO)₃).

**2-Methyl-2-hexanol (40).** 48.6 gm of magnesium (2.0 mole) was placed between two pieces of clean, dry filter paper and crushed between two dry wooden blocks. The magnesium was then added to a 2000 ml three necked flask equipped with condenser, stirrer and additional funnel. 550 ml of anhydrous ether which contained several drops of ethylene bromide was added followed by the dropwise addition of n-butyl bromide (2.0 mole). After all the bromide was added, the mixture was refluxed on a steam bath for one hour, and the resulting solution then cooled via an ice water bath. Acetone (116 gm, 2.0 mole) was added dropwise over a three hour period and the mixture refluxed for one additional hour and cooled to room temperature. Saturated NH₄Cl solution was added until the mixture was clear.
The resulting suspension of magnesium salts was filtered and the organic layer washed twice with water and dried over sodium sulfate. Distillation under reduced pressure afforded 186 g (80% yield) of compound 40 as a colorless liquid.

nmr (CCl₄): 6 3.98 (broad s, 1H, hydroxyl proton), 1.18 (s, 6H, methyl) and 1.70-0.50 (m, 9H).

2-Methyl-2-hexene (41a) and 2-Methyl-1-hexene (41b). 186 gm of compound 40 (1.60 mole) was placed in a 1000 ml flask equipped with a condenser. 10 gm of NaHSO₃ was then added and the mixture refluxed for 24 hours. The olefins were co-distilled with water at 80-90°C. After the distillation was complete, the organic layer was separated from water and dried over Na₂SO₄. Distillation afforded 148 g of product, b.p. 92-94°C. From the glpc and nmr analyses, the ratio of compound 41a and 41b was 71:29.

Compound 41a: nmr (CCl₄) 6 1.59 (s, 3H, methyl), 1.67 (s, 3H, methyl), 0.70-2.20 (m, 7H) and 5.30-4.90 (m, 1H, olefinic).

Compound 41b: nmr (CCl₄) 6 0.70-2.20 (m, 12H) and 4.55-4.75 (m, 2H), olefinic).

Base-induced Isomerization of 2-methyl-1-hexene (41b). To a mixture of 17 gm of t-BuOK (0.15 mole) in 200 ml DMSO was added 147 gm (1.50 mole) of the mixture of 41a and 41b. After one hour the reaction was stopped by addition of 1000 ml of water and the product extracted into pentane. Distillation afforded a colorless liquid, b.p. 92-94°C, 142 gm, 97% yield.
1,1-Dichloro-2,2-dimethyl-3-n-propylcyclopropane (42). Using the same procedure as described for the synthesis of (36)\textsuperscript{11}, compound 42, a colorless liquid, b.p. 45°C/2.30 mm Hg, 90 gm (46% yield) was synthesized from 103.5 gm (1.08 mole) of compound 41a, 127 gm (1.08 mole) of CHCl\textsubscript{3} and 121 gm of t-BuOK (1.08 mole) in 800 ml of pentane.

nmr (CCl\textsubscript{4}) δ1.18 (s, 3H, methyl), 1.38 (s, 3H, methyl) and 0.60-2.10 (m, 8H).

ir (neat) 2940 (s), 2870 (s), 1455 (s), 1375 (s), 1010 (s), 995 (s) and 800 (s) cm\textsuperscript{-1}.

Synthesis and Separation of the syn-(43a) and anti-(43b) stereoisomers of 1,1-dimethyl-2-allylidene cyclopropane (43). Compound 43 was synthesized as a mixture of syn and anti isomers as described by Billups et al.\textsuperscript{16}

Separation of the two geometrical isomers by glpc was carried out on an Aerograph Autoprep A-700 instrument with thermal conductivity detector using a 15 ft x 1/4 in. column packed with 15% \(\beta\),\(\beta\)-oxydipropionitrile on chromosorb P (non-acid washed 80-100) at 45°C with helium as carrier gas (flow rate 30 ml/min).

Isomer A: nmr (CCl\textsubscript{4}) δ 0.94 (broad s, 2H, cyclopropyl), 1.19 (s, 6H, methyl), 4.64-5.40 (m, 2H, olefinic) and 6.04-6.74 (m, 2H, olefinic).

ir (neat) 3100 (w), 3045 (w), 2980 (s), 2965 (s), 2895 (m), 2877 (m), 1790 (w), 1613 (m), 1447 (w), 1367 (w), 1255 (w), 1120 (w), 995 (m) and 891 (m).

Isomer B: nmr (CCl\textsubscript{4}) δ 1.01 (broad s, 2H, cyclopropyl), 1.23 (s, 6H, methyl), 4.68-5.63 (m, 2H, olefinic) and 6.00-6.75 (m, 2H, olefinic).

ir (neat) 3090 (w), 3035 (w), 2965 (s), 2950 (s), 2887 (m), 2869 (m),
1800 (w), 1617 (m), 1453 (w), 1373 (w), 1243 (w), 1120 (w), 995 (m) and 891 (m) cm$^{-1}$.

**Reaction of 1,1-dimethyl-2-allyldenecyclopropane (43) with Diiron Nona carbonyl.** 5.40 gm of 43 (0.05 mole) and 70 ml of benzene were placed in a three necked flask equipped with nitrogen flushing system, condenser, stirrer and a thermometer. 18.2 gm of Fe$_2$(CO)$_9$ (0.05 mole) was then added and the temperature allowed to rise from 25°C to 75°C. The homogeneous green solution was then refluxed at 81°C for 50 min., cooled and filtered through celite. After removal of benzene, distillation under reduced pressure afforded 3.96 gm (32%) of a green oil, b.p. 128-131°C/1.20 mm Hg. Glpc analysis showed two products in a ratio of 41:59. Separation of iron tricarbonyl complexes 44, 45 and 46 was achieved by repeated column chromatography (25 x 420 mm column, silica gel using CC$_4$ as eluent). The purity (>99%) of complexes 44 and 45 was shown by glpc (10 ft x 1/4 in. 10% UCON on chromosorb P using helium as carrier gas and operated at 130°C). Silver nitrate on silica gel (36 gm of silica gel mixed with 12.5 gm of AgNO$_3$ in 87.5 gm of water heated to 60-80°C for one hour) afforded a better separation, but the iron tricarbonyl complexes decomposed much faster on this column.

**Compound 44** is a yellow green oil with the following spectral properties. nmr (CDCl$_3$) δ 0.27 ($AB_q$, $J_{AB}=4.66$ Hz, 1H, cyclopropyl), 0.68 ($AB_q$, $J_{AB}=4.66$ Hz, 1H, cyclopropyl), 0.92 (m, 1H), 1.15 (s, 3H, methyl), 1.22 (s, 3H, methyl), 1.92 (m, 1H) and 5.00-5.70 (m, 2H).

ir (neat) 3040 (m), 3010 (m), 2045 (s), 1975 (s) and 985 (m) cm$^{-1}$.

mass spectrum: m/e 248 ($M^+$), 220 (-100), 192 (-200) and 164 (-300). Compounds 45 is a yellow oil which exhibits the following properties:
nmr (CDCl₃) δ 1.53 (s, 3H, methyl), 1.60 (s, 3H, methyl), 2.46 (d, J=2.43 Hz, 1H), 2.53 (s, 1H), 4.11 (d, d, J=2.43 Hz, 9.43 Hz, 1H) and 4.75-6.00 (m, 3H, vinyl).

ir (neat) 2045 (s), 1975 (s) and 1610 (m) cm⁻¹.

mass spectrum: m/e 248 (M⁺), 220 (c1CO), 192 (-2CO) and 164 (-3CO).

compound 46: This compound was not isolated in pure form but was found in several cuts mixed with compound 44.

nmr (CDCl₃) δ 1.46 (s, 3H, methyl), 1.48 (s, 3H, methyl), 2.20 (s, 1H), 2.24 (s, 1H), 3.47 (d, J=9.43 Hz, 1H) and 4.55-5.80 (m, 3H, vinyl).

Reactions of pure syn and anti 43 with Fe₂(CO)₉. These reactions were run using the procedure described above for the mixture of isomers. 0.15 gm of pure isomer A and 0.20 gm of pure isomer B were reacted with 1.80 gm and 2.40 gm of Fe₂(CO)₉ in 10 ml of benzene respectively. Product ratios were calculated from the relative nmr intensities of the methyl group absorptions. Isomer A gave compounds 44 and 45 in a ratio of 67:33 with a total yield of 46%, while isomer B gave 21% of compound 45 and only a trace of 46.

Reactions of Naphtho[b]cyclopropene (51) with Diiron Nonacarbonyl.
A mixture of naphtho[b]cyclopropene (0.70 gm, 0.005 mole) and Fe₂(CO)₉ (3.64 gm, 0.010 mole) in 250 ml well deoxygenated benzene was stirred at 40-45°C for 2.5 hr under an atmosphere of nitrogen. The mixture was then filtered through celite. After removal of solvent, the product 54 was purified by column chromatography (florisil using CHCl₃ as eluent) giving bright yellow crystals which decomposed around 140°C, 0.493 gm (yield 27%). An impurity (nmr singlet δ 1.56) was removed by refluxing in benzene.
nmr (CDCl₃) δ 3.57 (s, 2H), 7.25-8.25 (m, 6H, aromatic).

ir (KBr) 2115 (s), 2070 (s), 2020 (s) and 1660 (s) cm⁻¹.

mass spectrum: m/e 335.9731 (M⁺), calculated, 335.9719, 308 (-1CO), 280 (-2CO), 252 (-3CO), 224 (-4CO), 196 (-5CO), 168 (-Fe(CO)₄) and 140 (-Fe(CO)₅).

When an equimolar mixture of 51 and Fe₂(CO)₉ in well deoxygenated CH₂Cl₂ was stirred at room temperature, heat was evolved and product 54 was produced. The nmr spectrum of the crude product showed a singlet at δ 1.22 which disappeared during further purification. Reaction of 51 with Fe₂(CO)₉ for a shorter reaction time (45 min) allowed isolation of this material as a green oil. It was very unstable and appeared to rearrange to 54.

nmr (CDCl₃) δ 1.22 (s, 2H) and 6.80-7.90 (6H, m, aromatic).

ir (CDCl₃) 2270 (s), 2030 (s), 2010 (s), 1805 (s) and 1790 (s) cm⁻¹.

The instability of this compound has so far precluded mass spectral analysis and further characterization has not been achieved.

A trace of diketone 57 was isolated as a white solid from the reaction of 51 and Fe₂(CO)₉.

nmr (CCl₄) δ 4.56 (4H, s), 7.10-7.90 (10H, m, aromatic) and 8.17 (2H, s, aromatic).

ir (CHCl₃) 3060 (m), 3030 (m), 1672 (s), 1625 (m), 1590 (m) and 1335 (m).

mass spectrum: m/e 536 (M⁺), 310 (C₁₄H₁₀O₂⁺), 296 (C₁₃H₈O₂⁺) and 268 (C₁₂H₈O⁺).
REFERENCES


Appendix I

Spectra