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THE HEATS OF HYDROGENATION OF FIVE EXOCYCLIC-ENDOCYCLIC OLEFIN PAIRS

by

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INTRODUCTION
INTRODUCTION

The first interpretation of the stability differences encountered in cyclic compounds possessing rings of varying size was advanced by Adolf von Baeyer in 1885 (1). Baeyer assumed planar structures for all ring compounds and attributed the observed stability differences to variations in angle strain arising from distortion of the normal tetrahedral bond angles of carbon. The Baeyer strain theory failed to account for the greater stability of 6- as compared to 5-membered ring derivatives* since angles of 120° are required in the former system, if planar, whereas the 108° angles of the planar 5-ring closely approximate the tetrahedral value of 109° 28'. With subsequent recognition of the possibility of ring puckering by Sachse (3) and Mohr (4) and development of the method of conformational analysis, which assigns special importance to repulsive interactions between non-bonded substituents, the chemical behavior of saturated 5-, 6- and larger ring compounds has been satisfactorily explained. Thus, cyclohexane exists preferentially in the chair conformation (I), with adjacent hydrogens staggered as in the staggered form of ethane, whereas cyclopentane

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*The heats of combustion per methylene group for cyclohexane and for cyclopentane are 157.4 and 158.7 kcal., respectively (2).
approximates a planar structure (II) with hydrogens eclipsed, or nearly so*, and the lesser stability of cyclopentane derivatives is interpreted in terms of the higher energy of the eclipsed arrangement.

\[ \text{I.} \quad \text{II.} \]

The nature of the repulsive forces involved in the interaction of eclipsed non-bonded atoms has not been precisely defined. Eyring (7), in calculating the energy barrier to rotation in ethane, assumed the operation of van der Waals' repulsions, and obtained a value for the rotational barrier considerably lower than the currently accepted experimental value of 2.8 kcal./mole (8). More recently Lassette and Dean (9) have introduced a term for electrostatic repulsions of the electrons in the eclipsed bonds, and have concluded that such an effect contributes

*Various structures for cyclopentane, including the 5-carbon planar, 4-carbon planar (5), and 3-carbon planar (6) forms, have been discussed in the literature. In no case, however, is the proposed degree of non-planarity as large as that found in cyclohexane and eclipsing of hydrogens is a fundamental property of each of these models.
approximately equally with van der Waals' forces in determining the potential barrier. The most recently published information on the subject (10) is derived from microwave spectra and supports the view that the major fraction of the repulsive energy resides in bond interactions and is not due in any substantial measure to direct forces between substituent groups, at least in the case that these are hydrogens.

Introduction of a double bond, either endocyclic or exocyclic* to a 5- or 6-membered ring alters the structure of such a system with respect to both bond angles and non-bonded interactions. The conformational effects of these changes and the stability differences arising therefrom will be discussed in a later section of this thesis. It will suffice for the time being to note that the heat of hydrogenation of cyclopentene is 1.7 kcal./mole lower than that of cyclohexene (11, 12) despite the fact that the angle strain present in cyclopentene must clearly be greater than that in cyclohexene. It is therefore apparent that the enthalpy difference associated with repulsive interactions arising in the reduction products, cyclopentane and cyclohexane, is sufficiently large to obscure the strain difference in the corresponding olefins.

*The term "exocyclic" as used in this thesis refers to a bond joining a ring atom to an extraannular atom. The term "semicyclic" has been used in the older literature with the same connotation.
Calculations of "total strain energy" in cyclohexane, cyclopentane, cyclohexene and cyclopentene carried out by Pitzer (13) are consistent with this view.

In an attempt to rationalize the behavior of 5- and 6-membered ring compounds in situations involving a change in coordination number of a ring carbon atom from four to three and vice versa, Brown, Brewster and Shechter (14) proposed the following generalization: "reactions will proceed in such a manner as to favor the formation or retention of an exo double bond in the 5-ring and to avoid the formation or retention of the exo double bond in the 6-ring system." The validity of this statement has been challenged in several instances dealing for the most part with the question of relative stability of exo and endo unsaturated isomers in the 5-ring series (15, 16, 17). The objections, in general, result from the rule's implication that 5-ring compounds possessing exo double bonds are more stable than those possessing endo unsaturation. This implication was accepted by Wheeler (18), a colleague of Brown, in a communication in which the Brown rule was invoked as support for the prediction that at equilibrium 2-methylene-cyclopentanol (III) should be strongly favored over 1-cyclopentenylcarbinol (IV), whereas the reverse relationship should hold for the corresponding 6-membered
derivatives.* Brown (20), however, has maintained the position that the generalization was never intended to apply to the question of relative stability of exocyclic versus endocyclic unsaturation within a given ring system. In this event the interpretation to be placed on the acknowledgement in Wheeler's paper which reads, "The author is indebted to Drs. H. C. Brown and J. H. Brewster for helpful discussions and comments," is not entirely clear.

In an effort to clarify the issue raised by the generalization in its original form, Brown (20) has offered the following revision: "Double bonds which are exo to a 5-ring are less reactive and more stable

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*It has since been shown that both the 5- and 6-membered 2-methylenecycloalkanols rearrange in the presence of acid to the corresponding 2-methylcycloalkanones (19).
(relative to the saturated derivatives*) than related double bonds which are exo to a 6-ring. Reactions which involve the formation or retention of an exo double bond in a 5-ring derivative will be favored over corresponding reactions which involve the formation or retention of an exo double bond in a 6-ring derivative. Reactions which involve the loss of an exo double bond will be favored in the 6-ring as compared to the corresponding 5-ring derivative."

Although the first sentence of this statement appears to be a justifiable conclusion from the available evidence, the remainder of the revision, as well as the generalization in its original version, is inconsistent with the data presented in this dissertation. The generalization's emphasis upon exo unsaturation is particularly objectionable since it implies that special properties associated with exo double bonds provide the basis for interpretation of various stability relationships. In fact, as will be shown later, the major effect resides in the saturated derivative, since eclipsing in the cyclopentane, but not in the cyclohexane compounds, is relieved by the introduction of unsaturation, either exocyclic or endocyclic. In view of the confusion that has arisen in the interpretation of the Brown rule, it

*Italics inserted.
will be appropriate to review the areas of evidence on which this generalization is based.

Numerous observations indicate that reactions involving a change in the structure of a ring atom from tetrahedral to trigonal hybridization proceed more rapidly for cyclopentane derivatives than for those of cyclohexane. Thus, 1-methylcyclopentyl chloride undergoes solvolysis in 80% aqueous ethanol at a rate one hundred times faster than does 1-methylcyclohexyl chloride (21). On the other hand, reactions in which the rate-determining step involves a change from trigonal to tetrahedral hybridization proceed more rapidly in the 6-ring cases. Examples are provided by the relative rates of formation of the semicarbazones of cyclohexanone and cyclopentanone (22), and the relative rates of reduction of these cyclic ketones by sodium borohydride (23). From consideration of these facts, Brown has proposed that "in the 5-membered ring the trigonal structure for one of the ring atoms is strongly favored over the tetrahedral arrangement, whereas the reverse is true in the 6-membered ring." It will be noted that this conclusion goes considerably beyond the facts, which indicate only a greater tendency for the tetrahedral to trigonal conversion in the 5- than in the 6-membered ring, the reverse being true for trigonal to tetrahedral transformations.
Reactions involving ring expansion or ring opening have likewise been interpreted as providing support for the Brown generalization. Cyclohexanone undergoes the Baeyer-Villiger reaction with perbenzoic acid at a rate six times greater than cyclopentanone (24). The mechanism of the reaction has been studied by Doering (25), who established that the first stage of the process is an addition of perbenzoic acid to the carbonyl group (A).

\[
\text{A. } R\text{C}=O + \text{C}_6\text{H}_5\text{CO}_3\text{H} \rightarrow R\text{C}=O + \text{C}_6\text{H}_5\text{CO}_2\text{H}
\]

If this step is rate determining, as seems probable, the fact that cyclopentanone is oxidized less rapidly than cyclohexanone is a reflection of the severe eclipsed interactions expected to occur in the perbenzoic acid adduct of the 5-ring compound. The data does not, however, furnish any information on the stability of a 5-ring compound possessing exo unsaturation as compared to the corresponding 6-ring system.

Other examples that have been cited by Brown include the dimethylene and trimethylene carbonates, (V) and (VI).
The former compound is a highly stable substance which shows no tendency to polymerize (26). The latter compound, on the other hand, is thermally unstable and is readily converted by heat into a linear polymer (27).

In these cases the atoms \( \equiv \) to the carbonyl group are oxygens and any non-bonded interactions at these positions must involve the unshared oxygen electrons. Although the exact configuration of these electrons is difficult to assign it can certainly be assumed that the hybridization of the oxygen atoms is not pure \( sp^3 \) as is the case for an analogous methylene group. These facts complicate any theoretical argument which attributes stability in the 5-ring to a reduced number of eclipsed interactions.* Similarly, \( \delta \)-lactones (VII) and \( \delta \)-thiolactones (VIII) undergo hydrolysis (28, 29) and polymerization (30, 31) more readily than do the corresponding \( \sigma \)-lactones (IX) and \( \sigma \)-thiolactones (X). Formaldehyde reacts with glycerol to yield as the major

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*It should be noted that resonance interaction between the carbonyl group and oxygen (with oxygen in the \( p-sp^2 \) state) would confer considerable double bond character on the endo carbon-oxygen bond. Hence it is possible that this effect and not exo unsaturation controls the cases considered by Brown.
product* the 1,3-formal XI (a 6-membered ring with no double bond) (32), whereas the product of the reaction of phosgene with glycerol has been identified as having structure XII (a 5-ring containing an exo double bond) (33). In an example from the field of sugar chemistry, Brown has noted that under ordinary circumstances sugars

VII

VIII

IX

X

XI

XII

exist in solution as equilibrium mixtures of hemiacetals in which the pyranose form predominates. Treatment of the mixture with methanol and hydrogen chloride yields initially the methyl furanosides (XIII), but on more extended treatment the methyl pyranosides (XIV) are

*Large amounts of the 1,2-formal are also obtained in this reaction.
-11-

obtained (34). Although this observation has little bearing on the Brown generalization, since no double bonds are involved, it has been interpreted as indicating greater reactivity and lesser stability for the

![Chemical structures XIII and XIV](image)

furanose, which is removed preferentially from the equilibrium mixture as the methyl furanoside. When the glycoside equilibrium has been established, however, the pyranoside with no exo double bond will be the more stable. More pertinent to the present discussion is the observation that sugar acids exist predominately as 1,4-lactones, while the 1,5-hemiacetal is the preferred form of sugar aldehydes (35). It may finally be noted that in aqueous dioxane solution a greater percentage of \( \delta \)-hydroxyvaleraldehyde exists as the 6-ring hemiacetal than is the case with \( \gamma \)-hydroxybutyraldehyde, the cyclic hemiacetal of which is 5-membered (36). Conversely, in aqueous solution a greater proportion of \( \gamma \)-hydroxybutyric acid exists as the lactone (a 5-ring
with a exo double bond) than is the case with \( \delta \)-hydroxyvaleric acid (a 6-ring with an exo double bond) (28).

Thermochemical evidence has also been advanced by Brown in support of the generalization (see Table I).

**TABLE I**

**THERMOCHEMICAL DATA FOR CYCLOPENTANE AND CYCLOHEXANE DERIVATIVES**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Heat of Formation (gas, (25^\circ))</th>
<th>Increment (\Delta H_f(6)-\Delta H_f(5))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclopentane</td>
<td>-18.46(^a)</td>
<td></td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>-29.43(^a)</td>
<td>-11.0</td>
</tr>
<tr>
<td>Cyclopentanol</td>
<td>-59.3(^b)</td>
<td></td>
</tr>
<tr>
<td>Cyclohexanol</td>
<td>-70.5(^b)</td>
<td>-11.2</td>
</tr>
<tr>
<td>Cyclopentanone</td>
<td>-47.2(^c)</td>
<td></td>
</tr>
<tr>
<td>Cyclohexanone</td>
<td>-55.6(^c)</td>
<td>-8.4</td>
</tr>
</tbody>
</table>

\(^a\) See reference (37).
\(^b\) See reference (38).
\(^c\) Reported by H. C. Brown, et al., (14) from calculations by E. J. Prosen, National Bureau of Standards, from heats of combustion of cyclopentanol and cyclohexanol (38) and heats of hydrogenation of the corresponding ketones (39), with estimated or literature values for heats of vaporization.

It is noted that the difference in the heats of formation of cyclohexane and cyclopentane is -11.0 kcal./mole as compared with the incremental value per methylene group
of -4.9 kcal./mole (40) found in the normal paraffins. The corresponding value for the cyclohexanol-cyclopentanol difference is -11.2 kcal./mole, an observation which suggests little effect from the replacement of a hydrogen atom by a hydroxyl group. The difference in the heats of formation of the ketones, however, is only -8.4 kcal./mole. Thus replacement of a methylene group by a carbonyl group must lower the strain in the 5-ring system, increase it in the 6-ring system, or both. Of the three possibilities the last was chosen by Brown as the most acceptable. The heat of reaction for the conversion of propane to acetone is -27.0 kcal./mole (calculated from heats of formation (40, 41)). The values for the cyclopentane to cyclopentanone and cyclohexane to cyclohexanone conversions are respectively -28.7 and -26.2 kcal./mole. It follows,
therefore, that the stabilities of the ketones relative
to those of the parent hydrocarbons fall in the order
cyclopentanone $\succ$ acetone $\succ$ cyclohexanone. While this
argument may have some merit, it should be noted that
the differences involved are small, and that variations
in hyperconjugative stabilization of acetone (with six
$\alpha$ hydrogens) and cyclohexanone (with four $\alpha$ hydrogens)
might be sufficient to reverse the order of these two
substances.*

The evidence that has been considered thus far has
involved compounds in which the exo double bond has been
incorporated as a carbonyl group. Information relating
to olefinic substances is less extensive. Data that has
been advanced as support for the Brown rule has been
drawn from work of Dieckmann, Linsestid and Kon on equili-
bra in tautomeric systems involving endo- or exocyclic
double bonds. The pertinent information is summarized
in Table II. In all cases but the last the percent of
exo isomer at equilibrium is significantly larger in
the 5- than the 6-ring system. Similarly the more stable
forms of the unsaturated cyclopentyl and cyclohexyl

---

*Kreevoy and Taft (42) have recently concluded that
stabilization by hyperconjugation amounts to approxi-
mately 0.5 kcal./mole per hydrogen.
TABLE II
PER CENT OF EXO FORM AT EQUILIBRIUM

<table>
<thead>
<tr>
<th>Z</th>
<th>R = H</th>
<th>R = CH₃</th>
<th>R = H</th>
<th>R = CH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>-COCH₃</td>
<td>84ᵃ</td>
<td>64ᵇ</td>
<td>30ᶜ</td>
<td>ca 0ᵇ</td>
</tr>
<tr>
<td>-COCH₂CH₃</td>
<td>85-90ᵃ</td>
<td>--</td>
<td>30ᶜ</td>
<td>--</td>
</tr>
<tr>
<td>-CO₂CH₂CH₃</td>
<td>60ᵈ</td>
<td>88ᵈ</td>
<td>38ᶜ</td>
<td>5ᵈ</td>
</tr>
<tr>
<td>-CO₂H</td>
<td>14ᵉ</td>
<td>38ᵇ</td>
<td>12ᶠ</td>
<td>32ᵇ</td>
</tr>
</tbody>
</table>


Malonic esters have been shown to be XV and XVI respectively (49). The major products of self-condensation of cyclopentanone and cyclohexanone are indicated by structures XVII and XVIII (50), and it has been further established that distillation of the acid chloride XIX results in isomerization to the α, β-unsaturated isomer, whereas acid chloride XX yields the β, γ-unsaturated form under these conditions (51). In all these examples the issues raised by the Brown generalization are somewhat

.
obscured by the intervention of conjugative resonance, and a more detailed discussion of the problem will be deferred for consideration in a subsequent section of this dissertation.

[XV]

[XVI]

[XVII]

[XVIII]

[XIX]

[XX]
The best case for that portion of the revised Brown rule which seems acceptable as applied to olefins is based on examination of the results of various olefin forming eliminations. Iodine catalyzed dehydration of the tertiary alcohol XXI furnishes XXII as the major product in violation of the Saytzeff rule. Only 2.5% of isopropylidenedicyclohexane (the normal Saytzeff product)
was found in this reaction. Similar dehydration of dimethylcyclohexylcarbinol (XXIII) affords largely 1-isopropenylcyclohexane (XXIV) (52). It has been observed further (53) that optically active \( \alpha \)-terpineol (XXV), when dehydrated with either potassium bisulfate or alcoholic sulfuric acid, yields optically active limonene (XXVI). All of these reactions indicate a general reluctance on the part of the cyclohexane ring to accommodate an isopropylidene substituent. The formation of limonene in high optical purity in the dehydration of \( \alpha \)-terpineol is particularly informative since it demonstrates that equilibration of limonene with terpinolene (XXVII) does not occur under the conditions of dehydration.

With reference to analogous eliminations in 5-ring compounds, Brown has cited two cases in which exo olefins are reported as major products. Dimethylcyclopentylcarbinol (XXVIII), when heated in a sealed tube with fuming hydrogen bromide, affords the unstable bromide XXIX along with a product of rearrangement. Distillation of XXIX leads to isopropylidene cyclopentane (XXX) (54). Similarly, the hydroxy acid XXXI, when distilled in vacuo, yields the unsaturated acid XXXII and the lactone (55). In any case it is clear that if in these cases elimination involves abstraction of hydrogen from a
methyl group the resulting isopropenyl derivative (XXXIII), possessing a saturated 5-ring, would suffer eclipsed interactions involving not only hydrogen, but also the bulky isopropenyl group.

\[
\begin{array}{ccc}
\text{XXVIII} & \text{XXIX} & \text{XXX} \\
\text{XXXI} & \text{XXXII} & \text{+ lactone}
\end{array}
\]
Brown has proposed that the Mills-Nixon effect operates in accordance with his generalization. The Mills-Nixon effect describes the apparent proponderance of one Kekule structure for the aromatic ring in hydridene and tetrailin systems. Certain evidence exists which suggests that in hydridene there is a preference for the Kekule structure XXXIV, containing double bonds exo to a 5-ring, while in tetrailin the preference lies with structure XXXV, possessing no double bonds exo to the 6-ring (56). It may be noted that in each of these systems the two alternate structures contain the same number of ring substituents, and where exo unsaturation is present it necessarily involves two adjacent exocyclic double bonds.

\[ XXXIV \quad XXXV \]

Since data to be presented in this thesis is in conflict with important implications of the Brown generalization, it is necessary to examine the basis for Brown's emphasis upon stability differences of exo double bonds in the two ring systems, and, in particular, the assumptions that led him to suggest (a) that the exo-endo
difference for 5-ring olefins should be less than for 6-ring olefins, and (b) that a 5-ring compound possessing an exocyclic double bond is inherently more stable than a similarly constituted 6-ring derivative. The argument is as follows.

The difference between the heats of hydrogenation of cyclopentene (-26.9 kcal./mole) and cyclohexene (-28.6 kcal./mole) is 1.7 kcal./mole (11, 12). The corresponding difference between cyclopentanone and cyclohexanone is 2.9 kcal./mole (39). Since in methylenecyclohexane (XXXVI) there will be additional interactions between the methylene hydrogens and the equatorial hydrogens of the ring \((a \rightarrow b \text{ and } c \rightarrow d)\) not found in methylenecyclopentane (XXXVII), and since in the reduction products the resulting methyl group will

\[ \text{XXXVI} \]

\[ \text{XXXVII} \]

be eclipsed in the 5- but not in the 6-ring case, the difference in the heats of hydrogenation "will actually be considerably greater than 2.9 kcal./mole in the methylene compounds." The following sentence summarizes Brown's position. "However, even without allowing for
this further increase, the calculation fully justifies the neglect, as a first approximation, of the differences in stability of endo bonds in the two cyclic systems in favor of the larger difference in stability of the exo double bonds."

The present investigation was undertaken in order to provide quantitative data on stability (enthalpy) differences in various cyclic compounds possessing exo or endo unsaturation.
RESULTS AND DISCUSSION
RESULTS AND DISCUSSION

The fact that 1-alkylcyclohexenes are thermodynamically more stable than the corresponding alkylidenecyclohexanes is well established. Wallach and his associates accomplished the acid-catalyzed isomerization of methylenecyclohexane, ethylidenecyclohexane (57) and 4-methylisopropylidenecyclohexane (58) into the isomeric 1-alkylcyclohexenes. A value of -3.1 kcal./mole has been obtained for the heat of isomerization of methylenecyclohexane into 1-methylcyclohexene from the early combustion data of Roth* (59). The fact that 1-alkylcyclohexanols on dehydration give endocyclic olefins under conditions where equilibration may be expected (see page 17) suggests greater stability for the endo forms. Further information is available from studies of equilibria between \( \alpha, \beta \)- and \( \beta, \gamma \)-unsaturated carbonyl compounds possessing exocyclic (cyclohexylidene) and endocyclic (cyclohexenyl) double bonds, which indicate greater stability for the unconjugated, endocyclic forms (see page 14).

*It should be noted in this connection that the accuracy of Roth's data is open to some question since in an earlier publication (60) a value of -21 kcal./mole was reported for the heat of this isomerization. The value of -3.1 kcal./mole is based on a redetermination of the heat of combustion of 1-methylcyclohexene (1047.9 kcal./mole (61) as compared to the original figure of 1029 kcal./mole) and data for methylenecyclohexane that has never been published. The reason for the discrepancy has not been established but is probably assignable to problems of purity.
The stability differences between exo and endo isomers of the 6-ring series have been attributed to differences in the conformational properties assigned to these structures by Barton, Cookson, Klyne and Shoppee (62) and by Corey and Snee (63). Although quantitative estimation of the relative energies of the cyclohexenyl and cyclohexylidene systems on such a basis is not possible, it is clear that structure XXXVIII possesses fewer ring interactions than does XXXIX, and that the additional repulsions $a \rightarrow b$ and $c \rightarrow d$ in the exocyclic olefin (XXXIX) may be expected to contribute to the lesser stability of this form.

XXXVIII

XXXIX

In comparing the relative stabilities of 1-methylcyclohexene and methylenecyclohexane a further effect must be considered. Kistiakowsky and his collaborators (64) observed that the heat of hydrogenation of trimethylethylene
(-26.9 kcal./mole) is 1.5 kcal./mole lower than that of isobutene (-28.4 kcal./mole). The reduction in the heat of hydrogenation that accompanies increased substitution of the double bond has been variously ascribed to hyper-conjugation (65), to a combination of polar and hyper-conjugative effects (42), and to adjacent bond interactions involving C-C as well as C-H bonds (66). Irrespective of the details of the interpretation, it would appear that approximately half of the heat of isomerization calculated for the conversion of methylenecyclohexane into 1-methycyclohexene from the combustion data must be attributed to the substitution effect. A further discussion of this point will be found in a subsequent section of this thesis.

Evidence relating to the exo-endo stability relationship in 5-membered rings is not extensive. Wallach and Fleischer (67) have reported that treatment of a sample of isopropylidenecyclopentane of undetermined purity with ethanolic sulfuric acid affords in unspecified yield an olefinic fraction from which a crystalline derivative could be obtained by the action of nitrosyl chloride. This derivative, after dehydrochlorination, was hydrolyzed to a ketone. However, the yields of the products were not indicated and the only physical constant recorded in the experiment was the melting point of the semicarbazone of the ketone. The nature of the olefinic material, as well
as its origin, is therefore in doubt. Apart from these inconclusive experiments, no studies concerned directly with equilibration of alkylidene cyclopentanes and 1-alkylcyclopentenes appear to have been undertaken, and pertinent thermochemical data for these substances are not available. However, the complete isomerization of methylenecyclopentane and vinylcyclopentane into the corresponding 1-alkylcyclopentenes by passage over an alumina-supported chromium oxide catalyst at 250°C. has been reported (68). Collins and Schaeffer (69) have proposed a mechanism involving an exo- to endocyclic double bond migration in a 5-membered ring to account for the 32% yield of 1-benzylcyclopentene from the dehydration of trans-2-phenylcyclohexanol with phosphoric acid. The observation that cyclopentylideneacetone and ethyl cyclopentylideneacetate are energetically favored over the corresponding cyclopentenyl derivatives, in contrast to the behavior of the related 6-ring compounds (see page 14), is not relevant to the present discussion in view of resonance stabilization present in the conjugated exocyclic isomers (15).

The literature reveals other scattered observations which suggest that 1-alkylcyclopentenes are more stable than the corresponding alkylidene cyclopentanes. The evidence is not decisive, however, and much of the
available data suffers materially from lack of informa-
tion on yields and on kinetic as opposed to equilibrium
control of the reactions in question, from inadequate
characterization of product composition, and from
mechanistic ambiguities. Thus, although 1-methyl-
cyclopentene (70), 1-ethylcyclopentene (71, 72) and
1-isopropylcyclopentene (73) of authenticated structure
have been obtained by acid-catalyzed dehydration of the
corresponding 1-alkylcyclopentanols, the yields are either
unreported or are too low to permit a reliable assessment
of the stability problem. The formation of 1-methyl-
cyclopentene as the sole product of the dehydration of
cyclobutylmethylcarbinol by anhydrous oxalic acid has
also been noted (74), but the question of whether or not
equilibration of the 1-methylcyclopentene initially formed
on rearrangement can occur under these conditions has not
been examined. A special case of the dehydration of a
substituted 1-alkylcyclopentanol under non-equilibrium
conditions (POCl₃-pyridine) to give 71% of the exo olefin
is available in the steroid literature (75). Of greater
interest in the present connection are the more recent
observations that acid hydrolysis of 1-methylcyclopentyl
chloride furnishes 1-methylcyclopentene in 75% yield (76),
and that dehydration of 1-benzylcyclopentanol with oxalic
acid yields 1-benzylcyclopentene in 66% yield with no de-
tectable amount of the conjugated, but exocyclic benzal-
cyclopentane (69).
The development of the technique of measuring heats of catalytic hydrogenation of organic compounds has provided much thermochemical data of theoretical interest. Heats of hydrogenation afford a valuable supplement to combustion data since the heat change per mole is much smaller than that observed in combustion determinations. Differences in stability assigned on the basis of hydrogenation data are therefore less sensitive to the relative precision of the measurements than those based on heats of combustion.

The initial work in this field was carried out by Kistiakowsky and his associates (11, 12, 39, 64, 77 - 80) who measured the heats of hydrogenation of fifty-one compounds in the gas phase at 82°C. The limitation of this technique to substances of appreciable volatility called for an extension of the method to the liquid phase. This was accomplished by Williams (81), who measured the heats of hydrogenation of nine additional compounds in solution at 29°C. More recently Turner and coworkers (82 - 87) have inaugurated an extensive examination of the heat changes involved in reactions of the type

\[ X \text{ (dissolved)} + H_2 \text{ (gas)} \rightarrow Y \text{ (dissolved)} \]

conducted in acetic acid solution at 25°C. The data reported in this thesis is a part of this general program. The present work involves no alteration of
the apparatus or experimental procedure employed previously and discussion of the precision and accuracy of the method has already been given (82).

The compounds included in this study are methylene-cyclopentane, 1-methylcyclopentene, methylenecyclohexane, 1-methylcyclohexene, methylenecycloheptane, 1-methyl-cycloheptene, ethylidene cyclopentane, 1-ethylcyclopentene, ethylidene cyclohexane and 1-ethylcyclohexene. The purity of the samples employed has been variously checked by boiling point, refractive index, infrared spectra, vapor phase chromatography and peroxide tests.

Exclusion of isomeric olefins in the preparation was achieved in so far as possible by choosing the most specific route of synthesis, and by purification of the final product by careful distillation and, in some cases, by vapor phase chromatography. Methylene cyclohexane and methylenecycloheptane were both prepared by a Hoffman degradation of the appropriate N,N-dimethycycloalkyl-methylamine methyhydroxides. Hoffman degradation of N,N-dimethylcyclopentylmethylamine methyhydroxide proved to be an unsatisfactory method for the preparation of methylenecyclopentane, the major product in this instance being N,N-dimethylcyclopentylmethylamine resulting from displacement on a methyl group rather than elimination of the quaternary nitrogen function. The pyrolysis of
the amine oxide of N,N-dimethylcyclopentylmethylamine proved to be a satisfactory route to methylenecyclo-
pentane. This method has recently been shown by Cope (88) to yield no isomeric olefins in the preparation of
methylenecyclopentane.* Samples of 1-methylcyclopentene
and 1-methylcyclohexene of high purity rating were ob-
tained from the American Petroleum Institute and 1-
methylcycloheptene was obtained from iodine catalyzed
dehydration of 1-methylcycloheptanol. Ethylidenecyclo-
pentane and ethylidenecyclohexane were both prepared by
pyrolysis of the unsaturated acid resulting from the de-
hydration and hydrolysis of the Reformatsky product of
ethyl α-bromopropionate and the appropriate cyclic
ketone. 1-Ethylcyclopentene and 1-ethylcyclohexene were
obtained by iodine catalyzed dehydration of the corre-
ponding tertiary alcohols.

The results of the hydrogenation work are listed in
Table III. The heats of hydrogenation of methylenecyclo-
pentane, methylenecyclohexane and 1-methylcyclohexene were
re-examined with special regard to the question of peroxide
contamination. Hence data on these compounds are recorded

*A detailed study of the comparison of the amine
oxide and Hoffman degradations in alicyclic compounds
was carried out in this connection.
for two separate samples, the figures for sample 2 in each instance referring to more recent measurements, which were carried out on specimens showing a negative peroxide test. The largest variation, 0.3 kcal./mole, was observed in the case of 1-methylcyclohexene, for which the values of the first and second determinations were $-25.70 \pm 0.10$ and $-25.41 \pm 0.11$ kcal./mole, respectively. Since a discrepancy of this magnitude lies only slightly outside the limits of experimental error, it is assumed that peroxide contamination of the original samples, if any, was insignificant. The results of the second determinations are employed in the following discussion.

The values derived for the heats of hydrogenation of methylenecyclohexane (-27.8 kcal./mole) and of 1-methylcyclohexene (-25.4 kcal./mole) are consistent with the established greater stability of the endocyclic isomer in this series, and the heat of isomerization calculated from the hydrogenation data (-2.4 kcal./mole) does not differ appreciably from that obtained by the combustion method (-3.1 kcal./mole) (see page 23). The results for methylenecycloheptane (-26.3 kcal./mole) and for 1-methylcycloheptene (-24.0 kcal./mole) closely parallel those for the 6-membered ring derivatives, the heat of isomerization of exo- to endocyclic olefin being -2.3 kcal./mole in this case.
### TABLE III

**HEATS OF HYDROGENATION IN ACETIC ACID SOLUTION**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mmoles</th>
<th>PtO₂ (mg.)</th>
<th>$-\Delta H$ (Kcal./mole, 25°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylenecyclopentane</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 1</td>
<td>3.986</td>
<td>99.31</td>
<td>26.92</td>
</tr>
<tr>
<td></td>
<td>3.061</td>
<td>99.97</td>
<td>26.78</td>
</tr>
<tr>
<td></td>
<td>4.402</td>
<td>99.96</td>
<td>26.76</td>
</tr>
<tr>
<td><strong>Average, $-\Delta H = 26.82 \pm 0.08^a$</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 2</td>
<td>3.872</td>
<td>99.06</td>
<td>26.88</td>
</tr>
<tr>
<td></td>
<td>3.539</td>
<td>98.61</td>
<td>26.87</td>
</tr>
<tr>
<td><strong>Average, $-\Delta H = 26.88 \pm 0.02$</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-Methylocyclopentene</td>
<td>3.480</td>
<td>99.67</td>
<td>22.99</td>
</tr>
<tr>
<td></td>
<td>3.620</td>
<td>99.69</td>
<td>23.06</td>
</tr>
<tr>
<td></td>
<td>3.181</td>
<td>99.90</td>
<td>22.98</td>
</tr>
<tr>
<td><strong>Average, $-\Delta H = 23.01 \pm 0.04$</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Methylenecyclohexane</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 1</td>
<td>3.602</td>
<td>99.35</td>
<td>27.75</td>
</tr>
<tr>
<td></td>
<td>3.543</td>
<td>99.47</td>
<td>27.89</td>
</tr>
<tr>
<td><strong>Average, $-\Delta H = 27.82 \pm 0.07$</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 2</td>
<td>3.096</td>
<td>98.09</td>
<td>27.62</td>
</tr>
<tr>
<td></td>
<td>2.942</td>
<td>99.44</td>
<td>27.87</td>
</tr>
<tr>
<td><strong>Average, $-\Delta H = 27.75 \pm 0.13$</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
TABLE III (Cont.)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mmoles</th>
<th>PtO₂ (mg.)</th>
<th>-ΔH (Kcal./mole, 25°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Methylcyclohexene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 1</td>
<td>3.961</td>
<td>99.44</td>
<td>25.60</td>
</tr>
<tr>
<td></td>
<td>3.648</td>
<td>99.75</td>
<td>25.79</td>
</tr>
<tr>
<td>Average, -ΔH = 25.70 ± 0.10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 2</td>
<td>3.506</td>
<td>98.24</td>
<td>25.47</td>
</tr>
<tr>
<td></td>
<td>4.054</td>
<td>97.59</td>
<td>25.50</td>
</tr>
<tr>
<td></td>
<td>3.804</td>
<td>98.36</td>
<td>25.26</td>
</tr>
<tr>
<td>Average, -ΔH = 25.41 ± 0.11</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methylene cycloheptane</td>
<td>2.535</td>
<td>100.20</td>
<td>26.47</td>
</tr>
<tr>
<td></td>
<td>3.230</td>
<td>98.90</td>
<td>26.23</td>
</tr>
<tr>
<td></td>
<td>2.500</td>
<td>98.40</td>
<td>26.11</td>
</tr>
<tr>
<td>Average, -ΔH = 26.27 ± 0.14</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-Methylcycloheptene</td>
<td>2.913</td>
<td>99.75</td>
<td>23.93</td>
</tr>
<tr>
<td></td>
<td>2.898</td>
<td>99.82</td>
<td>24.11</td>
</tr>
<tr>
<td>Average, -ΔH = -24.02 ± 0.10</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Ethylidene cyclopentane</td>
<td>3.835</td>
<td>99.63</td>
<td>25.00</td>
</tr>
<tr>
<td></td>
<td>3.752</td>
<td>99.88</td>
<td>24.76</td>
</tr>
<tr>
<td>Average, -ΔH = 24.88 ± 0.12</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
TABLE III (Cont.)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mmoles</th>
<th>PtO₂ (mg.)</th>
<th>-ΔH (Kcal./mole, 25°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Ethylcyclopentene</td>
<td>4.837</td>
<td>100.51</td>
<td>23.66</td>
</tr>
<tr>
<td></td>
<td>4.602</td>
<td>101.11</td>
<td>23.46</td>
</tr>
<tr>
<td>Average, -ΔH = 23.56 ± 0.11</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethylidenecyclohexane</td>
<td>3.209</td>
<td>99.40</td>
<td>26.33</td>
</tr>
<tr>
<td></td>
<td>3.329</td>
<td>99.65</td>
<td>26.31</td>
</tr>
<tr>
<td>Average, -ΔH = 26.32 ± 0.04</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-Ethylcyclohexene</td>
<td>3.612</td>
<td>100.43</td>
<td>24.96</td>
</tr>
<tr>
<td></td>
<td>3.756</td>
<td>100.58</td>
<td>25.20</td>
</tr>
<tr>
<td>Average, -ΔH = 25.08 ± 0.13</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

-ΔH values include uncertainty in the heat of hydrogenation of the platinum oxide catalyst.

Of somewhat greater interest are the values obtained for methylenecyclopentane (-26.9 kcal./mole) and for 1-methylcyclopentene (-23.0 kcal./mole). It is clear from these results that, in terms of the enthalpy criterion, methylenecyclopentane is less stable than 1-methylcyclopentene. The data demonstrate further that the heat of isomerization (-3.9 kcal./mole) in this instance is appreciably greater than that observed in the analogous 6-membered ring system.
In view of the fact that the bonds in the exocyclic compounds thus far discussed are disubstituted, whereas those of the endocyclic isomers are trisubstituted, the exo-endo stability relationships derived above include a factor for the substitution effect. A comparison of the enthalpy values of exo-endocyclic olefin pairs of the same degree of substitution is therefore desirable, and the heats of hydrogenation of ethylidenecyclopentane, 1-ethylcyclopentene, and the corresponding 6-ring derivatives provide two such comparisons. In both series the substitution effect is clearly discernable. Thus, the heats of hydrogenation of methylenecyclohexane (-27.8 kcal./mole) and of ethylidenecyclohexane (-26.3 kcal./mole) differ by 1.5 kcal./mole, a figure that is identical with that obtained by Kistiakowsky (64) for the substitution factor in a structurally analogous open-chain system. A slightly larger value (2.0 kcal./mole) is obtained for the methylene-ethylidene difference in the 5-ring case.

Comparison of the result for ethylidenecyclopentane (-24.9 kcal./mole) with that for 1-ethylcyclopentene (-23.6 kcal./mole) indicates that, although greater stability is still retained in the endocyclic olefin, the enthalpy difference between exo and endo isomers, which now possess the same degree of double bond
substitution, is reduced from 3.9 kcal./mole to 1.3 kcal./mole. The exo-endo difference for the analogous members of the 6-ring series is similarly reduced from 2.4 kcal./mole to 1.2 kcal./mole.* In this case the heat of isomerization (exo to endo) in the 5-ring derivative is essentially equal to that found in the 6-ring compounds, and not considerably lower as implied by the Brown generalization.

The hydrogenation data may be explained in terms of the conformational properties of the molecules involved. Reduction of the cyclohexenyl system (A) involves the introduction of two staggered hydrogen atoms and the movement of the double bond substituents to staggered positions in the saturated 6-ring. Whatever strain is involved in partial eclipsing of the pseudoaxial and pseudoequatorial bonds in the cyclohexene ring is relieved at the same time. Reduction of the cyclohexylidene system (B) results in the introduction of a hydrogen atom and an alkyl group, both staggered, and relieves the \( a \rightarrow b \) and \( c \rightarrow d \) oppositions which are comparable to 1,3-diaxial interactions. Therefore, reduction of the latter system should produce the larger heat change. In the reduction of the cyclopentenyl system (C) six eclipsed interactions are formed whereas

*A value of -3.7 kcal./mole was obtained for this difference by Roth (59). This figure was based on unpublished data for ethylidene-cyclohexane.
only four are introduced by reduction of cyclopentylidene compounds (D). Again more heat will be evolved in the latter transformation. Similarly, the calculated heats of isomerization may be rationalized in terms of conformational properties. Conversion of cyclohexylidene compounds
to their cyclohexenyl isomers (E) relieves the $a \rightarrow b$ and $c \rightarrow d$ interactions at the expense of an increase in strain associated with the resulting pseudoaxial and pseudo-equatorial bonds. The cyclopentylidene to cyclopentenyl conversion (F) relieves two important eclipsed ring oppositions, and in the methylenecyclopentane to 1-methylcyclo pentene transformation gives rise to a more highly substituted double bond. It is not unreasonable that the heat change involved in the 5-ring isomerizations should be at least as great, if not greater, than those in the 6-ring cases.
It will be noted that the heat of hydrogenation of 1-ethylcyclopentene (-23.6 kcal./mole) is 0.6 kcal./mole higher than that of 1-methylcyclopentene (-23.0 kcal./mole), whereas the 1-ethylcyclohexene value (-25.1 kcal./mole) is 0.3 kcal./mole lower than the figure for 1-methylcyclohexene (-25.4 kcal./mole), although the olefins involved do not differ in degree of substitution. Since the heats of hydrogenation of simple alkyl-substituted ethylenes are relatively insensitive to changes in nature of the alkyl group (e.g., methyl to ethyl) (80), it is probable that the enthalpy variations observed in the cyclic olefins in question are of steric rather than of electronic origin. Some justification for this view can be drawn from examination of the conformational properties of these compounds and their reduction products. However, inasmuch as the differences in the heats of hydrogenation in this series are small, a detailed discussion of this problem is hardly warranted.

It should be recognized that since both starting material and product in the hydrogenation procedure are dissolved, the heat evolved in the reaction includes a term representing any difference in heats of solution in acetic acid of the two compounds. Any heat of isomerization calculated from the hydrogenation data is similarly affected. Although data is not available for calculating
this solution effect, the differences involved are probably small. Furthermore, a correction for this effect does not seem desirable since the interest in stability relationships of such compounds generally involves solution situations.

Stability relationships derived in the present investigation for isomers possessing exo and endo unsaturation are based upon enthalpy data. However, "stability" is more properly defined in terms of free energies, the thermodynamic relationship between the two being:

\[
\Delta F = \Delta H - T \Delta S,
\]
at constant temperature. It was desirable, therefore, to obtain further evidence supporting the conclusion of the hydrogenation work. For this purpose a qualitative study of the equilibrium behavior of methylenecyclopentane, methylenecyclohexane, ethyldenecyclopentane, and of ethyldenecyclohexane in the presence of acid was undertaken. These olefins undergo extensive polymerization in the presence of strong acid when undiluted, and the isomerization experiments were therefore carried out in acetic acid solution with p-toluenesulfonic acid as the catalyst. The resulting products were analyzed by vapor phase chromatography or by infrared absorption measurements. Both methylenecyclopentane \( \Delta H_{\text{isom.}} = -3.9 \text{ kcal./mole} \) and methylenecyclohexane \( \Delta H_{\text{isom.}} = -2.4 \text{ kcal./mole} \) appeared to be
quantitatively isomerized into the corresponding 1-methylcycloalkenes. The infrared spectrum of the 1-methylcyclopentene obtained in this way indicated trace contamination by acetate ester, but no residual methylenecyclopentane could be detected. Ethyldienecyclopentane ($\Delta H_{\text{isom.}} -1.3$ kcal./mole) and ethyldienecyclohexane ($\Delta H_{\text{isom.}} -1.2$ kcal./mole) both furnish mixtures of exocyclic and endocyclic products in which the endocyclic compounds largely predominate. The enthalpy criterion therefore provides a valid basis for the qualitative estimation of stability relationships in cyclic systems of this type where entropy differences are expected to be small.

The hydrogenation data described above constitutes a major contradiction to the Brown Rule in either its first or second versions. In particular it will be observed that the difference between the heats of hydrogenation of methylenecyclohexane and methylenecyclopentane is considerably less and not considerably greater than the corresponding difference between cyclohexanone and cyclopentanone. The reasons for this apparent discrepancy are not entirely clear. Although it is possible that the carbonyl and methylene groups may differ in their abilities to accommodate the angular distortion required in the 5-ring compounds, no calculations are available which would permit estimation of the magnitude, or even the
direction, of such an effect. An alternative suggestion is based on the assumption that cyclopentanone derives special stability from hyperconjugation, since its geometry is presumably more favorable for such a phenomenon than is that of cyclohexanone,* while the electron demand of the carbonyl function is greater than that of the methylene group. Arguments have recently been advanced by Kreevoy and Taft (42) to the effect that the hyperconjugation phenomenon is relatively insensitive to electron demand, but data of Brown and associates (91) on the solvolysis of alkylated phenyldimethylcarbinyl chlorides support the contrary view.

The fact that in the 5-ring compounds the heat of isomerization, exo to endo, is either approximately equal to (ethylidene case) or greater than (methylene case) that in the corresponding 6-ring derivatives represents a further contradiction of the Brown generalization. It is especially noteworthy that the difference in the heats of hydrogenation of 1-methylcyclohexene and 1-methylcyclopentene (2.4 kcal./mole) is 1.5 kcal./mole larger than the difference between the exo isomers (0.9 kcal./mole), and that the difference in the corresponding 1-ethylcycloalkenes (1.5 kcal./mole) is

---

*Evidence relating to the stereochemical requirements of hyperconjugation has been provided by Shiner (89), and by Streitwieser, Jagow and Suzuki (90).
approximately equal to the difference between their ethylidene isomers (1.4 kcal./mole). The experimental results are thus at variance with the fundamental assumption which provides the basis for the generalization, namely that the differences in stability of endo double bonds in the two cyclic systems are negligible with respect to those of exo double bonds.

The position that is adopted as a result of this investigation is as follows. The angular strain involved in placing a double bond exocyclic or endocyclic with respect to a 5-membered ring will make such a double bond less stable than a similarly situated olefinic linkage in a 6-membered ring system. The stability of molecules possessing unsaturation of this type may, of course, involve other factors as well. The following argument will serve to illustrate the point. The heats of hydrogenation (acetic acid solution, 25° C.) of the isomeric compounds ethylidene cyclopentane and methylene-cyclohexane are -24.9 kcal./mole and -27.8 kcal./mole, respectively. The heats of formation (liquid state, 25° C.) of the corresponding reduction products are, for ethylcyclopentane, -39.1 kcal./mole, and for methyl-cyclohexane -45.5 kcal./mole (92). If the heats of solution of ethylcyclopentane and methylcyclohexane are assumed to be substantially identical, the heat of
isomerization of ethylidene cyclopentane into methylenecyclohexane can be calculated and is found to be -3.5 kcal./mole. It follows that methylenecyclohexane is energetically favored over ethylidene cyclopentane, despite the stabilizing effect of the methyl substituent in the latter compound. Similar calculations for 1-ethylcyclopentene and for 1-methylcyclohexene give a heat of isomerization of -4.6 kcal./mole for the endocyclic pair. The point that requires special emphasis is the fact that replacement of a trigonal by a tetrahedral carbon atom in this series results in the introduction of non-bonded interactions that are eclipsed in the 5- and staggered in the 6-ring compounds. Cyclopentane derivatives are therefore less stable than the isomeric cyclohexanes, the difference in general being greater than that between the unsaturated substances. Thus, the heat of isomerization of ethylcyclopentane into methylocyclohexane is -6.4 kcal./mole as compared with the value of -3.5 kcal./mole for the exocyclic, and -4.6 kcal./mole for the endocyclic olefins (see Diagram I).

In a previous section of this thesis mention was made of the fact that at equilibrium cyclopentylideneacetone and ethyl cyclopentylideneacetate are favored over the corresponding cyclopentenyl derivatives. The stability order in the analogous 6-membered ring compounds
is reversed (see Table II, page 15). However, cyclopentylideneacetic acid, in contrast to the ethyl ester, furnishes cyclopenteny lacetic acid as the major product of base-catalyzed equilibration. These observations may
now be clarified in the light of the present data. The heat of isomerization of ethylideneacyclopetane into 1-ethylcyclopentene is $-1.3 \text{ kcal./mole.}$ Assuming a similar value for the heat of isomerization of a hypothetical, resonance-free cyclopentylideneacetone into cyclopentenylacetone* and a stabilization of the order of $2 \text{ kcal./mole}$ for the resonance-stabilized molecule,** a difference of roughly $1 \text{ kcal./mole}$ is obtained in favor of the conjugated, exocyclic form. Since resonance interaction between the carbonyl group and the double bond should decrease somewhat in the series ketone, ester, carboxylate anion (42), the amount of exocyclic isomer present at equilibrium is expected to diminish in the same order. The experimental results are in accord with this prediction. In the 6-ring compounds the planar arrangement required for maximum resonance in the unsaturated carbonyl system is subject to repulsive strains involving the interaction of an equatorial ring hydrogen atom and the carbonyl substituent.

*From the point of view of hyperconjugative and inductive effects (42) ethylideneacyclopetane does not constitute an entirely satisfactory model for the cyclopentylideneacetone system. Its choice in this instance was dictated by steric considerations.

**A value of $2.4 \text{ kcal./mole}$ is reported for the resonance energy of crotonaldehyde (79).
Resonance stabilization of the exo (conjugated) modification is thereby reduced and hence also the amount of this substance present at equilibrium.
EXPERIMENTAL
EXPERIMENTAL

Materials

Acetic acid. J. T. Baker reagent grade acetic acid was stirred with platinum catalyst under hydrogenating conditions for a few hours, filtered, and distilled through a short column, discarding the forerun. Used acetic acid solvent from all the hydrogenation calorimetry in this laboratory was periodically recovered by distillation through a Vigeux column, discarding both forerun and residue. After each recovery the entire supply of solvent was combined to ensure uniformity.

Catalyst. Baker and Company platinum dioxide, activity #380, was thoroughly mixed to ensure homogeneity. The catalyst was equilibrated with atmospheric moisture, and samples were weighed in open ampoules. The filled ampoules, each containing approximately 100 mg. platinum dioxide, were evacuated to a pressure of less than 1 mm. and sealed off. The volume of the ampoules was determined by displacement of water so that this amount could be subtracted from the apparent decrease in volume of the hydrogenation system. The heat of hydrogenation and hydrogen uptake were determined experimentally because of the indefinite composition of the catalyst.

Hydrogen. Houston Oxygen Company electrolytic hydrogen was used after passing it through a Deoxo Purifier to remove oxygen.
Methylenecyclopentane, Sample 1. Cyclopentylcarbinol, prepared from cyclopentylmagnesium bromide and formaldehyde, on treatment with phosphorus and iodine yielded material boiling at 75-90° (30 mm.), which was dissolved in an acetone solution of trimethylamine. A crystalline material, m.p. 175-185° (dec.), separated upon standing. However, repeated recrystallization of this material afforded a fraction, m.p. 253-256° (dec.), the infrared spectrum of which was identical with that of N,N-dimethylcyclohexylamine methiodide, m.p. 253-256° (dec.) (literature value (93) 277°), prepared from cyclohexyl iodide and trimethylamine. Since it was evident that some degree of rearrangement had occurred in the preparation of the iodide, this method of synthesis was abandoned as a route to N,N-dimethylcyclopentylmethyamine methiodide. In its place the following approach was adopted.

Diethyl cyclopentylmalonate (29 g.), b.p. 114-118° (1 mm.) (literature value (94) b.p. 115-117° (2 mm.)), prepared by the reaction of 62 g. of cyclopentyl bromide and sodiomalonlic ester by the procedure of Verwey (95), upon basic hydrolysis furnished 15 g. cyclopentylmalonic acid, m.p. 163-165° (dec.) (literature value (95) m.p. 162-163°), which was decarboxylated by heating at
170-180° to afford 10 g. cyclopentylacetic acid, b.p. 105° (1 mm.) (literature value (95) 139-140° (26 mm.)).

Cyclopentylacetic acid (10 g.), dissolved in 350 ml. chloroform and 120 ml. concentrated sulfuric acid, was treated with 8 g. of sodium azide according to the method of von Braun (96). The mixture was stirred at 50-55° for 4 hours, then poured over cracked ice, made basic with sodium hydroxide and steam distilled. From the distillate there was obtained 7 g. of cyclopentylmethylamine. The N-benzoyl derivative, m.p. 79° (literature value (96) m.p. 75°), was prepared.

Cyclopentylmethylamine (6 g.) was heated under reflux for 8 hours with 100 ml. of 38% aqueous formaldehyde, 100 ml. of 98% formic acid and 200 ml. of water. The mixture was then cooled, made basic with sodium hydroxide solution, saturated with sodium chloride, and extracted with ether. The resulting ethereal solution was dried over anhydrous magnesium sulfate, and the N,N-dimethylcyclopentylmethylamine was isolated by distillation through a 30 cm., 75-plate center-rod column, b.p. 150-151°, n_D^29.5 1.4355 (literature values (88) b.p. 149.5°, n_D^25 1.4385). This material proved to be rather hygroscopic, and analysis was therefore carried out on the picrate, m.p. 143-143.4° (from
ethanol)*.

**Anal.** Calcd. for C_{14}H_{20}N_{4}O_{7}: C, 47.16; H, 5.66; N, 15.73.

**Found:** C, 47.34; H, 5.91; N, 15.70.

The product was further characterized as the crystalline methiodide, m.p. 206.2-206.4° (from ethanol-ether).

**Anal.** Calcd. for C_{9}H_{20}I-N: C, 40.12; H, 7.49; N, 5.20.

**Found:** C, 40.19; H, 7.53; N, 5.33.

Hoffman degradation of the methyhydroxide of N,N-di-methylcyclopentylmethylamine proved unsatisfactory as a preparative route to methylene cyclopentane, since analysis of the pyrolysis products by vapor phase chromatography revealed a mixture containing olefin and regenerated tertiary amine in an approximately 25:75 molar ratio. In the analogous 6-ring case the olefin:tertiary amine ratio was about 55:45.** An acceptable procedure was found in the amine oxide degradation (98). A solution of 7 g. of N,N-dimethylcyclopentylmethylamine in

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*Mousseron and coworkers (97) report a melting point of 168-169° for a substance of this presumed structure, but no analytical data were given. Cope and associates (88) report a melting point of 142.8-143.8°, but did not give an analysis.

**These figures agree in order, but differ considerably in magnitude with the olefin:amine ratios of 64:36 for the 5- and 76:24 for the 6-ring compounds which are reported by Cope, et al (88). The discrepancies could easily result from differences in reaction conditions and analytical method.
30 ml. of methanol was accordingly treated with 30 g. of 30% hydrogen peroxide. After standing at room temperature for 40 hours, the excess hydrogen peroxide was destroyed by stirring with 0.5 g. of platinum black. The catalyst was removed by filtration, and the solution was concentrated under reduced pressure to a viscous oil. Treatment of a small sample of this material with an ethanol solution of picric acid furnished the picrate of N,N-dimethylcyclopentylmethylamine oxide, which was recrystallized from ethanol, m.p. 126-126.5°C.

Anal. Calcd. for C_{14}H_{20}N_{4}O_{8}: C, 45.16; H, 5.41; N, 15.05.

Found: C, 45.21; H, 5.48; N, 14.86.

Pyrolysis of the remaining amine oxide (180°C, 3 mm.) gave volatile material which was collected as two layers in a Dry Ice trap. After thorough washing with water, the olefin layer was distilled, yielding 2.5 g. of methylene cyclopentane, b.p. 76.0°C, n_D^{25} 1.4332 (literature values (77) b.p. 75.7°C, n_D^{20} 1.4355).

Comparison of the infrared spectrum of this material with that of 1-methylenecyclopentene (see below) revealed no detectable contamination by the latter substance, the distinctive absorption bands of 1-methylenecyclopentene at 1382, 1335, 1298, 1000 and at 787 cm^{-1} being completely missing from the spectrum of methylene cyclopentane. It was determined by the examination of known mixtures
that the method is capable of detecting 2% of 1-methylcyclopentene in methylenecyclopentane.

Sample 2. Material for a second determination of the heat of hydrogenation of methylenecyclopentane was prepared by the procedure described above. Twenty-nine grams of tertiary amine afforded 13 g. of olefin which was distilled through a 75-plate center-rod column. The material boiled flat at 76.2° (761 mm.) and was arbitrarily divided into three fractions: fraction 1, n_D^25 1.4333; fraction 2, n_D^25 1.4332; fraction 3, n_D^25 1.4333. The infrared spectra of the three fractions were identical. The center cut (fraction 2) was employed for the hydrogenation runs. A sample was tested for peroxide by the sodium iodide-starch technique (99). No iodine was liberated under conditions which would have detected 0.05 mole % of peroxide. Infrared analysis of material that had been allowed to stand in acetic acid solution at room temperature for 3 days indicated that no isomerization into 1-methylenecyclopentene occurs under these conditions.

1-Methylenecyclopentene. The 1-methylenecyclopentene employed in this investigation was obtained from the American Petroleum Institute, Sample No. 1046-5S, impurity 0.14 ± 0.08 mole %.

Methylenecyclohexane, Sample 1. Cyclohexylcarbinol (108 g.), b.p. 98-102° (30 mm.) (literature
value (100) b.p. 88-93° (18 mm.), prepared from cyclo-
hexyl chloride and formaldehyde by the procedure of
Gilman and Catlin (100), was treated with phosphorus
and iodine to yield 85 g. of iodomethylocyclohexane (101),
b.p. 175-178°, which was added to a solution of 40 g.
of trimethylamine in 150 ml. of acetone. The reaction
mixture was allowed to stand at room temperature for
6 days, at the end of which time 90 g. of N,N-dimethy-
cyclohexylmethylamine methiodide, m.p. 225-226° (litera-
ture value (102) m.p. 225°), had separated. This pro-
duct was dissolved in water, and freshly prepared silver
oxide was added until no further silver iodide was formed.
The solution was then filtered, and the water was removed
under reduced pressure with gentle warming. The resi-
due was finally pyrolyzed at atmospheric pressure (bath
temperature, 180°) and the volatile product was collected
and washed with dilute acetic acid to remove trimethyl-
amine and N,N-dimethylocyclohexylmethylamine. After
thorough washing with water, the methylenecyclohexane
was dried and distilled, b.p. 102.5°, n_D^25 1.4461 (lit-
erature values (72) b.p. 103.3°, n_D^20 1.4497).

**Sample 2.** A second sample was prepared by the pro-
cedure described above except that pyrolysis was carried
out under reduced pressure with a nitrogen purge. Dis-
tillation through a 75-plate center-rod column gave
material boiling flat at 102.8° (756 mm.) which was
collected in three fractions: fraction 1, $n_D^{25} 1.4469$; fraction 2, $n_D^{25} 1.4470$; fraction 3, $n_D^{25} 1.4463$. The infrared spectra of the three fractions were identical. Fraction 2, which was employed for the hydrogenation studies, was tested for the presence of peroxide with negative results. The material further showed a symmetrical peak on passage through a Perkin-Elmer Vapor Fractometer, using a 2 m. B column, with helium as the eluant. Under identical temperature ($82^\circ$) and flow conditions methylenecyclohexane gave a retention time of 11.2 minutes as compared to 13.8 minutes for 1-methylcyclohexene (see below). Examination of known mixtures established that 0.2% contamination by 1-methylcyclohexene was easily detectable by this procedure. The fact that methylenecyclohexane is stable in acetic acid solution was established by vapor chromatography of a sample that had remained in contact with acetic acid for 3 days at room temperature. No trace of 1-methylcyclohexene could be detected after this treatment.

1-Methylcyclohexene, Sample 1. 1-Methylcyclohexanol, prepared from methylmagnesium iodide and cyclohexanone, was dehydrated as described by Mosher (52) to yield 1-methylcyclohexene, b.p. 110.2$^\circ$, $n_D^{25} 1.4478$ (literature values (103) b.p. 110$^\circ$, $n_D^{20} 1.45067$).
Sample 2. American Petroleum Institute Sample No. 1040-5S, impurity 0.18 ± 0.08 mole % was employed in the second determination. The peroxide test on this material was negative.

Methylenecycloheptane. The methylenecycloheptane employed in the calorimetric experiments was prepared by D. W. Wiley, Department of Chemistry, Yale University, and its method of preparation is given in reference 86.

1-Methylcycloheptene. 1-Methylcycloheptanol, prepared from cycloheptanone and methylnagnesium iodide, was dehydrated by distillation in the presence of a small amount of iodine. The olefin in the distillate was separated and, after washing with water and drying over anhydrous sodium sulfate, was distilled through a 75-plate center-rod column. 1-Methylcycloheptene, b.p. 136°, n_D^25 1.4563 (literature values (104) b.p. 137.5-138.5°, n_D^25 1.4581) was obtained by this method. The infrared spectrum of this material was substantially different from that of methylenecycloheptane.

Ethylidenecyclopentane. Ethylidenecyclopentane was synthesized by the method of Wallach and von Martius (71). Ethyl 1-hydroxy-α-cyclopentylpropionate, prepared by the Reformatsky reaction of cyclopentanone (25 g.), ethyl α-bromopropionate (50 g.) and activated
zinc (10 g.), was dehydrated by heating with sodium bisulfate at 150° for 2\(\frac{1}{2}\) hours to yield 10 g. of unsaturated ester, b.p. 111-115° (35 mm.). Basic hydrolysis of this material afforded unsaturated acid which was decarboxylated by slow distillation at atmospheric pressure. The hydrocarbon distillate was washed successively with dilute sodium hydroxide solution and water, and was dried over anhydrous magnesium sulfate. Distillation of this material gave 3.5 g. ethylidenecyclopentane, b.p. 110-111° (literature value (72) 112.6°). However, vapor phase chromatography of the product gave two peaks with a peak area ratio of approximately 3:10. The retention time of the first and smaller peak was identical with that of a sample of 1-ethylcyclopentene (see below). The entire product was passed through the column in small portions and the material represented by the two peaks collected separately. The material of the first peak had an infrared spectrum identical with that of 1-ethylcyclopentene. The infrared spectrum of the material from the second peak was significantly different from that of 1-ethylcyclopentene and this material was employed for the hydrogenation work on ethylidenecyclopentane.

**1-Ethylcyclopentene.** 1-Ethylcyclopentanol (31 g.), prepared by the action of ethylmagnesium bromide on cyclopentanone, and 0.6 g. of iodine were heated in a
distillation flask at atmospheric pressure. The olefin fraction that distilled was washed with water, dried over anhydrous magnesium sulfate and distilled. The crude product (12 g.) was redistilled through a 75-plate center-rod column and furnished 9 g. of 1-ethylcyclopentene, b.p. 106.2-106.9°, (literature value (72) 107.3°). The product gave a single peak on vapor phase chromatography.

**Ethylidenecyclohexane.** The procedure of Wallach and Evans (57) was employed in the preparation of ethylidenecyclohexane. Reaction of cyclohexanone (15 g.), ethyl α-bromopropionate (50 g.) and zinc (10 g.) afforded 25 g. of ethyl 1-hydroxy-α-cyclohexylpropionate, b.p. 150° (35 mm.) (literature value (57) b.p. 135-136° (20 mm.)), which was dehydrated with sodium bisulfate at 150° to yield 19 g. of unsaturated ester, b.p. 125-130° (35 mm.) (literature value (57) b.p. 108-112° (12 mm.)). This material was hydrolyzed in aqueous potassium hydroxide and the resulting unsaturated acid was decarboxylated by slow distillation at atmospheric pressure to yield 5.4 g. of ethylidenecyclohexane. Distillation of the product through a Podbielniak column furnished material boiling at 136.8°, n_D 27 1.4656 (literature values (72) b.p. 136.8°, n_D 20 1.4623). The infrared spectrum of the product was substantially different from and revealed no contamination with 1-ethylcyclohexene (see below).
1-Ethylcyclohexene. 1-Ethylcyclohexene was obtained by the iodine-catalyzed dehydration of 1-ethylcyclohexanol according to the method of Mosher (52). Fractionation of the crude product in a 75-plate center-rod column gave material boiling at 136.2° (literature values (105) b.p. 135.7-136.6°).

Measurement of Heats of Hydrogenation

A detailed description of the calorimeter employed in this study and a discussion of the precision and accuracy of results obtained from it have been published (82). In brief, the heats of hydrogenation are determined by the following method: (1) the change in temperature of the calorimeter and its contents due to the hydrogenation reaction is measured by means of a resistance thermometer; (2) the calorimeter is cooled and electrically calibrated over the temperature range and time interval recorded in the hydrogenation experiment.

Hydrogenation Run. The calorimeter containing 225 ml. of acetic acid is assembled with evacuated ampoules of catalyst and of the test substance, wired to small magnets, suspended in the supporting tubes by means of externally mounted magnets. After the apparatus is tested for leaks, the entire system is evacuated and filled with hydrogen. Hydrogen is allowed to bubble slowly through the solvent for 10 minutes with stirring
to remove dissolved air. At the end of this period the evacuation and filling process is repeated several times, and the system is finally closed under 3 mm. positive pressure. After heating the contents of the calorimeter to a point slightly above the bath temperature by means of the electric heater, the stirring rate is adjusted to the desired speed, and the system is allowed to come to equilibrium as indicated by the linearity of the time-temperature curve. The ampoule of the test substance is then broken by allowing it to drop to the bottom of the calorimeter, and the time-temperature curve is followed until a constant slope is again obtained. At this point the volume of hydrogen in the buret (measured under 3 mm. positive pressure) and atmospheric pressure are noted, and the catalyst ampoule is broken. Temperature measurements are made at intervals until the time-temperature curve is once again linear. The pressure of hydrogen in the calorimeter is maintained slightly above atmospheric pressure throughout the reaction.

**Calibration Run.** At the end of the hydrogenation run, the calorimeter and its contents are cooled by allowing the temperature of the bath (refrigerated) to fall to about 18°. The bath is then returned to 24.6°, and the calorimeter is brought to thermal equilibrium. The rating period is followed as before, and when the
temperature at which the hydrogenation reaction was initiated is reached, the volume of hydrogen in the buret (3 mm. positive pressure) and atmospheric pressure are again recorded. The calorimeter heater is turned on, and the voltage drop across the heater and across the standard resistance, as well as the temperature of the calorimeter, are noted at intervals. The voltage applied to the heater is chosen so that the rate of heating in the hydrogenation run is duplicated as nearly as possible. When the temperature reaches a point approximating the maximum achieved during the hydrogenation run, the heater is switched off, the time being noted, and the time-temperature curve is followed until it is finally linear. The calorimeter is then dismantled and thoroughly cleaned with aqua regia in preparation for the next run.

**Calculations.** The temperature rise during a reaction or electrical calibration is calculated by use of the following formula (106):

\[
\Delta T = \Delta T_x + \frac{V_r - V_a}{\phi_r - \phi_a} (\phi_x - \phi_r) t_x;
\]

wherein if

\[ t_1 \] = time at beginning of the first rating period,
\[ t_2 \] = time at the end of the first rating period, that is, when catalyst ampoule is broken,
\[ t_3 \] = time at beginning of second rating period,
\[ t_4 = \text{time at end of the second rating period,} \]
and \( T_1 \ldots T_4 \) are temperatures at these times;

then:

\[ T = \text{calculated temperature rise,} \]
\[ T_x = T_3 - T_2, \]
\[ t_x = t_3 - t_2, \]
\[ v_a = (T_1 - T_2)/(t_1 - t_2), \]
\[ v_r = (T_3 - T_4)/(t_3 - t_4), \]
\[ \phi_a = (T_1 + T_2)/2, \]
\[ \phi_b = (T_3 + T_4)/2, \]
\[ \phi_x = t_x^{-1} \int_{t_2}^{t_3} T \, dt. \]

The integral is evaluated by cutting out and weighing a plot of thermistor resistance against time.\(^*\)

The electrical energy input is calculated by the formula:

\[ \text{Energy input (in defined calories)} = \frac{(E_H \cdot E_S \cdot t)}{(R_S \cdot 4.1833)}, \]

where

\[ E_H = \text{potential drop across the heater,} \]
\[ E_S = \text{potential drop across the standard resistor,} \]
\[ t = \text{duration of application of voltage across the heater,} \]
\[ R_S = \text{resistance of the standard resistor.} \]

\(^*\)Resistances are used in place of temperatures throughout the calculations by prefixing the absolute values of resistance differences with the algebraic signs of temperature differences.
The potential readings are the averages of measurements made at approximately uniform intervals during the heating period. The potential divider, used in measuring $E_H$, is calibrated at the conclusion of each electrical calibration run, and the factor obtained is employed in the calculations. The electrical energy input is corrected for the estimated heat dissipation inside the calorimeter of the copper leads to the heater.

The total heat change for the reaction is determined from the temperature rise of the hydrogenation by making a linear extrapolation from the electrical calibration. No serious error is introduced if $T_3 - T_2$ is nearly the same for reaction and calibration runs. The experimentally determined heat of hydrogenation of the amount of catalyst used is subtracted from the total heat change. A correction is also applied for the heat evolved upon condensation of acetic acid in the calorimeter, which results from the decrease in volume of the system due to absorption of hydrogen. The molar heats of hydrogenation are computed on the basis of the volume of hydrogen absorbed. This volume is corrected for the opening of the evacuated catalyst ampoule and is converted to standard conditions. The hydrogen pressure is computed from the mean of barometer readings at $t_2$ in the hydrogenation and calibration runs, taking into account the vapor pressure of acetic acid and the 3 mm. positive pressure inside the system.
Isomerization Experiments

Samples (0.5 ml.) of methylenecyclopentane, methylenecyclohexane, ethylidenecyclopentane, and ethylidenecyclohexane were dissolved in 1.0 ml. portions of glacial acetic acid containing catalytic amounts of p-toluene-sulfonic acid. The mixtures were sealed under vacuum in bent tubes arranged in such a manner that total reflux could be obtained during the reaction period. The solutions were then heated to 100° for 6 hours, at the end of which time the tubes were tilted, and the contents were distilled into a second limb which was cooled in liquid nitrogen. In the cases of methylenecyclohexane and ethylidenecyclopentane the distillate was analyzed directly by vapor phase chromatography. Since methylenecyclopentane and 1-methylenecyclopentene, as well as ethylidenecyclohexane and 1-ethylcyclohexene, were not separable under the chromatographic conditions employed, the products obtained in these experiments were separated from the acetic acid by water dilution, and, after thorough washing with water and drying, were analyzed in the infrared.
SUMMARY

Stability differences of five isomeric olefin pairs possessing exocyclic and endocyclic double bonds have been evaluated by the hydrogenation method. The heats of hydrogenation (kcal./mole) have been measured in acetic acid solution at 25° C. for the following compounds: methylenecyclopentane (-26.9), 1-methylcyclopentene (-23.0); methylenecyclohexane (-27.8), 1-methylcyclohexene (-25.4); methylenecycloheptane (-26.3), 1-methylcycloheptene (-24.0); ethylidenecyclopentane (-24.9), 1-ethylcyclopentene (-23.6); ethylidenecyclohexane (-26.3), 1-ethylcyclohexene (-25.1). The data indicate that in each pair the endocyclic modification possesses the greater stability. The stability relationships derived from the hydrogenation work have been confirmed in several instances by studies of acid-catalyzed isomerization. The results are discussed in terms of the conformational properties of the molecules involved and the relevance of the data to other cases of exocyclic and endocyclic unsaturation is considered.
REFERENCES

(1) A. Baeyer, Ber., 18, 2277 (1885).
(3) H. Sachse, Ber., 23, 1363 (1890); Z. physik. Chem., 10, 203 (1892).
(4) E. Mohr, J. prakt. Chem., 98, 349 (1918); 103, 316 (1922).


(22) F. Price and L. P. Hammett, ibid., 63, 2387 (1941).


(26) D. Vorlander, Ann., 280, 186 (1894).


(29) E. Schjanberg, Ber., 75, 468 (1942).


(31) F. Fichter and A. Beisswenger, Ber., 36, 1200 (1903).


(33) A. Contardi and A. Ercoli, Gazz. chim. ital., 64, 522 (1934).


(35) loc. cit., p. 10.


(44) G. A. R. Kon and R. S. Thakur, ibid., 2217 (1930).


(47) A. A. Goldberg and R. P. Linstead, ibid., 2343 (1928).

(48) R. P. Linstead, ibid., 2579 (1927).

(49) G. A. R. Kon and E. A. Speight, ibid., 2727 (1926).


(51) R. S. Thakur, ibid., 2157 (1932).


(53) F. Flawitzky, Ber., 20, 1956 (1887).


(55) F. W. Semmler, Ber., 42, 246 (1909).


(58) O. Wallach, Ber., 39, 2504 (1906).
(59) W. A. Roth, Landolt-Bornstein, Hauptw., Vol. II. pp. 1587-1611.
(60) W. A. Roth, Z. Elektrochem., 17, 791 (1911).
(67) O. Wallach and K. Fleischer, Ann., 353, 304 (1907).
(71) O. Wallach and K. von Martius, Ann., 405, 142 (1909).
(73) H. Meerwein and H. Probst, Ann., 405, 142 (1914).
(75) A. Butenandt, J. Schmidt-Thome and H. Paul, Ber., 72, 1112 (1939).


(89) V. J. Shiner, ibid., 78, 2653 (1956).

(90) A. Streitwieser, R. H. Jagow and S. Suzuki, ibid., 77, 6713 (1955).


(93) A. Skita and H. Rolfes, Ber., 53, 1242 (1920).


(95) A. Verwey, Ber., 29, 1997 (1886).

(96) J. von Braun, ibid., 66, 1375 (1933).


(101) J. Gutt, Ber., 40, 2067 (1907).

(102) O. Wallach, Ann., 353, 284 (1907).


(104) O. Wallach and H. Kohler, Ann., 345, 139 (1906).
