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THE SYNTHESIS AND CHEMISTRY OF 1,4-BRIDGED
BICYCLO[2.1.0]PENTANES AND RELATED SYSTEMS

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By

Eugene Arthur Armour, B.S.

The Ohio State University
1973

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To my loving wife
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The author is especially thankful for the tremendous sacrifice of his wife during his labors here. Her never ceasing love, patience, and support were of immeasurable value.

Finally, the author wishes to thank Him for whom all of this was accomplished. "For God so loved the world that he gave his only begotten Son, that whosoever believeth in Him should not perish, but have everlasting life". Amen.
Eugene Arthur Armour, the son of George A. and Lois J. Armour, was born in Mercer, Pennsylvania, on September 21, 1946. He obtained his elementary and secondary education in the South Bend, Indiana, area. He entered Purdue University in September, 1964, and received his B.S. in chemistry in June, 1968. On August 17, 1968, he married Janis Ann Thielke of South Bend, Indiana. He entered the Graduate School of The Ohio State University one month later. In August, 1973, he received his Ph.D. in organic chemistry from that institution.
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INTRODUCTION

The synthesis and study of strained ring systems has fascinated chemists for nearly a century since Baeyer first published his theory on angle strain in 1885. More recently, especially in the past 15 years, interest has again been intensified, as evidenced by the more than 1000 papers on the subject of strained rings which have appeared during this time. The renewed interest in strained carbocyclics is largely due to recent improvements in synthetic and analytical techniques which have allowed the synthesis and characterization of many such strained ring structures.

Strain in a molecule exists when bonds in that molecule are constrained in such a fashion that they cannot achieve "normal" bond angles. Such angle distortions result in a higher energy than would occur without such distortions. The increased strain is manifested in some of the unusual properties which such compounds exhibit. Much work has gone into the elucidation of the nature of strained carbon sigma bonds. Before a discussion of the more complex members of strained ring systems is attempted, it is desirable to look briefly at the simpler systems.

1. A. von Bayer, Ber., 2277 (1885).
The simplest such case, cyclopropane, serves as a good example of what effects strain can have on carbon-carbon single bonds. It has been known for a long time, for example, that unlike simple alkanes, cyclopropane can be pyrolyzed at 450-500°C to give propene, it can be brominated to 1,3-dibromopropane, or it can be hydrogenated to propane. This unusual reactivity is a result of constraining the three carbon atoms to form 60° angles as measured from straight lines joining the carbon nuclei, as compared to a "normal" tetrahedral angle of 109.5°. Considerable theoretical work has

been done on the nature of the bonding in cyclopropane. One such model, developed by Coulson and Moffit, would have the center of electron density associated with the bonding orbitals lying outside a straight line drawn between the carbon atoms (Figure 1). In this model, the orbitals would be distorted about $22^\circ$ from a linear bond between carbon atoms. Fritchie's electron density map for 2,5-dimethyl-7,7-dicyanonorcaradiene concurred with this model.


with the "banana bonds" being distorted about 20°.

As one moves down the series to cyclobutane, one might expect somewhat less strain. This is born out by the fact that cyclobutane is not as easily brominated as cyclopropane, nor is it as easily hydrogenated to butane. Nonetheless, a cyclobutane ring is still more strained than the next higher homolog, cyclopentane. By the time one reaches cyclohexane, nearly normal tetrahedron bond angles are obtained and hence cyclohexane is nearly strain free, i.e., one observes "normal" carbon-carbon sigma bonds.

Another method which can be used to distort carbon-carbon sigma bonds is to fuse two ring systems together along a common edge, as shown in Figure 2, where m and n are small. The first

\[
\begin{align*}
R & \quad (\text{CH}_2)_n \quad (\text{CH}_2)_m \\
R & \quad (\text{CH}_2)_n \quad (\text{CH}_2)_m
\end{align*}
\]

Figure 2.


report of a bicyclobutane \( (m = n = 1) \) came in 1959.\(^9\) A derivative of bicyclopentane \( (m = 2, n = 1) \) was reported as early as 1954\(^10\) while bicyclopentane itself was characterized in 1957.\(^11\) Similarly, the first bicyclo[2.2.0]hexane was obtained in 1940,\(^12\) but its structure was not totally established until 1959.\(^13\) The parent hydrocarbon was first synthesized in 1960.\(^14\) It will be noted that most of these syntheses are quite recent. This is a reflection of the amount of strain involved and thus the difficulty in synthesis. As might be expected, numerous examples of less highly strained bicyclics occur in the older literature. For example, bicyclo[3.1.0]hexane systems are quite common in natural products,\(^15\) while a simple derivative of bicyclo[3.2.0]heptane was correctly reported

in 1907.\(^{18}\)

Although only recently synthesized, considerable chemical\(^{17}\) and theoretical\(^{18}\) work has been carried out on these highly strained bicyclic molecules. The chemistry of the simplest member of this series, bicyclo[1.1.0]butane (1), does indeed reflect the unusual nature of its bent carbon-carbon single bonds which result

\(^{16}\) H. Staudinger, Ann., 356, 51 (1907); H. Staudinger and E. Suter, Ber., 52, 1092 (1920).


from the fusion of two small rings. Depending on various substitution, bicyclobutanes have been shown to react in the presence of acids, bases, free radicals, olefins, transition metals, and:


and heat. Theoretical studies likewise suggest that the C1-C3 bond of \( \text{I} \) may consist of overlap between two nearly pure 2p orbitals. Evidence in agreement with these calculations was obtained by Flygare and coworkers, who measured the electronic charge distribution of \( \text{I} \), and by Harmony and Cox, who found \( \text{I} \) to have an unusually large dipole of 0.67D. Thus, we do not see a normal carbon-carbon sigma bond, but rather, a highly strained, highly reactive sigma bond.

As was the case with monocyclic strained rings, increasing the ring size decreases the strain, and hence, as is often the case, decreases the reactivity. Thus, bicyclo[1.1.0]butane derivatives react almost instantly in very dilute acid, whereas bicyclo[2.1.0]pentane only reacts slowly with glacial acetic acid under conditions where bicyclo[3.1.0]hexane does not react at all.

We shall now turn our attention to still another ring system by which we can observe the effects of strained sigma bonds.

---

23. For a discussion, see ref. 16c, p. 196.


as one observes fascinating chemistry by fusing one small ring to another along a carbon-carbon single bond, one might expect equally unique chemistry by fusing still a third small ring along the same carbon-carbon bond, as shown in Figure 3. If \( l, m, \) and \( n \) are small enough, then the effects of bridging \( C_1 \) and \( C_2 \) as compared to the corresponding bicyclic systems should lead to additional information concerning these atypical sigma bonds.

A list of the propellanes \(^{27,28}\) which might be expected to be somewhat strained is shown in Chart I. At the onset of the present work, the smallest member of this class which had been isolated and characterized was tricyclo[3.2.1.1^5]octane (7). \(^{29,30}\) An even

---


smaller member of this class, $6$, may also have been observed as a reaction intermediate. $31$ Among the larger ring systems, $9, 10, 33$ and $11, 34$ and a derivative of $14, 35$ had been reported. Since this work was undertaken, $8, 36, 12, 37, 13, 38$ and $14, 38a$ have also been successfully synthesized. There are, as yet, no reported isolations of $2-6$.

The unusual nature of the bonding and the expected reactivity of such highly strained systems is dramatically illustrated by $7$. The hydrocarbon reacts with a wide variety of reagents under very

For $\ell = 1$:

- **$m = 1$**
  - $n = 1$
  - $n = 2$
  - $n = 3$
  - $n = 4$

- **$m = 2$**
  - $n = 2$
  - $n = 3$
  - $n = 4$

- **$m = 3$**
  - $n = 2$
  - $n = 3$
  - $n = 4$

- **$m = 4$**
  - $n = 2$
  - $n = 3$
  - $n = 4$

For $\ell = 2$:

- **$m = 2$**
  - $n = 2$
  - $n = 3$
  - $n = 4$
mild conditions as shown in Chart II. Many of the reactions are similar to those which occur with double bonds. The

**CHART II**

![Chemical Structures]

R.T. = room temperature


spontaneous reaction of 7 with molecular oxygen at room temperature is unprecedented. The corresponding oxa-derivatives likewise are quite strained. This is reflected by the strain energy of 15 (∼ 60 kcal/mole), and the ready conversion of 15 and 16 into 17 and 18, respectively. An X-ray diffraction study of 8,8-dichlorotricyclo[3.2.1.0^1,5]octane (19) confirmed the unusual arrangement of atoms which can result from fusing three small rings.

---


along one carbon-carbon single bond. In this case, it was found that C₂, C₅, C₇, and C₈ all lie on one side of an imaginary plane which could be drawn through C₁. The bridgehead carbon was actually displaced 0.093Å from a plane defined by C₂, C₇, and C₈. However, it was suggested, on the basis of theoretical considerations, that the "inverted" tetrahedral geometry of 19 was more readily explained in terms of angles between corresponding bond hybrids, rather than interatomic vectors (as was the case with cyclopropane). These angles were found to range between 101° and 116°, closer to what might be expected for a tetracoordinate carbon atom. The bridgehead-bridgehead bond was considered to be the overlap of two nearly pure p orbitals.

As has been illustrated in the monocyclic and bicyclic series, moving to the next higher homologue, tricyclo[4.2.1.0₁₅]nonane (8), leads to decreased strain, and as is usually the case, decreased reactivity. Thus, 8 requires heat to initiate reaction
with glacial acetic acid, whereas 7 reacted spontaneously at room temperature. That 8 is still quite reactive is indicated by its instantaneous uptake of bromine even at -78°. Even more interesting is the fact that the unsaturated analogue 20 reacts preferentially with bromine at the sigma bond rather than the pi bond.

Another structure quite related to 8 is that of 1,3-dehydroadamantane (21a). It, too, has the "inverted" tetrahedral

geometry and is quite reactive, as shown below. The strain energy of a derivative, 21b, is approximately 29 kcal/mol. As pointed out by Scott and Pincock, this is nearly identical to the 28 kcal/mol strain energy for cyclopropane. Furthermore, "Even if the unusual bonding in 1,3-dehydro adamantane and related compounds results in no great increases in energies, the reactivities of these propellane compounds are much greater than that of any simple
cyclopropane'. That is, the geometry of and nature of bonding in such systems can lead to high reactivity in spite of the seeming lack of significant strain. This then, is an exception to the general rule that decreased strain leads to decreased reactivity.

Although the present work deals only with 1,4-bridged bicyclo[2.1.0\(^1\)]pentanes and 1,5-bridged bicyclo[3.1.0\(^1\)]pentanes, a brief discussion of 1,4-bridged bicyclo[2.2.0\(^1\)]hexanes is in order for completeness. As expected, the tricyclo[n.2.2.0\(^{n+2}\)]alkanes are reactive. The first such example, 22, prepared by Applequist and Searle and overlooked by later workers,\(^{38,46}\) reacts slowly with bromine in refluxing carbon tetrachloride.\(^{47}\) The parent compound, 1\(^4\,), and the next lower homologue, 1\(^3\,), are both reactive with bromine at room temperature, requiring 10-20 minutes at room temperature for completion.\(^{38}\) Hence, 1\(^4\,) and 1\(^3\,) are less reactive to bromine than their counterparts in the 1,4-bridged bicyclopentane series (7 and 8).

Only recently has a derivative of the smallest member of 1,4-bridged bicyclo[2.2.0\(^1\)]hexanes in this series been reported.\(^{37}\) Although very little chemistry has been investigated, one very important reaction, heretofore undiscussed, has been observed.


\(^{47}\) This is probably a free radical reaction,\(^{46}\) and not an electrophilic addition as in the case of 7 and 13.
for this small ring propellane, namely, its thermal ring opening. Whereas \( \text{I}, \text{I} \), \( \text{I} \), \( \text{II} \), \( \text{I} \), and \( \text{II} \) were all reported thermally stable at reasonably high temperatures, \( \text{II} \) readily fragmented to give a mixture of \( \text{II} \) and \( \text{II} \).
Theoretical studies on strained propellanes were in good agreement with the observed behavior. Hoffmann and Stohrer noted that collapse of 26 to give 12 is symmetry forbidden, as is the fragmentation of 12 to give 27, while fragmentation of 26 to give 27 is a symmetry allowed process. In addition, 26 and 12

are considered to be isomers of one another, and not merely stretched conformations. Similar conclusions concerning two energy minima corresponding to $12$ and $26$ were reached by Newton and Schulman, who suggested before Eaton's report, that $12$, when made, might have a lifetime of several hours at room temperature.

In contrast, the calculations of Hoffman and Stohrer showed that the diradical forms $28$, $29$, $30$, and $31$ are '...but stretched
conformations of their collapsed σ-bonded tricyclics...", 2, 3, 6, and 7, respectively. Thus, 2, 3, 6, and 7 represent energy minima. In addition, 3, 6, and 7 should not undergo fragmentation via a symmetry forbidden process to 1,3-dimethylenecycloalkanes (32, 33, and 34, respectively). The aforementioned fragmentation of 23 to give 24 and 25, coupled with the thermal stability of 7 and lack of fragmentation products for 6 and 7 are thus important since they give experimental evidence to corroborate the theoretical results.

In view of the intriguing possibilities for study in these small ring propellanes, the initial goal of this work was to synthesize some new, highly strained derivatives. Of particular interest to us, were compounds of the type shown in Figure 4 resulting from 1,4-bridging of bicyclo[2.1.0]pentanes, and 1,5-bridging of bicyclo[3.1.0]hexanes. It was desired to prepare sufficiently stable derivatives of these types in order that the chemistry of such systems could be investigated. It was hoped that the knowledge thus gained could lead to a better understanding of the
nature of bonding in such systems.
PART I
SYNTHESIS AND METAL CATALYZED REARRANGEMENTS
OF THE TRICYCLO[3.2.1.015]OCTANE RING SYSTEM

Introduction

The chemistry associated with tricyclo[3.2.1.015]octane (I) has been the subject of several investigations, as previously discussed. During the course of these investigations, important discoveries were made concerning transition metal promote.
rearrangements of several strained ring skeletons. For example, bicyclobutanes\textsuperscript{51} were easily isomerized, as were bicyclopentanes,\textsuperscript{52} a derivative of bicyclo[3.1.0]hexane,\textsuperscript{53} quadracyclane,\textsuperscript{54} and cubane.\textsuperscript{55} In view of the uncertain nature of these transformations, it was of interest to determine whether \( I \) would undergo a similar type of reaction. This is the subject of the first part of this section.

In another study of the [3.2.1]propellane system, unrelated to the metal catalysis work, it was desired to prepare a functionalized derivative of \( I \). Previously, only 8,8-dichloro derivative

\[ \begin{array}{c} \text{R} \\ \text{R} \end{array} \]

\( I \)

\( 19 \) had been reported.\textsuperscript{23,43} Whereas \( 19 \) is not readily adaptable

---


for studying the chemistry of the [3.2.1.0^1,5]tricyclic system, it was hoped that by putting a functionality in the C_6 position of \( \mathcal{D} \), useful information could be obtained. In particular, functionalizing the C_6 position would allow direct comparisons between the chemistry of systems related to \( \mathcal{I} \) and the corresponding derivatives of its bicyclic analogue, bicyclo[2.1.0]pentane. The successful attempt to prepare such a functionalized derivative is the subject of the second part of this section.

Metal Catalysis

The synthesis of \( \mathcal{I} \) was accomplished according to literature procedures\(^4\) as shown in Chart III. The cuprous chloride catalyzed decomposition of diazomethane\(^3\) gave much higher yields (50-60\%) of \( \mathcal{I} \) than Wiberg's reported\(^2\) two step conversion of \( \mathcal{E} \) into \( \mathcal{I} \) via \( \mathcal{J} \) (15-20\% total). The complete synthesis from \( \mathcal{E} \) to \( \mathcal{I} \) could be carried out in about 2\% overall yield.

When \( \mathcal{I} \) was exposed to 5 mole percent of chlorotricarbonyliridium(I) dimer in chloroform solution for 24 hr at 50-55\(^\circ\), it was completely isomerized to a 36:64 mixture of 4-methylenecycloheptene (36) and 5-methylenecycloheptene (38) in 52\% yield.\(^5\)

Catalytic reduction of the product mixture with 5\% palladium on carbon gave only methylcycloheptane, which was in all ways identical.

---

CHART III

\[ \text{KOH} \quad \text{KOH} \]

1) BrCH\(_2\)CH\(_2\)Br
2) HBr, Δ

\[ \text{TsNHNNH}_2 \]
2) NaOC\(_2\)H\(_3\), hv

\[ \text{CH}_2\text{N}_2 \]
CuCl

\[ \text{Na}/\text{NH}_3 \]
to an authentic sample. In order to confirm the structures assigned to the initially formed dienes, both were independently synthesized.

\[
\begin{align*}
I & \quad \frac{[\text{IrCl(CO)}_3]_2}{\text{CHCl}_3} \\
& \quad \begin{array}{c}
\text{CH}_2 \\
\text{CH}_2
\end{array} + \\
& \quad \begin{array}{c}
\text{CH}_3
\end{array}
\end{align*}
\]

\[
\begin{align*}
\text{37} + \text{38} & \quad \text{H}_2 \\
& \quad 5\%, \text{Pd/C}
\end{align*}
\]

The preparation of 38 was relatively straightforward. The known alcohol, 39, was converted to the tosylate 40 utilizing p-toluenesulfonyl chloride in pyridine. Reaction of 40 with

\[
\begin{align*}
\text{CH}_2\text{OH} & \quad \begin{array}{c}
\text{CH}_2\text{OTS}
\end{array} \\
& \quad \begin{array}{c}
\text{CH}_2
\end{array}
\end{align*}
\]

\[
\begin{align*}
\text{39} & \quad \begin{array}{c}
\text{TsCl}
\end{array} \quad \text{pyridine} \\
& \quad \begin{array}{c}
\text{CH}_2\text{OTS}
\end{array}
\end{align*}
\]

\[
\begin{align*}
\text{40} & \quad \begin{array}{c}
\text{KOT-Bu}
\end{array} \quad \text{DMSO} \\
& \quad \begin{array}{c}
\text{CH}_2
\end{array}
\end{align*}
\]

57. An authentic sample of methylcycloheptane was purchased from Chemical Samples Co., Columbus, Ohio.

potassium t-butoxide in dimethyl sulfoxide gave 38. The synthesis of the isomeric diene, 37, proved considerably more difficult.

Cyclohepten-4-one (41) was prepared according to the literature directions. When the conversion of 41 into 37 via the classical Wittig procedure proved unsuccessful in our hands, 42 was synthesized via reaction of 41 with trimethylsulfonium ylid.60 When 42 was treated with sodium iodide and zinc powder in acetic acid buffered with sodium acetate, 61 4-methylene cycloheptene (37) was formed. The independently synthesized samples of 37 and 38 were


in all respects identical to the products obtained from the isomerization of \( \mathcal{I} \).

The isomerization of \( \mathcal{I} \) in the presence of the transition metal complex is thought to involve cleavage of the \( C_1-C_8 \) and \( C_1-C_5 \) bonds of \( \mathcal{I} \) to give a complex of the transition metal and a carbene, probably best represented as a resonance hybrid \( \underline{43a-c} \) where \( \underline{43a} \) and \( \underline{43b} \) are the most important contributors. Migration of a hydrogen from either \( C_2 \) or \( C_7 \) with simultaneous loss of the metal would lead to the production of \( \underline{38} \) and \( \underline{37} \), respectively.

\[
\begin{align*}
\text{CH}_2 & \quad \text{M} & \quad \text{CH}_2 & \quad \text{M} \\
\underline{43a} & \quad \text{M} & \quad \text{CH}_2 & \quad \text{M} \\
\underline{43b} & \quad \text{M} & \quad \text{CH}_2 & \quad \text{M} \\
\underline{43c} & \quad \text{M} & \quad \text{CH}_2 & \quad \text{M}
\end{align*}
\]

Since various transition metal catalysts have been shown to isomerize olefins, it was desirable to show that \( \underline{37} \) and \( \underline{38} \) were

62. For a recent discussion on the relative importance of each resonance contributor in a similar case, see R. Noyori, Tetrahedron Lett., 1691 (1973), and references therein.

the initially formed dienes, and not the result of some anomalous rearrangement of other initially formed diene(s). This was tested by subjecting 1-deuteriocyclopentene\(^{64}\) to the reaction conditions. After 24 hr at 55-60\(^\circ\)C, almost no deuterium scrambling was observed. This is taken as evidence that some similar hypothetical precursor(s) to \(37\) and \(38\) likewise would probably not rearrange under the reaction conditions. Thus, \(37\) and \(38\) are indicated as the initial products of the isomerization.

It was thought that the first step in the reaction might be the oxidative addition\(^{65}\) of the metal to \(7\) to give \(44\) or \(45\),

\[
\begin{align*}
7 & \rightarrow \begin{array}{c}
                 \text{CH}_2 \\
                \text{M} \\
                 \text{M}^-
\end{array} \\
\text{or} & \begin{array}{c}
                 \text{CH}_2 \\
                \text{M} \\
                 \text{M}^-
\end{array} \\
\rightarrow & \begin{array}{c}
                 \text{CH}_2 \\
                \text{M} \\
                 \text{M}^-
\end{array}
\end{align*}
\]

followed by collapse to \(43\). In an attempt to trap such an intermediate, the reaction was repeated under identical conditions in methanol. This time, just one product, 1-methoxybicyclo[3.2.1]-octane (46) was obtained in 70\% isolated yield. The structure of 46 was established via an independent synthesis. The bridgehead

64. The author wishes to thank Dr. T. Atkins for providing the 1-deuteriocyclopentene used in this experiment.

acetate \( \text{I} \), prepared from the reaction of \( \text{I} \) with glacial acetic acid, was reduced to the alcohol \( \text{II} \), which in turn was converted to \( \text{IV} \) by its reaction with sodium hydride and methyl iodide. Compound \( \text{IV} \) prepared in this manner was identical in all respects to the product of the transition metal promoted rearrangement of \( \text{I} \) in methanol. However, in view of the recent findings of Gassman and Reitz, it is questionable whether \( \text{IV} \) arises from direct capture of \( \text{III} \). Instead, it is possible that \( \text{IV} \) is merely the result of acid catalyzed addition of methanol to \( \text{I} \).

**C₆ Functionalized Tricyclo[3.2.1.0¹⁵]octane**

Synthesis of the desired C₆ functionalized tricyclo[3.2.1.0¹⁵]octane was accomplished in the following manner. The tricyclic ketone \( \text{V} \) was readily obtained in 75% yield from the known bicyclo-
[3.3.0]oct-1(5)-en-2-one \(^{49}\) by reaction with trimethylsulfonium ylid \(^{69}\) in dimethylsulfoxide. The ketone \(50\) was converted to the hydroxymethylene compound \(51\) in 59\% yield. When \(51\) was treated with sodium hydride and tosyl azide,\(^{70}\) a nearly quantitative conversion into the \(\alpha\)-diazoketone, \(52\), was obtained.

The key step in this sequence was the hoped for photochemical Wolff ring contraction of \(52\). There was, at the time of this work, ample precedence for the ability of this contraction to introduce strain into a ring system.\(^{71}\) In view of the expected lability of the products to dilute acids and to oxygen, the reaction was run under argon in purified tetrahydrofuran (distilled from lithium aluminum hydride) containing dimethyl amine. Irradiation with a


68. The author wishes to thank Badische Anilin- and Soda-Fabrik for a generous gift of \(49\).


bank of 15-watt Sylvania "Blacklite" fluorescent tubes for 10 days led to a 25% yield of exo \(53\) and 13% yield of endo \(54\). This corresponds to about a 65:35 ratio of \(53:54\). Preparative vpc allowed isolation of \(53\) and \(54\).
Evidence to confirm the structures of 53 and 54 was obtained from their spectral properties. The infrared spectrum of 53 (neat) showed absorptions at 3.22 μ (cyclopropane CH str) and 6.06 μ (amide C = O str). An nmr spectrum gave absorptions at δ\text{CDCl}_3 2.97 (s, 3H), 2.90 (s, 3H), 1.17-2.33 (m, 9H), 1.06 (d, J = 6 Hz, 1H), and 0.55 (d, J = 6 Hz, further split into a multiplet, 1H). Compound 54 gave an ir spectrum (neat) with absorptions at 3.23 μ (cyclopropyl CH str) and 6.07 μ (amide C = O str). An nmr spectrum gave δ\text{CDCl}_3 3.00 (s, 3H), 2.97 (s, 3H), 1.15-2.73 (m, 9H), 1.01 (d, J = 6 Hz, 1H), and 0.77 (d, J = 6 Hz, 1H). Both 53 and 54 gave correct exact mass molecular weights, and the fragmentation patterns of the mass spectra of the two isomers were very similar. Finally, chemical evidence for the structures of 53 and 54 comes from the fact that both 53 and 54 turned dark and polymerized quite readily, even on standing under argon at -10°C.

The stereochemical assignments for 53 and 54 are based on two
arguments. First, having the electronegative amide group in close proximity to the C₈ hydrogen (Hₐ) only leads to an increase in the difference in chemical shifts between Hₐ and Hₐ (i.e., Hₐ-Hₐ) relative to the parent hydrocarbon (7). On the other hand, orienting the amide group away from Hₐ leads to a slight decrease in the chemical shift difference between Hₐ and Hₐ. As it will be demonstrated later in this thesis, this behavior is a general phenomenon of these strained propellanes.

The second reason for assigning the stereochemistry of 5₂ and 5₄ is by analogy to two somewhat similar systems. The intermediate ketenes derived from 5₂, 5₂,72 and 5₆,38a all give similar exo:endo product ratios. It might be expected that similar stereoc-  

investigation. In addition, some difficulty was encountered in securing needed starting material (49). This attack at studying highly strained ring systems, was therefore, set aside. However,
synthesis of \( \underline{53} \) and \( \underline{54} \) did serve to demonstrate that entry could be made into the tricyclo[3.2.1.0\(^1\,\underline{5}\)]octane ring system by means other than that reported originally, \(^{29,30}\) and that the derivatives of \( \underline{7} \) thus obtained have the high reactivity associated with such tricyclic carbo skeletons.
PART II

PREPARATION OF A SIMPLE TRICYCLO[4.2.1.0_1^3,6]-
NONANE RING SYSTEM

Introduction

As has already been discussed, the effects of 1,4-bridging on a bicyclo[2.1.0]pentane ring system (where \( n = 3 \)) are manifested in a tremendous increase in reactivity, so much so, in fact, that such systems are somewhat difficult to handle. Many reactions which one might wish to examine (for example, the kinetics of hydrolysis, or the solvolysis of suitable derivatives) are limited because of competing processes. Thus, it was desirable to prepare a system somewhat less reactive than \( \text{I} \) or \( \text{II} \) and \( \text{III} \).

One approach which immediately presented itself was to decrease the amount of strain in the 1,4-bridged bicyclo-pentane by increasing the length of the bridge. The discussion of this section will center on a successful approach to this goal, i.e., the synthesis of a tricyclo[\( n \cdot 2 \cdot 1 \cdot 0 \cdot 1_3, n+2 \)]alkane where \( n = 4 \).
Results and Discussion

As shown in Chart III, the synthesis of \( I \) proceeds quite directly from \( 35 \) in greater than 50% isolated yield. By analogy, one would expect that \( 62 \) should lead to \( 8 \) in a straightforward manner. The bicyclic olefin, \( 62 \), was prepared from \( 52 \) as shown in Chart IV according to literature procedures \(^{73}\) in 22% yield. Two of these steps deserve comment. We, as others, \(^{74}\) noted that the product ratio of \( 65 \) and \( 66 \) from \( 64 \) was quite dependent on the stirring speed of the reaction mixture. Secondly, although the photolysis of the lithium salt of \( 67 \) did give \( 62 \) as reported


CHART IV

\[
\text{[Reactions and structures as depicted in the image.]}\]
(~ 30%), we found that pyrolysis as described by Shechter et al.\textsuperscript{75} was superior both in yield (> 80%) and in purity of the product.

In our hands, reaction of 62 with a large number of carbenes and carbenoids failed, however, to yield any of the desired propellane.\textsuperscript{76} The reasons for this are, to say the least, unclear. It must be a combination of electronic and/or stereochemical factors. That 62 does not react is particularly perplexing in view of the ease with which it epoxidizes.\textsuperscript{74} Whatever the reasons be, a new approach to the synthesis of \( \mathcal{A} \) was decided upon.

If steric hindrance plays a role in the failure of 62 to react with a carbene (or carbenoid), then, it was reasoned, this effect might be overcome by a suitable "flattening" of the six-membered ring. One method of accomplishing this would be to introduce a second double bond into the molecule, as in the case of 68. Vogel and coworkers\textsuperscript{77,78a} had previously shown that carbene addition could be made to occur exclusively with the tetrasubstituted


\textsuperscript{76} This lack of reaction was observed by another laboratory, J. J. Bloomfield, private communication.


\textsuperscript{78} (a) E. Vogel and H.D. Roth, \textit{Angew. Chem.}, 76, 145 (1964).
central bonds in both 68 and 70 rather than with the disubstituted double bonds. Reaction of a carbene with 68 might therefore be expected to occur at the central, tetrasubstituted double bond in preference to the disubstituted olefin. In addition, the increased strain of the central double bond resulting from its incorporation into a four-membered ring might be expected to aid in the selectivity.

The synthesis of 68 was adapted from that outlined by Garrett and Fonkin. The trans diacid 71, readily obtainable by hydroly-
sis of the ester derived from a Diels-Alder reaction of 1,3-butadiene and diethyl fumarate, was treated successively with phosphorous pentachloride, dimethyl amine, and lithium aluminum hydride. Compound \( T_2 \) was converted into the di-N-oxide via its oxidation with hydrogen peroxide. The di-N-oxide was pyrolyzed to give \( T_3 \), which was irradiated \( \text{hv} \) to give \( 68 (T_1 \rightarrow 68, \sim 10\%) \). Both \( T_3 \) and \( 68 \)

\[
\begin{align*}
\text{EtO} & \overset{\text{EtO}}{\text{EtO}} \\
\text{H} & \overset{\text{H}}{\text{H}} \\
\text{CO}_2\text{Et} & \overset{1)}{\Delta \rightarrow} \text{CO}_2\text{H} \\
\text{EtO} & \overset{2)}{\text{OH}} \\
\text{H} & \overset{3)}{\text{H}^+} \\
\text{LiAlH}_4 & \text{CON(CH}_3\text{)}_2 \\
\text{CON(CH}_3\text{)}_2 & \text{CO}_2\text{H} \\
\text{POCl}_3 & \text{COCl} \\
\text{COCl} & \text{HN(CH}_3\text{)}_2 \\
\text{CH}_2\text{N(CH}_3\text{)}_2 & \text{CH}_2\text{N(CH}_3\text{)}_2 \\
\text{CH}_2\text{N(CH}_3\text{)}_2 & \text{hv} \rightarrow \text{68} \\
\end{align*}
\]

79. A 450 watt high pressure Hanovia lamp was used for this purpose.
were remarkably stable, remaining unchanged after standing six months at 5°.

When 68 was treated with diazomethane in the presence of cuprous chloride, it was observed that the initial products of

\[
68 + \text{CH}_2\text{N}_2 \rightarrow 68 + 20 + 75
\]

the reaction were tricyclo[4.2.1.0{1,8}]non-3-ene (20) and tricyclo-[5.2.0{1,7}.0{3,5}]non-1(7)-ene (75) in roughly equal amounts through about 50% reaction. Longer reaction times led to the formation of endo-tetracyclo[5.2.1.0{1,7}.0{3,5}]decane (76) and, in smaller amounts, exo-tetracyclo[5.2.1.0{1,7}.0{3,5}]decane (77). At this point, the amount of 20 began to decrease, while 75 increased only slowly. Vpc yields confirmed this observation. After an estimated 50% conversion, 68, 20, 75, and 76 were formed in yields of 37, 15, 18,
and ~2.7%, respectively, along with a trace of 7I. After an estimated 70% conversion, vapor phase chromatography showed that 68, 20, 75, 76, and 7I were present in yields of 19, 13, 26, ~6, and ~1%, respectively.

All components could be separated by preparative vapor phase chromatography. Compound 20 showed infrared spectrum (neat) absorptions at 3.25 μ (vinyl CH str and/or cyclopropyl CH str) and at 6.05 μ (C=C str). Its nmr spectrum was quite definitive and agreed exactly with that later described by Warner and LaRose. Compounds 20, 75, and 76 gave correct m/e parent peaks and either correct analyses and/or exact mass spectra. Compound 75 gave an ir spectrum absorption at 3.30 μ (cyclopropyl CH str). Compounds 76 and 7I gave very simple ir spectra which were quite similar, with no C=C str around 6.1 μ. The mass spectral fragmentation patterns for 76 and 7I were nearly identical. The nmr spectra of the various compounds are shown in Table 1.

The spectral data are consistent with the structures of 72, 76, and 7I. The only question which arises is the assignment of exo and endo stereochemistry of 76 and 7I. Examination of the nmr spectrum for 7I is particularly informative for this purpose. Molecular models of 7I indicate that the molecule is fairly rigid and that only one reasonable conformation is likely, in which H₂ is in the plane of both cyclopropyl rings. Proton H₂ should therefore be expected to be somewhat deshielded. Proton H₂, on the other
hand, lies slightly over the plane of the two cyclopropyl rings and should be somewhat shielded. This is in fact observed. Likewise \( H_1 \) lies directly over the face of the \( C_1-C_7-C_{10} \) cyclopropane ring and is considerably shielded to -0.22 \( \delta \). A detailed analysis of the various coupling constants confirms the assignments. This data is only consistent with the \textit{exo} stereochemistry. In the case of the \textit{endo} isomer, \( 76 \), all four \( H_e \) protons would be expected to show similar environments relative to the two cyclopropyl rings. Models seem to indicate that this is the case. None of the \( H_e \) protons can get into the plane of both three-membered rings, and one therefore doesn't expect the deshielding to lower field for any of the \( H_e \) protons in \( 76 \) that was observed for \( H_f \) in \( 77 \). Thus, in \( 76 \), \( H_e \) appears above 1.98 \( \delta \), almost 0.3 ppm upfield from \( H_f \) in \( 77 \).

Examination of the cyclopropyl methine protons is also informative. In the \textit{exo} isomer, \( 77 \), \( H_g \) should occupy a relatively "normal" position (0.96 \( \delta \)). In the \textit{endo} isomer, \( 76 \), the corresponding protons, \( H_h \), are directly over the \( C_1-C_7-C_{10} \) cyclopropyl ring. They are correspondingly shielded to 0.69 \( \delta \). This shift (~0.3 ppm) is also consistent with the assigned structures.

Implied in the change in observed product ratios as the reaction proceeds, although not rigorously proved, is that \( 76 \) is the initially formed tetracyclic, and that it is formed from \( 20 \). If

---

Table 1

<table>
<thead>
<tr>
<th>Position</th>
<th>Coupling Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ha 0.45</td>
<td>( J_{a-b} = 5; J_{a-d} = 2 )</td>
</tr>
<tr>
<td>Hb 0.73</td>
<td>( J_{b-a} = 5 )</td>
</tr>
<tr>
<td>He, Hf 1.68</td>
<td></td>
</tr>
<tr>
<td>He 1.16</td>
<td></td>
</tr>
<tr>
<td>Ha 0.52</td>
<td>( J_{a-b} = 4; J_{a-d} = 2 )</td>
</tr>
<tr>
<td>Hb 0.69</td>
<td>( J_{b-a} = 4 )</td>
</tr>
<tr>
<td>Hc, Hd 1.83</td>
<td></td>
</tr>
<tr>
<td>He 2.26</td>
<td>( J_{d-a} = 2 )</td>
</tr>
<tr>
<td>Hf 5.40</td>
<td></td>
</tr>
<tr>
<td>Ha 0.63</td>
<td>( J_{a-b} = 4.5; J_{a-d} = 2 )</td>
</tr>
<tr>
<td>Hb 0.11</td>
<td>( J_{b-a} = 4.5 )</td>
</tr>
<tr>
<td>Hc 2.05-2.54</td>
<td></td>
</tr>
<tr>
<td>Hd 2.05-2.54</td>
<td></td>
</tr>
<tr>
<td>He 0.94</td>
<td></td>
</tr>
<tr>
<td>Ha 0.28</td>
<td>( J_{a-b} = 4.5; J_{a-d} = 2 )</td>
</tr>
<tr>
<td>Hb 0.85</td>
<td>( J_{b-a} = 4.5 )</td>
</tr>
<tr>
<td>Hc, Hf 1.51-1.86</td>
<td></td>
</tr>
<tr>
<td>He 1.86-1.98</td>
<td></td>
</tr>
<tr>
<td>Hf 0.08</td>
<td></td>
</tr>
<tr>
<td>Hg 0.69</td>
<td></td>
</tr>
<tr>
<td>Hh 0.69</td>
<td></td>
</tr>
<tr>
<td>Ha 0.22</td>
<td>( J_{a-b} = 4.5; J_{a-d} = 2 )</td>
</tr>
<tr>
<td>Hb 0.76</td>
<td>( J_{b-a} = 4.5 )</td>
</tr>
<tr>
<td>Hc, Hf, He 1.56-2.07</td>
<td></td>
</tr>
<tr>
<td>Hf 2.26</td>
<td></td>
</tr>
<tr>
<td>Hg 0.96</td>
<td></td>
</tr>
<tr>
<td>Hh 0.57</td>
<td></td>
</tr>
<tr>
<td>Hl -0.22</td>
<td></td>
</tr>
</tbody>
</table>

a) Positions given in units of \( \delta \) relative to TMS or CHCl\(_3\) as internal standards.

b) Coupling constants given in Hz.
this is the case, then it appears that attack on the double bond of 20 is preferentially on the side cis to the four-membered ring rather than cis to the three-membered ring. This result is similar to that for 78, which prefers attack cis to the five-membered ring rather than to the three-membered ring. The similarity of the two systems to methylene transfer again suggests that the stereochemical assignments for 76 and 77 are correct.

Some control over the reaction of 68 with diazomethane was possible. Thus, the yield of the desired isomer 20 was optimized by running the reaction only to 50% conversion. If the tetracyclic 76 and 77 were desired, then exhaustive reaction with diazomethane was carried out. As might be expected, however, the separation of isomers was somewhat laborious and not readily adaptable to the large scale needed for further study. Additionally, an easier route into this ring system became available (cf., Part IV), and further work on 20 was abandoned.

All of the new tricyclic and tetracyclic compounds prepared

in this section (20, 75, 76, and 77) were reasonably stable. They were thermally stable (could be distilled) and showed no appreciable reaction on standing in the presence of oxygen. Lengthening the methylene bridge of 7 did decrease the reactivity as predicted. It is interesting to note that 20 can be catalytically hydrogenated over platinum to give 38, which is also reasonably stable. Thus, the failure of carbenes to react with the olefin 62 is probably not a result of product instability.

\[ 74 \xrightarrow{H_2/Pt} 8 \]
PART III

SYNTHESIS AND SOLVOLYSIS OF EXO AND ENDO-7-TRICYCLO[4.3.1.015]DECYL p-NITROBENZOATES.

Introduction

In Part I, a ring contraction scheme, starting with 50, was devised for making entry into the 1,4-bridged bicyclopentane ring system. In a continuing effort to synthesize and study the chemistry of various tricyclo[n.2.1.01n.2]alkene derivatives, a similar sequence was decided upon in which 79 was a key intermediate. Conversion of 50 and 79 into the corresponding p-nitrobenzoates and subsequent solvolysis would then allow evaluation of the effects of 1,5-bridging on the bicyclo[3.1.0]hex-2-yl cation.
This bicyclic cation has been the subject of much recent discussion. In particular, considerable attention has been given to the question of whether different cations result from the ionization of a suitable leaving group from the exo and endo sides of the 2-position of the bicyclo[3.1.0]hexane nucleus. It was hoped that solvolyses of the tricyclic analogues might lead to a better understanding of this and other considerations concerning the nature of these various systems.

**Synthesis**

The synthesis of 79 was initially accomplished according to the method of Williams and Ziffer, who reported that irradiation of the β-2 unsaturated ketone (80) in tert-butyl alcohol gave 79 as a major product. The overall sequence (Method A), starting with β-naphthol, was somewhat lengthy and certainly not readily adaptable to scaling up. An alternate sequence (Method B), starting with


readily available cyclohexanone, was therefore worked out (Chart V). The key step in this sequence was the addition of dimethyl-
loxosulfonium ylid to the known bicyclo[4.3.0]non-1(6)-en-7-one (81). Unfortunately, the yield for conversion of 81 into 79 was
a somewhat disappointing 36%. The overall yield for Method B was
only one percent better than for Method A (10% vs 11%). However,
in terms of the number of operations and ease of scaling up,
Method B was superior, and allowed the ready synthesis of sizable
quantities of the tricyclic ketone 79.

\[
\begin{align*}
79 & \xrightarrow{\text{Al(Oi-Pr)₃}} \begin{array}{c}
\text{79} \\
\text{1-PrOH, } \Delta \\
\text{51/₄ hr}
\end{array} \quad \begin{array}{c}
82 \\
\sim 95
\end{array} \\
79 & \xrightarrow{\text{Al(Oi-Pr)₃}} \begin{array}{c}
\text{79} \\
\text{1-PrOH, } \Delta \\
\text{20 hr}
\end{array} \quad \begin{array}{c}
50
\end{array}
\end{align*}
\]

When 79 was treated with lithium aluminum hydride, the pre-
dominate product (~95%) was the exo alcohol, 82. On the other
hand, treatment of 79 with aluminum isopropoxide in refluxing

CHART V

Method A:

\[
\begin{align*}
&\text{Method A:} \\
&\text{1) } \text{CH}_3\text{OH/H}^+ \\
&\text{2) } \text{H}_2/\text{Raney Ni} \\
&\Delta/\text{pressure}
\end{align*}
\]

\[
\begin{align*}
&\text{Method B:} \\
&\text{1) } \text{ZnCl}_2 \\
&\text{HOOAc} \\
&\text{Ac}_2\text{O} \\
&\text{2) } \text{H}^+(-\text{CO}_2)
\end{align*}
\]
isopropyl alcohol gave initially a predominence (> 80%) of the endo epimer, 83. Control experiments were able to demonstrate that continued refluxing yielded a nearly 50:50 mixture of exo and endo epimers. The exo-\( p \)-nitrobenzoate (84) and endo-\( p \)-nitrobenzoate (85) were then obtained in pure form by standard techniques.

The stereochemistry of 82 and 83 was based on two arguments. The first was by direct analogy to the tricyclo[3.3.1.01,5]nonyl ring system which was similarly reduced, derivatized, and solvolyzed. Treatment of 50 with lithium aluminum hydride gave exo

\[
\text{LiAlH}_4 \rightarrow \begin{array}{c}
\text{H} \\
\text{CH}_2\text{I}_2
\end{array}
\]

\[
\text{Al(Oi-Pr)}_3
\]

---


86. P.G. Gassman and R.N. Steppel, unpublished results.
86, while treatment with aluminum isopropoxide in refluxing isopropyl alcohol yielded endo 87. This behavior of 50 thus paralleled that of 72, as would be expected. The structure of 86 was unequivocally established by its preparation from the allylic alcohol 88. When 88 was treated with a modified Simmons-Smith reagent, the product with the cyclopropyl ring syn to the alcohol was formed (86) in accordance with the known directing effect of these methyle transfer reagents in smaller ring systems.87

A second argument was based upon nmr chemical shifts. It has been known for some time that, in general, a low-field shift of ca 0.1-0.6 ppm (and sometimes as large as 1-4 ppm) is observed for a proton attached to a carbon atom when that proton is sterically compressed.88 The effect is deshielding irrespective of the nature of the atom which is responsible for the crowding. Furthermore, when the atom is oxygen, the proton of a CH₂ unit away from the sterically compressed proton becomes shielded to higher field. Examination of the compounds under consideration (82 and 83) suggested that the same effects might be operative in this rigid, strained ring system.

87. For example, see W.G. Dauben and G.H. Berezin, J. Amer. Chem. Soc., 85, 468 (1963)
88. For a good discussion, see: S. Winstein, P. Carter, F.A.L. Anet, and A.J.R. Bourn, ibid., 87, 5247 (1965) and references therein.
The parent hydrocarbon (10) is taken as the model compound. Proton $H_a$, being adjacent to the smaller five-membered ring, would be more compressed than $H_b$, which is adjacent to the larger, more flexible, six-membered ring. By our argument, $H_a$ should be more deshielded ($0.38 \delta$) than $H_b$ ($0.16 \delta$). In the case of the exo epimer 82, the large, electronegative hydroxyl group should increase the steric compression on $H_a$, thereby increasing the deshielding of $H_a$ ($0.68 \delta$), and perhaps even shielding $H_b$ ($0.10 \delta$). At any rate, the net difference between $H_a$ and $H_b$ (i.e., $\Delta H_a - \Delta H_b$) should be larger than in the model compound 10. Thus, $\Delta \delta$ in this case is positive. On the other hand, the endo

---

89. The change in chemical shifts, $\Delta \delta$, was chosen as a better judge of the effects of steric compression rather than the absolute values of $\delta$. This was done because some of the spectra were recorded vs TMS as internal standard and others were recorded vs chloroform as internal standard. The difference, $\Delta \delta$, of less than 1 ppm should be less subject to drift in the pmr signal than the absolute values. Note also that $\Delta \Delta \delta$ is most informative, since the effects of exo and endo substitution on $H_a$ and $H_b$ work in opposite directions.
epimer, $\delta_3$, should only have a small effect relative to the parent $\delta_0$. It might be expected that placing the hydroxyl group syn to the six-membered ring might force the six-membered ring into a more rigid position, increasing slightly, perhaps, its interaction with $H_b$. At any rate, the change in $H_\alpha$ should be slight, and the change in $H_\beta$ should be slight, and, if anything, deshielding. The net effect, i.e., $\delta H_\alpha - \delta H_\beta$, should be small, and $\Delta\Delta\delta$ relative to $\delta_0$ should be zero or negative. This is the observed case.

As was suggested in Part I, this behavior proved to be quite general. Listed in Table 2 are the results for several compounds discussed in this section, Part I, and Part IV of this thesis. The results are totally consistent with the predicted behavior. It might be argued that the assignments for $H_\alpha$ and $H_\beta$ could be reversed in the case of $\delta_2$ and $\delta_3$, and thus the exo and endo hydroxyl assignments are reversed. However, in the case of the 1,4-bridged bicyclopentanes ($\delta_7, \delta_8, \delta_{24}, \delta_{29} \rightarrow \delta_{95}$), the $H_\beta$ proton is easily assigned by means of its readily observable long range $W$-coupling with the endo hydrogens of the cyclobutyl ring. In view of the total consistency of this series, the assignments for $\delta_2$ and $\delta_3$ are certainly correct, in agreement with the chemical evidence already given.

**Kinetic Results**

Table 3 lists the rates of solvolysis for the p-nitrobenzoates.
Table 2 (con't.)

\[ \begin{align*}
0.36 & \quad H_b & \quad Ha & \quad 1.00 \\
\delta & \quad 0.64 \\
\Delta \delta & \quad (+) \\
\end{align*} \]
Table 2 (cont.)

\[
\begin{align*}
\Delta \delta &= 0.59 \\
\Delta \Delta \delta &= (+)
\end{align*}
\]

- a) Positions are given in units of \( \delta \) relative to TMS or CHCl\(_3\) as internal standards.

- b) \( \Delta \delta \) is equal to the difference, \( H_a - H_b \).

- c) \( \Delta \Delta \delta \) is determined from the difference \( (\delta H_a - \delta H_b) \) exo or endo-(\( \delta H_a - \delta H_b \)) model.

- d) See reference 36.

- e) The parent hydrocarbon is unknown. However, \( H_a \) and \( H_b \) are expected to be equal for the parent.

- f) See reference 32.

- g) See reference 86.

- h) See reference 33.
of 82, 83, 86, 87, 97 (endo-bicyclo[3.1.0]hexan-2-ol), and 98 (exo-bicyclo[3.1.0]hexan-2-ol), corresponding to 84, 85, 99, 100, 101, and 102, respectively, in 70:30 v/v acetone:water. As can be seen from this data, bridging of the 1,5-positions of 101 and 102 provides for a considerable increase in the solvolysis rates. In the case of 85 and 100, this acceleration might conceivably be associated with the change in steric environment of the leaving group. However, an analogous argument cannot be made for the similarly accelerated rates observed for the solvolysis of 84 and 99 relative to 101. Examination of the rate ratios of the epimeric pairs 101 and 102, 99 and 100, and 84 and 85, shows that these ratios (3.8, 3.4, and 1.9, respectively) vary very little. This indicates that the effect of the trimethylene bridge in the tricyclo[3.3.1.01,5]nonane derivatives and of the tetramethylene bridge in the tricyclo[4.3.1.01,8]decane derivatives was probably the same for both the exo and endo p-nitrobenzoates.

Recently, the solvolyses of 103 and 104 were found to be 22 and 18 times faster than those of the corresponding nonmethylated cases. Although this was interpreted in terms of a highly delocalized structure such as 105, the authors indicated that the effect of methyl substitution was primarily an entropy effect. Our data indicate that the trimethylene bridge in the case of 99 and 100, and the tetramethylene bridge in the case of 84 and 85 do not have much of an effect on the entropy of the reaction, even
Table 3. Rates of Solvolysis of Derivatives of Bicyclo[3.1.0]hexane in 70:30 v/v Acetone:Water.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temp (±0.02 °C)</th>
<th>Rate (sec⁻¹)</th>
<th>$k_{rel}^{\circ}25$° (kcal/mol)</th>
<th>$\Delta H^\ddagger$</th>
<th>$\Delta S^\ddagger$ (e.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>![Diagram 84]</td>
<td>115.00</td>
<td>(2.22 ± 0.07) x 10⁻³</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>100.00</td>
<td>(6.82 ± 0.09) x 10⁻⁴</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>85.00</td>
<td>(1.55 ± 0.03) x 10⁻⁴</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>25.0</td>
<td>1.54 x 10⁻⁷</td>
<td></td>
<td>23.9</td>
<td>-9.5</td>
</tr>
<tr>
<td>![Diagram 85]</td>
<td>115.00</td>
<td>(1.12 ± 0.02) x 10⁻³</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>100.00</td>
<td>(3.29 ± 0.01) x 10⁻⁴</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>85.00</td>
<td>(7.89 ± 0.01) x 10⁻⁵</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>25.0</td>
<td>8.26 x 10⁻⁸</td>
<td></td>
<td>23.7</td>
<td>-11.5</td>
</tr>
<tr>
<td>![Diagram 89]</td>
<td>130.00</td>
<td>(2.75 ± 0.02) x 10⁻³</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>115.00</td>
<td>(9.63 ± 0.12) x 10⁻⁴</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>100.00</td>
<td>(2.56 ± 0.07) x 10⁻⁴</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>25.0</td>
<td>9.02 x 10⁻⁸</td>
<td></td>
<td>22.9</td>
<td>-14.1</td>
</tr>
</tbody>
</table>
Table 3 (cont.)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temp (±0.02 °C)</th>
<th>Rate (sec⁻¹)</th>
<th>$k_{rel}^{25°}$</th>
<th>ΔH⁺ (kcal/mol)</th>
<th>ΔS⁺ (e.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Compound 1" /></td>
<td>130.00</td>
<td>$(1.66 \pm 0.01) \times 10^{-3}$</td>
<td></td>
<td>24.6</td>
<td>-10.7</td>
</tr>
<tr>
<td></td>
<td>115.00</td>
<td>$(5.76 \pm 0.09) \times 10^{-4}$</td>
<td></td>
<td></td>
<td>25.0</td>
</tr>
<tr>
<td></td>
<td>100.00</td>
<td>$(1.31 \pm 0.01) \times 10^{-4}$</td>
<td>$(1.31 \pm 0.01) \times 10^{-4}$</td>
<td>210</td>
<td></td>
</tr>
<tr>
<td></td>
<td>25.0</td>
<td>$2.62 \times 10^{-8}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><img src="image2.png" alt="Compound 2" /></td>
<td>160.00</td>
<td>$(8.91 \pm 0.04) \times 10^{-4}$</td>
<td></td>
<td>26.7</td>
<td>-11.4</td>
</tr>
<tr>
<td></td>
<td>145.00</td>
<td>$(2.90 \pm 0.04) \times 10^{-4}$</td>
<td></td>
<td></td>
<td>29.2</td>
</tr>
<tr>
<td></td>
<td>130.00</td>
<td>$(8.21 \pm 0.16) \times 10^{-5}$</td>
<td>$(8.21 \pm 0.16) \times 10^{-5}$</td>
<td>3.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>25.0</td>
<td>$4.78 \times 10^{-10}$</td>
<td></td>
<td></td>
<td>1.0</td>
</tr>
<tr>
<td><img src="image3.png" alt="Compound 3" /></td>
<td>160.00</td>
<td>$(8.30 \pm 0.13) \times 10^{-4}$</td>
<td></td>
<td>29.2</td>
<td>-6.0</td>
</tr>
<tr>
<td></td>
<td>145.00</td>
<td>$(2.40 \pm 0.05) \times 10^{-4}$</td>
<td></td>
<td></td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>130.00</td>
<td>$(6.20 \pm 0.03) \times 10^{-5}$</td>
<td>$(6.20 \pm 0.03) \times 10^{-5}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>25.0</td>
<td>$1.25 \times 10^{-10}$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) Extrapolated from higher temperatures.
b) See reference 86.
though rate accelerations of greater than $10^2$ result from this bridging.

Product studies on 99 and 100 at 100° indicated that both 99 and 100 gave a 2:1 mixture of 86 and 87 on solvolysis in aqueous acetone. Solvolysis at higher temperatures, or the heating of 86 and 87 in the presence of acid, resulted in the formation of small amounts of additional products, which were not identified. These studies indicated that 99 and 100 probably solvolyzed to give the same ion.

Product studies on 84 and 85 were somewhat more complicated because the ratio of products changed during the course of the reaction due to the instability of some of the products under the reaction conditions. Thus, after 10 half-lives at 85°, 84 gave 106 (59%), 82 (7%), 83 (7%), and 107 (20%). In contrast, after 10% reaction the ratio of 106:82:83:107 was 70:25:4:1. This indicated
to us that 106 and 82 were the primary products of the solvolysis and that they were converted into 83 and 107 under the reaction conditions. After 10 half-lives at 85°, 85 also gave 106 (63%), 82 (8%), 83 (6%), and 107 (11%). At 10% reaction the ratio of 106:82:83:107 from 85 was 68:30:1:trace, which shows that the product ratios from the solvolysis of 84 and 85 are essentially within experimental error of each other. This indicates that the primary products from both 84 and 85 are the same, and suggests that 84 and 85 probably ionize to give the same cationic intermediate.

The structures of 82 and 83 were established by comparison with the starting alcohols. Bicyclo[4.4.0]dec-1(6)-en-3-ol (107) was identified by comparison with an authentic sample prepared by lithium aluminum hydride reduction of 80 according to the
A combination of spectral and chemical evidence was used to elucidate the structure of \( \text{106} \). Nmr and ir spectral data established the presence of a tertiary alcohol and of a trisubstituted double bond [one proton triplet at \( \delta 5.54 \) \((J = 5.5 \text{ Hz})\)].\(^{91}\) In addition, the nmr spectrum showed six allylic type protons at \( \delta 2.34-1.85 \). Catalytic hydrogenation of \( \text{106} \) gave a saturated tertiary alcohol, whose ir spectrum compared well with that reported for bicyclo[4.3.1]decan-1-ol.\(^ {92}\)

The similar product ratios obtained from \( \text{84} \) and \( \text{85} \), and from \( \text{99} \) and \( \text{100} \), indicate that the epimeric pairs of compounds are solvolyzing to the same intermediates. The significant difference


\(^{91}\) The position and coupling constant for this absorption were very similar to those reported for bicyclo[3.3.1]non-1-ene. J.R. Wiseman and W.A. Pletcher, \textit{J. Amer. Chem. Soc.}, 92, 956 (1970) report \( \delta 5.62 \) \((t, J = 7 \text{ Hz})\). J.A. Marshall and H. Faubl, \textit{ibid.}, 92, 948 (1970) report \( \delta 5.52 \) \((t, J = 3.5 \text{ Hz})\). The isolation and identification of the bicyclo[4.2.1]non-1(8)-ene system [J.R. Wiseman, H.-F. Chan, and C.J. Ahola, \textit{ibid.}, 91, 2812 (1969)] indicates that \( \text{106} \), which should be less highly strained, may not be very destabilized as a result of the bridgehead double bond.

in the primary products obtained from the two tricyclic ring system is of interest. The formation of 106 as the major product from 84 and 85 and the absence of analogous products from 99 and 100 can be rationalized in terms of the nine-membered ring of 106 being able to sustain a trans double bond. If a similar product were to be formed from 99 and 100, a trans-cyclooctene would be incorporated into the bicyclic skeleton. Although the parent olefin is known, the added strain energy which would result from such a trans double bond is probably sufficient to inhibit formation of products containing this moiety.
PART IV
SYNTHESIS AND SOLVOLYSES OF A FUNCTIONALIZED
TRICYCLO[4.2.1.0^1,8]NONANE RING SYSTEM

Introduction

In Part I, the synthesis of a C₆ functionalized [3.2.1]propellane system (53 and 54) was described. These epimers proved to be unsuitable for further study largely because of their high reactivity. In Part II, the larger, more stable [4.2.1]propellane was successfully made, but the synthesis proved to be inconvenient for large scale study. It was decided, therefore, to pursue another line of attack for entry into a functionalized [4.2.1]propellane system. The results of Part I indicated that considerable strain could be introduced into a ring system via a Wolff ring contraction, and thus, that 95 and 108 should be available by contraction of 57. Furthermore, the results of Part II (vide supra) suggested that 95 and 108, when made, ought to be reasonably stable. Compounds 95 and 108 were desired for two purposes. One purpose, the subject of the first part of this chapter, was for reduction to the corresponding carbinols. It was desired to convert the carbinols into tosylates in order to measure the solvolytic effects.
of constraining a cyclobutylcarbinyl cation into the tricyclic ring system.

The second purpose for preparing 95 and 108 was for a possible degradation to a 1,4-bridged bicyclo[2.1.0]pentane-2-ol. Wiberg and coworkers had shown that the endo-dinitrobenzoate of bicyclo-[2.1.0]pentan-2-ol solvolyzed $10^7$ faster than the exo-derivative.

93. Unlike the extensively studied cyclopropylcarbinyl cation system, very little information exists concerning the cyclobutylcarbinyl cation. The solvolysis of parent compound, as well as of some bridged derivatives, is discussed by K.B. Wiberg and B.A. Hess, Jr., J. Amer. Chem. Soc., 88, 4433 (1966) see also, W.G. Dauben and J.L. Chitwood, ibid., 90, 3835 (1968) and C.F. Wilcox, Jr., and M.E. Mesirov, ibid., 84, 2757 (1962).


It was of interest to us to determine the effects of 1,4-bridging on this solvolysis. The attempt to prepare the necessary ring system is the subject of the second part of this chapter.

Synthesis and Solvolyses of Carbinol Tosylates

The synthesis of the desired tosylates followed directly from the key intermediate, tricyclo[4.3.1.0^1,5]decan-7-one (79), as shown in Chart VI. The 8-hydroxymethylenetricyclo[4.3.1.0^1,5]decan-7-one was produced by the reaction of 79 with sodium hydride and ethyl formate (73%). Conversion to the diazoketone (57) was effected with sodium hydride and p-toluenesulfonyl azide (~90%). When 57 was irradiated in methanol, an approximately 75:25 mixture (52%) of the exo and endo methyl esters, respectively, was obtained, along with two unidentified isomers which were present to the extent of about 5% each. One of these may have been 110 (see Experimental), but this was not definitely established. The presence of the two impurities was important, however, since it was extremely difficult to separate them from either the esters (95 and 108) or the carbinols (89 and 90). The photolysis mixture
CHART VI

1) NaH, HCO₂C₂H₅
2) NaH, TsN₃

79 → 57

hv
CH₃OH

1) OH⁻
2) H₂O

109 → 95 + 108
exo
endo
75 : 25

LiAlH₄

pure 95 + 108

95 + 108

89 + 90

TsCl
pyridine

91 + 92

TsCl
pyridine

21 + 22
was therefore subjected to basic hydrolysis to yield the pure acid 109. The acid was fairly labile [mp 38-55°C (dec)] and was immediately esterified with diazomethane to afford a pure mixture of the epimeric esters (74% from the photolysis mixture). The carbine obtained by lithium aluminum hydride reduction of the pure esters (96%), could be separated by preparative vapor phase chromatography to give the pure epimers 89 and 90. The isomers 89 and 90 were converted by the reaction of p-toluenesulfonyl chloride in pyridine to 91 (83%) and 92 (86%), respectively. The overall yield was 21% from 72 (and 2.3% for 11 steps from cyclohexanone).

The ratio of carbinols obtained was still ~75:25 for 89 and 90, respectively, indicating no epimerization during the hydrolysis to the acid 109. When the methyl ester mixture (85 and 108) was subjected to sodium methoxide in refluxing methanol, no change in the product ratio was observed.

The nmr, ir, and mass spectra, as well as combustion analyses, were in agreement with the assigned structures of the new compounds. The assignment of stereochemistry at C7 was based on the same arguments presented in Part I (see p. 34) and in Part III (see, especially, Table 2, p. 58). In addition, the chemistry of the epimers, to be discussed, was consistent with the designated structures.

The solvolyses of the epimeric carbinol p-toluenesulfonates, 21 and 22, were carried out in 90:10 v/v acetone:water buffered
with 2,6-lutidine. As shown in Table 4, the rates of solvolysis, which were very similar, provide little indication of any difference in activation energy for the solvolysis of 91 and 92. The observed difference of a factor of about 9 at 80°C in the relative rate of solvolysis could be attributed to any one of a variety of effects.

Table 4. Rates of Solvolysis for exo and endo Tricyclo[4.2.1.01,6]nonane-7-methanol, p-Toluenesulfonates (91 and 92) in 90:10 v/v acetone:water Buffered with 2,6-Lutidine.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temp. (±0.02°C)</th>
<th>Rate (sec⁻¹)</th>
<th>H⁺ (kcal/mole)</th>
<th>S⁺ (e.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>91</td>
<td>80.00</td>
<td>(6.34±0.06)x10⁻⁴</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>70.00</td>
<td>(2.90±0.01)x10⁻⁴</td>
<td>20.50±0.2</td>
<td>-15.40±0.6</td>
</tr>
<tr>
<td></td>
<td>60.00</td>
<td>(1.04±0.01)x10⁻⁴</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₂OTs</td>
<td>25.0</td>
<td>2.54 x 10⁻⁶</td>
<td></td>
<td></td>
</tr>
<tr>
<td>92</td>
<td>100.00</td>
<td>(4.62±0.02)x10⁻⁴</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>90.00</td>
<td>(1.86±0.02)x10⁻⁴</td>
<td>23.2±0.1</td>
<td>-12.1±0.4</td>
</tr>
<tr>
<td>CH₂OTs</td>
<td>25.0</td>
<td>1.41 x 10⁻⁷</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) Extrapolated from higher temperatures.

96. Acetone-water was used as the solvolytic media rather than the more common buffered acetic acid because the highly strained tricyclic ring system was susceptible to acetic acid addition.
In contrast to the kinetic study, a product study indicated a high degree of involvement by the rest of the molecule in the ionization of \( \text{91} \) and \( \text{92} \). After 10 half-lives at \( 80^\circ\), \( \text{91} \) gave 91% of \( \text{111} \) and 9% of \( \text{96} \). It would appear that this is the kinetic product mixture, since on treatment with acid, either \( \text{111} \) or \( \text{96} \) is interconverted to give an equilibrium mixture consisting of 55% of \( \text{111} \) and 45% of \( \text{96} \). The structure of \( \text{96} \) was established on the basis of its spectral properties and through comparison of its mp (66.0-67.5°) and infrared spectrum with the reported values.

\[
\begin{align*}
\text{91} & \quad \text{111} \\
\text{H} & \quad \text{CH}_2\text{OTs} \\
\end{align*}
\]

The structure of \( \text{111} \) was established on the basis of its spectral properties. The infrared spectrum of \( \text{111} \) showed both free and hydrogen-bonded O-H stretching bands at 2.70 \( \mu \) and 2.92 \( \mu \), respectively. No absorption characteristic of a carbon-carbon double bond could be detected. The near infrared spectrum of \( \text{111} \) showed an absorp-

97. It was demonstrated that the carbinols \( \text{89} \) and \( \text{90} \) were stable to the reaction conditions and were not responsible for the production of the observed products from solvolysis of \( \text{91} \) and \( \text{92} \).

tion at 1.651 μ (¢ 0.2μ8) characteristic of a cyclopropyl methylene unit. The nmr spectrum of 111 showed a complex pattern of overlapping multiplets extending from δ 0.37 to 2.39 for the carbon-bonded protons. No evidence for the presence of either vinlyc hydrogens or protons bonded to a carbinol carbon could be detected. Thus, the alcohol must have been tertiary and a cyclopropyl ring must have been present. The spectral data, coupled with the interconversion of 111 and 96, was only consistent with structure 111.

Solvolysis of 92 gave 106 (56%), 82 (12%), 83 (12%), and 107 (11%), at 80° after 10 half-lives when a 2,6-lutidine buffer was used in 90:10 v/v acetone:water. In contrast, after 10% reaction, the ratio of 106:82:83:107 was 74:20:4:1. The primary products of the solvolysis of 92 appear to be 106 and 82, since the amounts of 83 and 107 increase as the solvolysis proceeds, presumably as a result of acid catalysis by the 2,6-lutidinium tosylate. The products were identified by comparison to those obtained in the solvolysis of 7-tricyclo[4.3.1.016]decyl p-nitrobenzoates 84 and 85.

The data presented support the contention that 91 and 92 solvolyze to give two completely different ions. It appears that


100. In unbuffered 90:10 v/v acetone:water, only 107 was obtained. It was demonstrated that 106, 82, and 83 were readily converted into 107 in the presence of acid.
91 gives products based on the migration of $C_6$ to the incipient cationic center to give 112, while 92 is converted into products resulting from the migration of $C_6$ to the site of developing charge to yield 113. Since there is no crossover of products, these rearrangements must be extremely stereospecific. The degree of stereospecificity is presumably controlled by the stability of the developing cation. Migration of $C_6$ in the solvolysis of 91 should lead to 112, which is stereochemically well arranged for stabilization by the neighboring cyclopropyl ring as shown in 114. Only products with the stereochemistry required by the intermediacy of 114 were found in the solvolysis of 91. Migration of $C_6$ in the
solvolysis of 92 would produce 115, which is not well situated for stabilization by the neighboring cyclopropyl group.

In the solvolysis of 92, migration of C₈ should give the cyclopropylcarbinyl cation 113. Support for this contention was provided by the solvolysis of the epimeric p-nitrobenzoates, 84 and 85 which gave similar mixtures of the same products as were obtained from 92. Migration of C₈ in the solvolysis of 91 would produce 116, which would be expected to have a destabilizing interaction of the hydrogen at C₈ and C₁₀ of 116.

These results indicate that the ring-expansion from a cyclobutylcarbinyl to a cyclopentyl type cation can be an extremely selective process. In propellanes such as 91 and 92, where the cyclobutane moiety is part of a more highly-strained ring system, interactions with the rest of the molecule can lead to products
with unusual carbon skeletons due to the overall relief of ring strain. Unfortunately, the exact role that the 1,4-bridging of the bicyclopentane nucleus plays in the solvolysis of $\text{91}$ and $\text{92}$ cannot be evaluated since the results for the solvolysis of the exo and endo-2-bicyclo[2.1.0]pentane methyl p-toluenesulfonates are not yet available. 101

**Attempted Degradation of 109**

The acid 109 was treated with methyl lithium to give an approximately 75:25 mixture of exo and endo methyl ketones 23 and 24. On treatment of this epimeric mixture with peracetic acid buffered with anhydrous sodium carbonate in methylene chloride under classical Baeyer-Villiger oxidation conditions, the exo epimer, 23, was observed to react immediately and quantitatively with two moles of peracid to give just one product (117). Under the reaction conditions, the endo-epimer 24 could be recovered unchanged. If 1.2 equivalents of peracid per mole of ketone were used, then ~50% of 23 could be recovered, plus some 117. No

101. P.G. Gassman, work in progress.
intermediate product was observed.

Compound 117 gave an ir spectrum (neat) with absorptions at 5.73 μ (C = O str) and 8.06 μ (C0 str of an acetate). An nmr spectrum gave δ_{CDCl₃} 2.92 (d, J = 4 Hz, 1H) and 0.97-2.63 (br, m, 15 Hz, with a methyl singlet at 1.96). A near infrared spectrum (CCl₄) indicated the lack of a cyclopropyl ring by the lack of any absorptions between 1.600 and 1.675 μ. A mass spectrum failed to give a parent peak as might be expected for an acetate but did give a base peak at m/e 136 corresponding to the loss of acetic acid. Finally, the combustion analysis of 117 confirmed that had incorporated two oxygen atoms into its formula upon reaction with the peracid. From this data, it would appear that 117 is either a tertiary acetate and trisubstituted epoxide, or else a tetrasubstituted epoxide with a secondary acetate whose proton on the same carbon bearing the acetate is anomalously shielded.

Originally, it was thought that perhaps the desired acetate, 118, was being initially formed, and was subsequently solvolyzing to give the cation 119. By analogy to 123, which slowly rearranges to 107, presumably through 124, 119 might be expected to rearrange to 120 which could be captured by the acetate anion to give 121.


Under the reaction conditions, 121, a tetrasubstituted olefin, should easily be epoxidized, preferably from the side opposite the acetate, 104 to give 122. The proton of 122 in this tetrasubstituted epoxide and secondary acetate might be unusually shielded by

the presence of the epoxide in the rigid tricyclic. To test this hypothesis, 4,5,6,7-tetrahydro-2-indanol, prepared according to the method of Starr and Eastman, was converted to the acetate (125) by reaction with acetic anhydride in pyridine. Epoxidation of 125 under the reaction conditions used for the Baeyer-Villiger reaction of 93 gave a 92% yield of a 60:40 ratio of 122:126.

\[
\begin{align*}
\text{OH} & \quad \text{Ac}_2\text{O} \quad \xrightarrow{\text{pyridine}} \quad \text{OAc} \\
& \quad \text{125} \\
\text{H} & \quad \text{OAc} \quad + \quad \text{OAc} \\
& \quad \text{122} \\
\end{align*}
\]

Neither isomer was the desired 117.

Again, by analogy, if cation 119 were produced, perhaps cation 127 would be an important resonance (or equilibrium) form, just as 123a was an important resonance (or equilibrium) form of 123. As the parent compound, bicyclo[4.2.1]non-1(8)-ene, has been isolated, it is not unreasonable that 128 could be formed from acetate anion attack on 127. Compound 128 with its highly strained double bond, could be expected to epoxidize readily to
give a trisubstituted epoxide and tertiary acetate (which turned out to be 117). To test this hypothesis, 117 was reduced with an excess of lithium aluminum hydride in ether to give just one component, 122, mp 158-159.5°C. An ir spectrum (CCl₄) gave absorptions at 2.71 μ (free OH str) and 2.88 μ (H-bonded OH str). An nmr spectrum gave δCCl₄ 3.13 (br s, 1H, variable in position and exchangeable in deuterium oxide), 2.84 (m, 1H), and 0.86-2.56 (br m, 12H).
A mass spectrum gave a parent peak at m/e 154. From this data, it is obvious that only an acetate has been cleaved, and not the epoxide. Refluxing 117 in an excess of lithium aluminum hydride for 12 hr in tetrahydrofuran still gave only 129. Models indicated that perhaps the epoxide ring of 129 was too hindered for rear-side attack with lithium aluminum hydride. Epoxide 129 was therefore treated with lithium in ethyl amine, conditions which allow for the opening of hindered epoxides and would favor tertiary alcohol formation. Only one product was produced, diol 130. Evidence for the structure of 130 was contained in its spectral and physical properties. An ir spectrum (CHCl₃) gave absorptions at 2.74 μ (free OH str) and 2.91 μ (H-bonded OH str). An nmr spectrum (CD₃)CO gave δ(TMS) 3.08 (very br m, 2H, readily exchanges with deuterium oxide), and 1.14-2.36 (m, 14H). A combustion analysis gave

the correct C, H, and O percentages. The physical properties of 130 are very revealing. The compound was very high melting [185-187° (sub)] and was not soluble in carbon tetrachloride, only slightly soluble in chloroform, and soluble in acetone and water. This and the preceding data are only consistent with structure 130 (and 117 and 122).

Wiberg found considerable difficulty in preparing the 3,5-dinitrobenzoate of endo-bicyclo[2.1.0]pentan-2-ol because it invariably partially rearranged to give some Δ3-cyclopentenyl-3,5-dinitrobenzoate, indicating the high reactivity of compounds such as 131. Even more pertinent to the present case is the observation by Brook and Brophy that peracid oxidation of endo-methyl ketone 132 gave, at best, a 95:5 mixture of 133 and 134. In addition, when 133 was hydrolyzed under basic conditions, 67% of 136 and only 33% of 135 were obtained. These results were explained in terms of the competitive solvolysis of the acetate group with resultant ring opening, again attesting to the high reactivity of compounds such as 131 and 133.

In the case of the endo-2-bicyclohexyl p-nitrobenzoate, a rate acceleration of 340 was observed when 1,4-bridging with a tetramethylene unit was introduced. If a 1,4-tetramethylene bridge has a similar accelerating effect on the solvolysis of endo-2-acetoxybicyclo[2.1.0]pentane, then the acetate 118 may be too reactive to isolate under ordinary reaction conditions. Instead,
it solvolyzes to cation 119 and subsequently reacts as already described. These results again demonstrate that in propellanes such as 93 and 118, where the bicyclopentane is part of a more highly-strained ring system, interactions with the rest of the molecule can lead to unusual reactivity and unusual products due to the overall relief of ring strain.
EXPERIMENTAL

Elemental analyses were performed by the Scandinavian Micro-analytical Laboratory, Herlev, Denmark. Melting points and boiling points are uncorrected. Infrared spectra were taken on a Perkin-Elmer Model 137 Infraord as neat liquids, solutions in A.R. carbon tetrachloride, or powdered solids in potassium bromide disks. Near-infrared spectra were obtained on a Cary Model 14 Recording Spectrometer from 0.5 M solutions in A.R. carbon tetrachloride. Nuclear magnetic resonance spectra were obtained on either a Varian Associates A-60A or JEOLCO MH 100 spectrometer and reported in delta (δ) units relative to tetramethylsilane (δ = 0.00) or deuteriochloroform (δ = 7.28) as the internal standards. Mass spectra were obtained on an AEI MS-9 spectrometer.

Isomerization of Tricyclo[3.2.1.015]octane(7)28,30,40 with Chlorotricarbonyliridium(I) dimer. In a typical procedure, 120 mg (5 mole percent) of chlorotricarbonyliridium(I) dimer was added to 398 mg of tricyclo[3.2.1.015]octane in 5 ml of chloroform (purified over basic alumina) in a test tube previously washed with a potassium hydroxide-ethanol solution. The sealed tube was heated to 50-55° for 24 hr. Analysis of the crude reaction mixture by vpc (10 ft, 10% SE-50 on Diaport S column at 80°) indicated one
major peak. Preparative vpc on a 4" x 1/4" 20% SE-30 on 60/80 Chrom W column after vacuum transfer yielded one major peak, a mixture of 4-methylenecycloheptene (37) and 5-methylenecycloheptene (38). The ir, nmr, mass spectrum (parent peak m/e 108), and gc retention times of the mixture were consistent with those of authentic samples of 37 and 38. By nmr analysis, the yield was 52%, consisting of 36% of 37 and 64% of 38.

Hydrogenation of 4-Methylenecycloheptene (37) and 5-Methylenecycloheptene (38) Mixture. To 10 ml of ether containing 25 mg of 5% palladium on carbon was added 82.1 mg of the mixture of 37 and 38. Hydrogenation at ambient temperature and slightly more than one atmosphere for 4 hr yielded only methylcycloheptane, 45.2 mg (51%), collected by preparative gas chromatography on a 4" x 1/4" 20% SE-30 on Diaport S column. The ir spectrum was as expected, and the nmr spectrum and vpc retention times were identical to those of an authentic sample (Chemical Samples).

4-Methylenecycloheptene (37). To 3.69 g (18.1 mmol) of trimethyl-sulfonium iodide in 60 ml of dry tetrahydrofuran under nitrogen was added slowly with stirring, 10.5 ml (18.1 mmol) of 1.75 N ether solution of methyl lithium, maintaining the temperature at -20°. After one minute, 1.53 g (13.9 mmol) of cyclohept-3-enone in 60 ml of dry tetrahydrofuran was added during a 10 min period.
The solution was stirred for 15 additional minutes at -20°, then warmed to room temperature for 1.5 hr. The solution was added to 100 ml of ice-water and extracted thoroughly with ether. The combined ether extracts were washed with water, saturated salt solution, and dried over anhydrous magnesium sulfate. Distillation gave 0.97 g of material, bp 74-75° (17 mm), containing the desired oxirane (δ^TMS = 2.47, typical of epoxide protons) contaminated with considerable ketonic material (about 60% by gc), presumably a mixture of the starting ketone and the isomerized α-β unsaturated ketone. The epoxide was then reduced to the olefin by the method of Cornforth, Cornforth, and Mathew. To 5 ml of glacial acetic acid was added 0.32 g of water, 2.10 g of sodium iodide, 0.70 g of anhydrous sodium acetate, and, with cooling, 2.10 g of zinc powder. After stirring for 3 minutes, 0.97 g of the oxirane mixture in 2 ml of glacial acetic acid was added dropwise. After 1 hr of stirring at room temperature, the remaining zinc was filtered, washing with 10 ml of acetic acid, then 10 ml of ether. The filtrate was diluted with ice-water and extracted thoroughly with ether. The combined ether extracts were washed thoroughly with saturated sodium bicarbonate solution, saturated salt solution, and dried over anhydrous magnesium sulfate. After filtration and concentration, preparative vpc on a 4' x 1/4'' 20% SE-30 on 60/80 Chrom W column yielded the desired 4-methylene-cycloheptene (37), in all respects identical to that obtained from
the isomerization of tricyclo[3.2.1.0^1,5]octane with chlorotri-carbonyliridium(I) dimer. The infrared (neat) had characteristic absorbances at 3.20 μ and 3.25 μ (vinyl CH str), 6.05 μ (C = C str) and 11.23 μ (terminal methylene CH bend); the nmr spectrum showed CCl₄ δTMS 5.65 (m, 2H, vinyl), 4.62 (s, 2H, vinyl, terminal methylene), 2.82 (br d, 2H, doubly allylic methylene), 1.99-2.57 (br m, 4H, allylic methylene), and 1.22-1.90 (br m, 2H, methylene).


5-Methylenecycloheptene (38). To a solution of 2.01 g (10.6 mmol) of p-toluenesulfonyl chloride in 5 ml of pyridine was added at 0°, 1.33 g (10.5 mmol) of 4-cycloheptene methanol in 5 ml of pyridine. After stirring at room temperature for 2 hr, and standing in the refrigerator overnight, 1 ml of water was added and the mixture stirred for 10 min. Further dilution with 10 ml of water was followed by thorough extraction with ether. The combined ether extracts were washed with 10% hydrochloric acid, saturated sodium bicarbonate solution, saturated salt solution, and dried over anhydrous magnesium sulfate. Filtration followed by removal of solvent and drying overnight in vacuo yielded 2.40 g (81%) of tosylate as white crystals, mp 46.0-48.5°. The tosylate, without further purification, was dissolved in 20 ml of dry dimethylsulfoxide (distilled from calcium hydride) and was added dropwise
over a period of 30 min to a solution of 1.45 g of potassium t-butoxide in 20 ml of dry dimethylsulfoxide, maintaining the temperature at 20-25°. After stirring for 30 min, 100 ml of pentane was added, the solution was stirred for 1 min, and was poured into 60 ml of ice-water slush. After thorough extraction with pentane, the extracts were washed with saturated salt solution and dried over anhydrous magnesium sulfate. The drying agent was filtered, the solution was concentrated, and a pure sample of 5-methylecycloheptene (38) was collected by preparative vpc on a 4' x ¼' 20% SE-30 Diaport S column. It was identical in all respects to that obtained from the isomerization of tricyclo-
[3.2.1.01,5]octane with chlorotricarbonyliridium(I) dimer. The infrared spectrum (neat) gave characteristic absorbances at 3.20 μ and 3.25 μ (vinyl CH str), 6.05 μ (C = C str), and 11.24 μ (terminal methylene CH bend); the nmr spectrum showed δ_{CCL4}^{TMS} 5.85 (m, 2H, vinyl), 4.72 (s, 2H, vinyl, terminal methylene), and 2.24 (s, 8H, allylic methylene). The mass spectrum gave m/e 108.


Reaction of Rhodium Dicarbonyl Chloride Dimer with Tricyclo-
[3.2.1.01,5]octane (7) in Methanol. Into 3 ml of purified methanol (passed through basic alumina) in a test tube was placed 311.0 mg (95 mol percent) of 7. To this solution was added 57.1
mg (5 mol percent) of rhodium dicarbonyl chloride dimer (exo-
thermic) and the volume brought up to 5 ml with additional methanol.
The ampoule was sealed under argon and heated to 50° for 24 hr.
The ampoule was then cooled, opened, and the solution distilled
to give 280 mg (70%) of a colorless liquid, bp 108° (78 mm).
Vpc on a 10' x 1/8'' 10% SE-30 on Diaport S column at 130° showed
the material to consist of just one component, 1-methoxybicyclo-
[3.2.1]octane (46). An ir spectrum (neat) showed an absorption
at 9.01 μ (CO str) as well as considerable fine structure between
6.8 and 11.5 μ; an nmr spectrum gave absorptions at $^6_{\text{CCl}_4}$ 3.15
(s, 3H), 2.04-2.44 (br m, 1H), and 1.09-1.92 (m, 12H); a mass
spectrum showed m/e 140. An analytical sample, $^{24}_D$ 1.4659, was
collected by preparative vpc on a 9' x 1/4'' 10% SE-30 on 60/80
Chrom W column at 125°.

Anal. Calcd for C_{9}H_{18}O: C, 77.09; H, 11.50. Found: C, 77.03;
H, 11.71.

Approximately 100 mg of 7 was added dropwise to 1 g of glacial
acetic acid and the reaction solution was stirred for 20 min.
The reaction mixture was poured into 15 ml of ether and the excess
glacial acetic acid was removed by shaking with cold saturated
sodium bicarbonate solution. The ether layer was then washed with
two portions of water, once with saturated sodium chloride solu-
tion, and dried over anhydrous magnesium sulfate. Evaporation of the solvent from a portion of the sample gave a sweet smelling liquid whose ir spectrum (neat) indicated the presence of the desired acetate \( \text{CH}_3\text{CO}_2 \) by absorptions at 5.72 \( \mu \) (C = O str) and 8.04 \( \mu \) (-CO\(_2\) str of an acetate). Vpc on a 10' x 1/8'' 10% SE-30 on Diaport S column at 170\(^\circ\) indicated just one component.

The remaining solution was added with ice cooling to 250 mg of lithium aluminum hydride in 5 ml of anhydrous ether. After gently refluxing overnight, the solution was cooled in an ice bath and 1.04 g of 10% sodium hydroxide solution was added dropwise. The solution was stirred for 1 hr at room temperature and the lithium salts were removed by filtration. The filtrate was dried over anhydrous magnesium sulfate and the drying agent was removed by filtration. Evaporation of the solvent from a portion of the sample gave an oil whose ir spectrum (neat) indicated the presence of the desired alcohol \( \text{CH}_3\) by absorptions at 3.01 \( \mu \) (OH str) and 9.08 \( \mu \) (CO str). Vapor phase chromatography on the aforementioned column indicated the presence of just one component.

The remaining solution was added dropwise with ice cooling to 350 mg of sodium hydride in ether. To the mixture was then added 14 g of methyl iodide and the solution was brought to a gentle reflux. The progress of the reaction was followed by vpc on the aforementioned column. After 86 hr, the reaction was complete, giving just one component. The solution was decanted and the
solvent distilled. The residue was collected by preparative vpc on a 9' x 1/4'' 10% SE-30 on 60/80 Chrom W column at 125° to give 46. This was identical to the product of rhodium dicarbonyl chloride dimer reaction with 7 in methanol by nmr, ir, and vpc retention times on three columns of widely differing polarity. These columns were a 10' x 1/8'' 10% SE-30 on Diaport S column at 130°, a 5'6'' x 1/8'' Carbowax 20M on Chrom W column at 170°, and a 10' x 1/8'' 7% XF 1150 on 60/80 Chrom G column at 90°.

Reaction of Rhodium Dicarbonyl Chloride Dimer with 1-Deuteriocyclopentene in the Presence of 7. Into 1 ml of purified deuteriochloroform (passed through basic alumina) was placed 1.2.8 mg of 1-deuteriocyclopentene, 64 22.3 mg of 7, and 8.3 mg of rhodium dicarbonyl chloride dimer (approximately 100:10:1 mole ratios, respectively). The solution was sealed under argon and heated to 55-60° for 24 hr. The solution was cooled and the cyclopentene-chloroform distilled from higher boiling material (pot <80°). An nmr spectrum (CDCl₃/CHCl₃) of the distilled material indicated an aliphatic H:olefinic H ratio of 5.65:1, compared to a ratio of 6.3:1 for the starting 1-deuteriocyclopentene, indicating very little, if any, deuterium scrambling.
Tricyclo[3.3.1.0^{1,5}]nonan-2-one (50). Dimethylloxosulfonium methylide (0.264 mol) was prepared in 240 ml of dry dimethylsulfoxide (distilled from calcium hydride) from 10.62 g (0.264 mol) of 60% sodium hydride in mineral oil and 58.32 g (0.264 mol) of trimethylloxosulfonium iodide according to the method of Corey and Chaykovsky, except that external cooling to 10° was necessary to keep the reaction under control during the addition of the dimethylsulfoxide. (CAUTION! In two other runs of somewhat larger scale, explosions occurred. For a superior method, see the preparation of tricyclo[4.3.1.0^{1,5}]decan-7-one, page 109.) After stirring at room temperature until the hydrogen evolution ceased, the reaction was cooled to and maintained at 10° while 29.28 g (0.300 mol) of bicyclo[3.3.0]oct-1(5)-en-2-one (42) in 60 ml of dry dimethylsulfoxide was added dropwise. The reaction was stirred 4.5 hr at room temperature, decanted into 120 ml of ice-water, and extracted thoroughly with ether. The combined ethereal extracts were washed with water and dried over anhydrous sodium sulfate. After filtration, the solution was distilled to give 24.51 g (75%) of 50 as a colorless liquid, bp 56-60° (0.25 mm).

This material was quite pure by vpc on a 6' x 1/8" F and M Hi-Pak 10% Silicone Gum Rubber SE-30 on Diatopor S column at 140°. Preparative vpc on a 9' x 1/4" 10% SE-30 on 60/80 Chrom W column at

106. The author wishes to thank Dr. R. Stepple for working out the synthesis of 50: R. Stepple and P.G. Gassman, unpublished results.
130° gave an analytical sample, $n_D^{24}$ 1.5030.


7-Hydroxymethylenetricyclo[3.3.1.0₁,₅]nonan-6-one (51). In a 250 ml, three-necked, round-bottomed flask equipped with a mechanical stirrer, reflux condenser, and argon inlet was placed 4.41 g (0.110 mol) of a 60% sodium hydride suspension in mineral oil. After washing the sodium hydride under argon with three 10-ml portions of anhydrous ether, 50 ml of anhydrous ether was added. To this mixture was added with stirring, a solution of 10.00 g (0.0735 mol) of 50, 13.60 g (0.184 mol) of ethyl formate, and 100 ml of anhydrous ether by means of a slow addition funnel over a period of 4 hr. The reaction mixture became quite pasty toward the end of the addition, and thus, an additional 50 ml of anhydrous ether was introduced. After stirring overnight, 1 ml of ethanol was added cautiously and the solution was stirred for 0.5 hr. The solution was then extracted with several portions of 0.025% sodium carbonate solution (750 ml total). The combined extracts were acidified to pH 4.5 with a 10% hydrogen chloride solution and then were immediately extracted, first with three 200-ml, then six 100-ml portions of methylene chloride. The combined organic layers were passed through a cone of anhydrous sodium sulfate and the methylene chloride removed on a rotary evaporator to
gave 9.06 g of crude material as a yellow-green solid. This material was sublimed at 60-80° (0.01 mm) to give 7.15 g (59%) of 51 as white amorphous crystals, mp 104.5-107°. An ir spectrum (CHCl₃) showed absorptions at 5.77 µ (aldehyde C = O str), 5.85µ (ketone C = O str), 5.99µ (conjugated ketone C = O str) and 6.24µ (conjugated ketone C = C str); an nmr spectrum gave absorptions at δCHCl₃ 10.34 (br s, 0.65 H), 9.70 (d, J = 13 Hz, 0.35 H), 3.56 (br m, 0.35 H), 2.56 (s, 0.65 H), 1.64-2.40 (m, 6.35 H), 1.32 (d, J = 6 Hz, 1H), and 1.05 (d, J = 6 Hz, 1H); a mass spectrum gave m/e 164. An analytical sample was prepared after two additional sublimations at 60° (0.05 mm) to give white crystals, mp 105.5-107°.


7-Diazotricyclo[3.3.1.0₁,₅]nonan-6-one (52). In a typical experiment, 70 366 mg (9.05 mmol) of a 60% sodium hydride suspension in mineral oil was placed in a 50 ml, 3-necked, round-bottomed flask equipped with a reflux condenser, mechanical stirrer, and nitrogen inlet. The mineral oil was removed by washing with several portions of anhydrous ether. To the washed sodium hydride was added 20 ml of anhydrous ether and the mixture was cooled to 0° in an ice bath. With stirring, 1.00 g (6.10 mmol) of 51 was added at such a rate as to maintain gentle hydrogen evolution. After the addition was
complete, the reaction mixture was allowed to warm to room temperature until gas evolution ceased (10-15 min). After cooling again to 0°, 1.20 g (6.10 mmol) of p-toluenesulfonyl azide in 10 ml of anhydrous ether was added dropwise in diffuse light. The reaction was subsequently stirred at room temperature in the dark for 24 hr. The reaction mixture was then filtered through Celite, taking care to keep the unreacted sodium hydride covered at all times with anhydrous ether. The filtrate was placed on a rotary evaporator and the solvent was removed to yield a bright yellow-orange oil, quite pure by nmr. An ir spectrum of $^2$ (neat) showed absorptions at 4.76 µ (CN$_2$, str) and 5.96 µ (C = 0 str); an nmr spectrum gave absorptions at $^\text{CDCl}_3$ 3.07 (s, 2H), 1.55-2.15 (m, 6H), 1.33 (d, J = 6 Hz, 1H), and 1.15 (d, J = 6 Hz, 1H). The yields from several runs ranged between 87 and 100%. The diazo-ketone was used for irradiation without further purification or characterization.

exo and endo-N,N-Dimethyl-6-carboxamidotricyclo[3.2.1.0$^3$5]octane

(53 and 54). The amides 53 and 54 were prepared using the procedure of Meinwald and Gassman. A solution of 1.48 g (9.13 mmol) of $^2$ in 220 ml of anhydrous tetrahydrofuran (distilled from lithium

aluminum hydride) was placed in a pyrex tube containing a magnetic stirring bar, and dimethyl amine was bubbled in until the volume of solution totaled 215 ml. The pyrex tube was then fitted with an argon inlet, reflux condenser, and argon exit leading to an inverted graduated cylinder for measuring nitrogen evolution. After argon was bubbled through the system for 15 minutes the irradiation was begun in a cold-room maintained at approximately -5°. Nitrogen evolution ceased after 10 days, when a total of 143 ml had been collected (70% of theory). The solvents were removed on a rotary evaporator under argon. The residue was taken up in ether, the insoluble polymers filtered off, and the solvent again removed on a rotary. All handling was accomplished under argon. Vpc of the crude mixture on a 10' x 1/8' ' 10% SE-30 on Diaport S column at 170° indicated three products. These were, in order of their elution from the column: an unidentified material, endo 54, and exo 53. Preparative vpc on a 4' x 1/4' ' 3% SE-30 on 100/120 Varaport 30 column at 120° allowed isolation of 68.2 mg (4.2%) of 54 and 153.4 mg (9.4%) of 53, each of which readily polymerized and turned dark on standing, even under argon at -10°.

Compound 54 gave an ir spectrum (neat) with absorptions at 108. Care was taken to base wash all glassware in this experiment in order to avoid any acidic surfaces which could polymerize the products.

108. A bank of eight 15-watt Sylvania 'Blacklite' fluorescent tubes was used for this purpose.
3.23μ (cyclopropane CH str) and 6.07μ (amide C = O str). An nmr spectrum of 54 showed absorptions at $\delta_{\text{CDCl}_3}$ 3.00 (s, 3H), 2.97 (s, 3H), 1.15-2.73 (m, 9H), 1.01 (d, $J = 6$ Hz, 1H), and 0.77 (d, $J = 6$ Hz, 1H).

Anal. Exact mass molecular weight, Calcd for C$_{11}$H$_{17}$NO: 179.1310. Found: 179.1307.

Compound 53 gave an ir spectrum (neat) with absorptions at 3.22μ (cyclopropane CH str), and 6.06μ (amide C = O str). An nmr spectrum of 53 showed absorptions at $\delta_{\text{CDCl}_3}$ 2.97 (s, 3H), 2.90 (s, 3H), 1.17-2.33 (m, 9H), 1.06 (d, $J = 6$ Hz, 1H), and 0.55 (d, $J = 6$ Hz, further split into a multiplet, 1H). The fragmentation pattern of a mass spectrum of 53 was very similar to that of 54.

Anal. Exact mass molecular weight, Calcd for C$_{11}$H$_{17}$NO: 179.1310. Found: 179.1307.

Product yields were determined on a 10' x 1/8' 10% SE-30 on Diaport S column at 170° using biphenyl as an internal standard. The yields were 25% of 53 and 13% of 54.

**trans-Δ^4-Tetrahydrophthaloyl Chloride (74).** In a 5l, three-necked, round-bottomed flask equipped with a mechanical stirrer, reflux condenser, and drying tube was placed 625 g (3.0 mol) of phosphorous pentachloride and 2.5 l of anhydrous ether. Under stirring, 225 g (1.5 mol) of trans-Δ^4-tetrahydrophthalic acid was added at such a rate as to maintain a gentle reflux (approximately 1 hours).
The solution was refluxed one hour on a steam bath. Distillation gave 244.5 g (79%) of \( T_4 \), bp 99° (1.2 mm) [lit.\(^{110}\) bp 114-115° (8 mm)]; infrared (neat), 5.58 (C = 0 str of acid chloride).

\( N,N,N',N' \)-Tetramethyl-trans-1,2-dicarboxamido-4-cyclohexene (137).\(^{11}\)

To 100 ml of dimethylamine was added dropwise with ice cooling a solution of 30.4 g (0.147 mol) of trans-\( \Delta^4 \)-tetrahydrophthaloyl chloride in 150 ml of absolute ether. The resulting dimethyl amine hydrochloride (22.0 g, 92%) was filtered, washed with anhydrous ether, and the filtrate distilled to yield 30.9 g (94%) of 137, bp 141° (0.17 mm). A second run using 244.5 g of \( T_4 \) gave 220.4 g (83%) of 137. The infrared of 137 (neat) gave an absorption at 6.06\( \mu \) (C = 0 str); the nmr gave \( \delta^{1} \text{CDCl}_3 \) 5.69 (2H, br m), 3.2 (1H, s), 3.12 (6H, s), 2.90 (6H, s), 2.57 (1H, br m), and 2.06 to 2.33 (4H, m); and \( n_D^{22} \) 1.5072.

\( N,N,N',N' \)-Tetramethyl-trans-1,2-bis(methylamino)-4-cyclohexene (72).

To 28.2 g (0.742 mol) of lithium aluminum hydride in 1.1 l of anhydrous ether was added dropwise, with ice cooling, 110.2 g

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(0.493 mol) of 137. The solution was refluxed overnight. After cooling in an ice-water bath, 112.8 g of 10 percent sodium hydroxide solution was added dropwise, the solution stirred for 2 hr at room temperature, and the lithium salts were filtered. The combined filtrate from two such runs was distilled to yield 148.9 g (77%) of 72, bp 69° (0.13 mm), n_D^20 1.4754 [lit. ^111 bp 78° (2.5 mm), n_D^20 1.4780]; ir (neat) 3.29 μ (C = C-H str); nmr δ _TMS^CCl_4 5.49 (2H, m), 1.77 to 2.37 (22H, m with sh s at 2.13).

4,5-Dimethylenecyclohexene (73). The method of Garrett and Fonkin^78a,112 was used to make 73. In a 1 l, three-necked, round-bottomed flask equipped with a reflux condenser, addition funnel, and magnetic stirring bar was placed 80.0 g (0.406 mol) of 72 in 160 ml of methanol. To the solution was added 75 ml of 30 percent hydrogen peroxide under ice cooling and stirring over a period of 4 hours. Two hours after the ice-water bath was removed, the solution came to reflux and was therefore again cooled in an ice-water bath for several more hr. The solution was then stirred at room temperature. After 2½ hr, the solution was tested for free amine by adding one drop of the reaction mixture to one drop of 1% phenolphthalein in ethanol. A positive test (free amine) was

evident by the purple color produced. The solution was cooled, and 40 ml of 30% hydrogen peroxide was added as before. After 48 hours, 20 ml of additional 30% hydrogen peroxide was added. After 72 hours, the phenolphthalein solution remained colorless, indicating complete oxidation. Platinum black (5-10 mg in 0.5 ml water) was added and the reaction stirred until the oxygen evolution stopped. The solvent was removed on a rotary evaporator to yield a very thick, viscous liquid which was used for pyrolysis without further purification. A 250-ml, round-bottomed flask containing a magnetic stirring bar and the di-N-oxide was equipped with a transfer tube connected to a 500-ml three-necked, round-bottomed flask immersed in a dry-ice-isopropanol bath and equipped with a stopper and a tube leading to additional traps and to a vacuum pump. The viscous liquid was heated slowly under vacuum with as much stirring as possible. The material solidified at 90° (0.2 mm) and decomposed at ~140° (0.2 mm) to give $\mathcal{T}_2$, which was collected in the trap. The collected material was taken up in ether, washed with water, and distilled. All glassware in this and the following experiment had been previously base-washed (10% methanolic potassium hydroxide). The yield was 17.2 g (40%) of $\mathcal{T}_2$, bp 70-75° (60 mm) [lit. bp 56-60° (59 mm)$^{113}$ and 90° (100 mm)$^{114}$], pure by vapor phase chromatography

$^{114}$ C.S. Marvel and E.E. Ryder, Jr., ibid., 77, 66 (1955).
Bicyclo[4.2.0]octa-1(6),3-diene (68). In a photolysis vessel equipped with a nitrogen inlet, a reflux condenser, and quartz immersion well, 17.2 g (0.162 mol) of 72 was irradiated78 as described by Fonkin and Garrett.78a The resulting mixture was distilled to yield 7.44 g (43%) of 68, bp 68° (20 mm), n D 1.4978.

An ir spectrum (neat) showed absorptions at 3.27μ (C = C-H str) and 6.12μ (C = C str); an nmr spectrum showed δCCL4 5.69 (2H, s) and 2.43 (8H, s).

Reaction of 68 with Diazomethane. In a typical experiment, 2.00 g (18.8 mmol) of 68 was put in 20 ml of anhydrous ether (distilled from lithium aluminum hydride) containing 0.25 g of freshly purified cuprous chloride.115 The reaction was carried out behind a safety shield in a 25 x 200 mm test tube containing a magnetic stirring bar and a two-holed neoprene stopper. In one hole was placed a reflux condenser (no ground-glass joints) with a potassium hydroxide drying tube. In the other hole was placed a glass tube for introducing the diazomethane. All glassware was scratch free. Diazomethane, generated in a separate vessel from the action of 90 ml of 50% potassium hydroxide solution on 150 ml of ether

containing 10 g of N-methyl-N-nitrosoourea at 0°, was passed through a potassium hydroxide drying tower and was bubbled continuously into the vigorously stirred reaction solution (kept at 0° with an ice water bath), with a slow stream of nitrogen. Approximately every 4 hr, 0.25 g of fresh cuprous chloride was added to the solution and the generator recharged. The solution, which became black as the reaction progressed, was monitored by vapor phase chromatography using a 10' x 1/8' 10% SE-30 on Diaport S column at 110°. Initially, tricyclo[4.2.1.01,6]non-3-ene (20) and tricyclo[5.2.01,7.03,5]non-1(7)-ene (T5) were formed in roughly equal amounts (up to an estimated 50:25:25 ratio of 68:20:T5). Longer reaction times led to the formation of endo-tetracyclo-
[5.2.1.01,7.03,5]decane (T6) and in smaller amounts, exo-tetra-
cyclo[6.2.1.01,7.03,5]decane (T7). At this point, the amount of 20 began to decrease, while T5 increased slowly. The reaction could then be stopped when the desired mixture of isomers was obtained (in this example, after 16.75 hr).\textsuperscript{116} Distillation gave 1.49 g of a colorless mixture of 68, 20, T5, T6, and T7, bp 64-70° (8-22 mm). In another run, after an estimated 50% conversion,

\begin{footnotesize}
\textsuperscript{116} The amount of time necessary to achieve a certain isomer ratio varied with the dryness of the solvent and the activity of the catalyst. In general, however, about 12 to 15 hr was necessary to achieve 50% conversion.
\end{footnotesize}
vpc yields were determined using a 10' x \( \frac{1}{8} \)" 10% SE-30 on Diaport S column at 80° with methylbenzoate as internal standard. The results showed 68, 20, 75, and 76 were formed in yields of 37, 15, 18, and \( \sim 2.5\% \), respectively, along with a trace of 77. Another run after an estimated 70% conversion gave yields of 19, 13, 26, \( \sim 6 \), and \( \sim 1\% \) for 68, 20, 75, 76, and 77, respectively. Preparative vpc on a 9' x \( \frac{1}{4} \)" 10% SE-30 on 60/80 Chrom W column at 90° allowed isolation of each component of the reaction mixture. The first component to be collected was identical to the starting material 68. The remaining compounds are listed below in the order of their elution from the column:

**Tricyclo[4.2.1.0\(^1\).8\]non-3-ene (20).** The ir spectrum (neat) showed absorances at 3.25\( \mu \) (C = C-H str and/or cyclopropyl str) and 6.05\( \mu \) (C = C str); the nmr spectrum (CDCl\(_3\)) was the same as reported by Warner and LaRose\(^{36}\) (see Table 1).

**Tricyclo[5.2.0\(^1\).7.0\(^3\).5\]non-1(7)-ene (75).** The ir spectrum (neat) gave an absorption at 3.30\( \mu \) (cyclopropyl CH str); the nmr spectrum (see Table 1) gave \( \delta_{\text{CDCl}_3}^{\text{CHCl}_3} 2.05-2.54 \) (8H, m), 0.44-1.24 (3H, br m) in which could clearly be seen a broad multiplet centered around 0.94 (2H, cyclopropyl methine protons, H\(_6\)) and around 0.63 (1H, H\(_a\) cyclopropyl hydrogen), and 0.11 (1H, m, shielded cyclopropyl proton, H\(_b\)); \( n_D^{22} 1.5003 \). Anal. Calcd for C\(_9\)H\(_{12}\): C, 89.94; H, 10.06. Found: C, 89.65; H, 10.16.
endo-Tetracyclo[5.2.1.0\(^1\)7.0\(^3\)5]decane (76). The ir spectrum (neat) was very simple, showing no \(\mathrm{C} = \mathrm{C}\) str around 6.1\(\mu\); the nmr spectrum (see Table 1) showed \(\delta_{\text{CDCl}_3} \) 1.86-1.98 (4H, m, methylene protons on cyclohexyl ring, \(\mathrm{H}_e\)), 1.51-1.86 (4H, m, methylene protons on cyclobutyl ring, \(\mathrm{H}_c\) and \(\mathrm{H}_d\)), 0.85 (1H, d, \(J = 4.5\) Hz, geminal coupling of the \(\mathrm{C}_{10}\) cyclopropyl proton \(\text{syn}\) to cyclobutyl ring, \(\mathrm{H}_b\)), 0.69 (3H, m, 2 cyclopropyl methine protons, \(\mathrm{H}_h\), and \(\mathrm{C}_4\) cyclopropyl proton \(\text{anti}\) to the cyclohexyl ring, \(\mathrm{H}_e\)), 0.28 [1H, d of t, \(J = 4.5\) Hz (geminal coupling) and \(J = 2.0\) Hz (W coupling with the cyclobutyl protons \(\text{anti}\) to the \(\mathrm{C}_1, \mathrm{C}_7, \mathrm{C}_{10}\) cyclopropane ring, \(\mathrm{H}_d\)) for the \(\mathrm{C}_{10}\) cyclopropyl proton \(\text{syn}\) to the cyclohexyl ring, \(\mathrm{H}_a\)], and 0.08 (1H, m, \(\mathrm{C}_4\) proton, \(\mathrm{H}_f\), \(\text{syn}\) to cyclohexyl ring); \(n_D^{21} \) 1.4950.

Anal. Exact mass molecular weight, Calcd for \(\text{C}_{10}\text{H}_{14}: 134.1095\). Found: 134.1097.

exo-Tetracyclo[5.2.1.0\(^1\)7.0\(^3\)5]decane (77). The ir spectrum (neat) was very simple, showing no \(\mathrm{C} = \mathrm{C}\) str around 6.1\(\mu\), and was nearly identical to that of 76 except for a few small changes in the position and intensity of bands in the fingerprint region. The nmr spectrum (see Table 1) showed \(\delta_{\text{CDCl}_3} \) 2.26 (2H, d of d of d, for the two cyclohexyl methylene protons, \(\mathrm{H}_f\), \(\text{anti}\) to the two cyclopropyl rings. Models show these \(\text{anti}\) protons to be in the plane of both cyclopropyl rings, and therefore, they would be expected to be deshielded relative to the \(\text{syn}\) protons.\(^{30}\) Each of these
anti protons is split into a doublet, $J = 1.4 \text{ Hz}$, geminal coupling, which is further split into doublets, $J = 5 \text{ Hz}$, vicinal coupling. The pattern is further split into doublets, $J = 2 \text{ Hz}$, by $W$-coupling with $H_h$. Other absorptions occur at $\delta 1.56-2.07$ (6H, m, 4 cyclobutyl protons, $H_c$ and $H_d$; and 2 cyclohexyl methylene protons 
\text{sym} to the two cyclopropyl rings, $H_e$), 0.82-1.09 (2H, m, cyclopropyl methine protons, $H_g$), and 0.76 (1H, d, $J = 4.5 \text{ Hz}$, geminal coupling of C_{10} cyclopropyl proton 
\text{syn} to cyclobutyl ring, $H_b$). Centered around 0.57 $\delta$ is the C_{4} cyclopropyl proton \text{anti} to the cyclohexane ring, $H_h$. It consists of a triplet, $J = 9 \text{ Hz}$, vicinal 
coupling, further split into a doublet, $J = 5 \text{ Hz}$, geminal coupling. It is further split by long range $W$-coupling into a complex pattern. At 0.22 $\delta$ is a doublet of triplets for the C_{10} cyclopropyl proton 
\text{syn} to the cyclohexyl ring, $H_a$ ($J = 4.5 \text{ Hz}$, vincinal coupling, and 
$J = 2.0 \text{ Hz}$, $W$ coupling with the two cyclobutyl protons \text{anti} to the C_{1}, C_{7}, C_{10} cyclopropyl ring). Finally, at -0.22 $\delta$ is a doublet of triplets for the C_{4} cyclopropyl proton \text{syn} to the cyclohexyl ring, $H_f$ ($J = 5 \text{ Hz}$, geminal coupling, and $J = 5.0 \text{ Hz}$, vicinal coupling).

\textbf{Anal.} Exact mass molecular weight, Calcd for C_{10}H_{14}: 134.1095
\text{Found: 134.1094.}

All the new compounds isolated (20, 75, 76, and 77) were thermally stable (could be distilled) and showed no appreciable reaction on standing in the presence of oxygen.
Tricyclo[4.3.1.0\(^1\).6]decan-7-one (79). Method A: Into a 3 ℓ photolysis vessel equipped with a water cooled pyrex immersion well, argon inlet, reflux condenser, and magnetic stirring bar was placed 2.0 ℓ of dry t-butanol (distilled from sodium) and 6.0 g (0.040 mol) of bicyclo[4.4.0]dec-1, (6)-en-3-one (80).\(^{90,117}\)

After flushing with argon for 10 min, irradiation was begun\(^{73}\) under vigorous stirring and a slow stream of argon. (CAUTION: care should be taken that the solvent does not freeze and plug the condenser).

The progress of the reaction was monitored by vpc on a 5′6″ x 1/8″ Carbowax 20 M on Chrom W column at 170° by following the disappearance of 80 and the appearance of 79. The reaction was stopped after 70 hr and most of the t-butanol removed by distillation at atmospheric pressure through a 12′′ vacuum jacketed Vigreaux column. The residue (~50 ml) was poured into 250 ml of ether and was washed with four 100-ml portions of water, 150 ml of saturated sodium chloride solution, and dried over anhydrous magnesium sulfate. After filtration, distillation yielded 4.62 g (77%) of a colorless liquid, bp 48-50° (0.15 mm) which was shown by vpc to consist of a mixture of 80, 79, and some unidentified impurities. Chromatography on 300 g of silica gel (MCB No. 923) with 4:96 ethyl acetate:hexane as eluent gave first the unidentified

impurities, then \( \text{80} \) (0.96 g, 16\% recovery), then a mixture of \( \text{80} \) and \( \text{79} \) (0.32 g, 7\%), and finally, \( \text{79} \). This last fraction was distilled to give 1.89 g (31\%) of \( \text{79} \), bp 49-51° (0.15 mm). The infrared and nmr spectrum of \( \text{79} \) were as described by Williams and Ziffer.83

**Method B:** Into a 1 l round-bottomed flask equipped with a mechanical stirrer, argon inlet, and reflux condenser was placed 350 ml of dry dimethylsulfoxide (distilled from calcium hydride) and 5.0 g of 57\% sodium hydride in mineral oil. While stirring under argon, 25 g of trimethyloxosulfonium iodide was added portionwise at such a rate that gentle hydrogen evolution was maintained. The reaction was cooled externally with an ice-water bath occasionally in such a manner as to maintain the temperature between 20° and 25°. When the addition was complete, an additional 5.0 g of 57\% sodium hydride in mineral oil was added, followed again by 25 g of trimethyloxosulfonium iodide. This process was repeated until a total of 23.2 g (0.55 mol) of 57\% sodium hydride and 121 g (0.55 mol) of trimethyloxosulfonium iodide had been added.

(\text{CAUTION!} When the method of Corey and Chaykovsky83 was used, i.e., when dry dimethylsulfoxide was added to a powdered mixture of sodium hydride and trimethyloxosulfonium iodide, on at least two occasions, an explosion ensued in which a large volume of hydrogen gas was evolved, fortunately, with no fire. The present
method gives product yields identical to those obtained by the method of Corey and Chaykovsky, only with a great deal more safety. After the hydrogen evolution ceased, the reaction was cooled to and maintained at 10° while 68.0 g (0.50 mol) of bicyclo[4.3.0]-non-1(6)-en-2-one \( ^{81} \) in 150 ml of dry dimethylsulfoxide was added dropwise. The reaction was subsequently stirred overnight at room temperature and poured onto a mixture of 500 g of ice and water. The aqueous layer was extracted with seven 400-ml portions of ether and the combined ethereal extracts were washed with two 1-l portions of water, 1 l of saturated sodium chloride solution, and dried over anhydrous sodium sulfate. The drying agent was removed by filtration and the ether removed via a rotary evaporator. Distillation of the remaining liquid from two such runs gave 125.3 g (84%) of a mixture, bp 62-75° (0.45 mm). The components of the mixture were separated via column chromatography, using a 3' x 3' dia column packed with 750 g of MCB grade 923 silica gel for each 35.0 g of the mixture. Ethyl acetate:hexane (4:96) was used as eluent. The first fraction was two impurities, followed by 79, and then 80. After all of the mixture was chromatographed, the combined fractions of 79 were distilled to give 53.9 g (36%) of a colorless liquid, bp 60-65° (0.2 mm), \( n_D^{24} = 1.5060 \) which was in all ways identical to 79 prepared by Method A.

exo-Tricyclo[4.3.1.0\(^{16}\)]decan-7-ol (82). Into a 25 ml one-necked,
round-bottomed flask equipped with a magnetic stirring bar, reflux condenser, and argon inlet was placed 0.13 g (3.4 mmol) of lithium aluminum hydride in 10 ml of anhydrous diethylether. To this mixture was added dropwise, with stirring, 1.00 g (6.7 mmol) of tricyclo[4.3.1.01,6]decan-7-one in 5 ml of anhydrous ether. After refluxing overnight under argon, the reaction was cooled in an ice bath and 0.52 g of 10% sodium hydroxide solution was added dropwise. The resulting mixture was stirred for an additional two hours at room temperature, filtered, and the filtrate concentrated on a rotary evaporator. Distillation yielded 0.99 g (98%) of a colorless liquid, bp 55° (0.1 mm), estimated by gas chromatography on a 6' x 1/8" 15% Carbowax 20M on Chrom W column at 190° to consist of ca. 95% of 82 and 5% of the endo alcohol 83. The ir spectrum of 82 (neat) gave the characteristic absorbance at 2.98 μ (OH str); the nmr spectrum showed δCDCl3 4.01 (tr t, 1H), 2.37 (s, 1H), 0.82 to 2.19 (br m, 12H), 0.68 (d, 1H), and 0.10 (d, 1H).


exo-7-Tricyclo[4.3.1.01,6]decanyl p-Nitrobenzoate (84). To a solution containing 2.69 g (14.5 mmol) of p-nitrobenzoyl chloride in 20 ml of anhydrous pyridine was added dropwise under ice cooling and with magnetic stirring, 2.00 g (13.2 mmol) of 82. After
standing in a refrigerator for 3 days, the reaction mixture was poured onto crushed ice and 200 ml of cold 10% hydrochloric acid was added cautiously, while keeping the solution cold. The reaction mixture was extracted with six 100-ml portions of ether. The combined ethereal extracts were washed successively with three 100-ml portions of 10% hydrochloric acid, two 300-ml portions of 20% sodium hydroxide, 300 ml of water, and 300 ml of saturated salt solution. After drying over anhydrous sodium sulfate, filtering, and concentrating on a rotary evaporator, the crude p-nitrobenzoate was recrystallized from pentane at low temperature (-78 °) to yield 3.43 g (86%) of a white powder, mp 70-72 °. The infrared spectrum of 8 4 \( (C\text{Cl}_4) \) gave characteristic absorbances at 5.78 μ (C = O str), 6.21 μ (C = C str), 6.54 μ (NO2 str), and 7.85 μ (CO str); the nmr spectrum showed 8 \( C\text{Cl}_4 \) 8.15 (s, 4H), 5.40 (br t, 1H), 0.95 to 2.44 (m, 12H), 0.87 (d, 1H) and 0.33 (d, 1H).

Anal. Calcd for C17H19NO4: C, 67.76; H, 6.35; N, 4.65. Found: C, 67.68; H, 6.43; N, 4.55.

endo-Tricyclo[4.3.1.01,6]decan-7-ol (83). In a 500 ml, three-necked, round-bottomed flask containing a magnetic stirring bar was placed 200 ml of isopropyl alcohol, 3.00 g (20 mmol) of tricyclo[4.3.1.01,6]decan-7-one, and 8.16 g (44 mmol) of aluminum isopropoxide. The flask was equipped with an addition funnel, glass stopper, and 10 cm vacuum jacketed Vigreax takeoff con-
denser, and brought to a gentle reflux. The acetone-isopropanol mixture was distilled slowly, adding sufficient isopropyl alcohol dropwise to maintain the reaction mixture at a constant volume. The course of the reaction was followed by vpc on a 6' x 1/8' 19% Carbowax 20M on Chrom W column at 190°C. The reaction was stopped after 3 1/4 hours, when an approximate ratio of >80% desired endo alcohol, <10% exo alcohol, and <10% starting ketone was achieved. Control experiments showed that further reaction times allowed additional equilibration of the exo and endo isomers to a roughly 50-50 mixture. The mixture was cooled, poured into 400 ml of ether, and washed thoroughly with 400 ml of 5% sodium hydroxide solution. The aqueous layer was additionally extracted with two 200-ml portions of ether, and the combined ethereal solutions were washed with water, saturated salt solution, and dried over anhydrous sodium sulfate. Filtration, concentration on a rotary evaporator (bath temperature 35°C), and distillation yielded 2.84 g (93%) of a colorless liquid, bp 63°C (0.3 mm) containing the aforementioned ratio of three isomers. The infrared of (neat) showed the characteristic absorbance at 2.91 μ (CH str); the nmr spectrum showed δCHCl₃ to 4.02 (m, 1H, methine adjacent to hydroxyl) and 0.24 (s, 2H, cyclopropyl protons). An analytical sample, nD 1.5043, was prepared by preparative vapor phase chromatography on an 8' x 3/8' 15% Carbowax 1500 3% KOH on 60/80 Chrom G column at 185°C.
endo-7-Tricyclo[4.3.1.0^(1,6)]decyl p-Nitrobenzoate (85). To a solution containing 3.34 g (18.1 mmol) of p-nitrobenzoyl chloride in 25 ml of anhydrous pyridine was added dropwise under ice cooling and magnetic stirring, 2.50 g (16.5 mmol) of endo 85 in 25 ml of anhydrous pyridine. After standing in the refrigerator for 3 days, the reaction mixture was poured onto crushed ice and 200 ml of 10% hydrochloric acid (cold) was added cautiously. It was subsequently extracted with six 100-ml portions of ether. The combined ethereal extracts were washed with three 100-ml portions of 10% hydrochloric acid, two 300-ml portions of 20% sodium hydroxide, 300 ml of water, and 300 ml of saturated salt solution. After drying over anhydrous sodium sulfate, filtration, and concentration with a rotary evaporator, the crude p-nitrobenzoate was recrystallized from pentane at low temperature (−78 °) to give 4.14 g (82%) of a white powder, mp 96.5-98 °. The infrared of 85 (CCl4) gave characteristic adsorptions at 5.78 μ (C = 0 str), 6.21 μ (C = C str), 6.53 μ (NO2 str), and 7.85 μ (CO str); the nmr spectrum showed δCHCl3 8.34 (s, 4H), 5.58 (br m, 1H), 0.41 to 2.11 (br m, 12H), and 0.18 (m, 2H).

Anal. Calcd for C17H19NO4: C, 67.76; H, 6.36; N, 4.65. Found: C, 67.73; H, 6.26; N, 4.65.
**Kinetics for 
Reagents. A stock solution of 70:30 (vol/vol) acetone-water was used as solvent. Baker reagent grade acetone was used.

Procedure. Approximately 59 mg of the p-nitrobenzoate (about 0.02 M) was dissolved in the 70% aqueous acetone in a 10 ml volumetric flask. Aliquots of 1.25 ml were transferred to Carius tubes which had previously been flushed with argon. The sealed ampoules were placed in a constant temperature bath and removed after 0.25, 0.5, 0.75, 1.0, 1.5, 2.0, 2.5, and 10.0 half-lives. They were immediately quenched in an ice-water bath. After warming to room temperature, the ampoules were opened and exactly 1 ml withdrawn with a constant volume automatic pipette. This was diluted to 10 ml with solvent and titrated with a Methrohm Herisan potentiograph, Model E 426, using 0.0108 N sodium hydroxide solution as titrant. The endpoint was taken to be at pH 8. Measured infinity titres agreed with calculated values. All runs gave linear pseudo first-order plots through 2.5 half-lives. Rate constants were calculated using a Wang Electronic Calculator, Model 360 K.

Products:

Products from Solvolysis of \textit{exo-Tricyclo[4.3.1.0^{1,6}]decan-7-ol}

\textit{p-Nitrobenzoate (8\#)}. Into 20 ml of 70% aqueous acetone was placed
226 mg (0.75 mmol) of $\text{8}_{4}$ in a Carius tube. After sealing under argon, the tube was allowed to stand at $85^\circ$ for two days. After cooling, the tube was opened and the contents poured into 80 ml of ether. The ether layer was washed with three 20 ml portions of saturated sodium bicarbonate solution, 40 ml of saturated sodium chloride solution, and dried over anhydrous sodium sulfate. After filtering and concentrating on a rotary evaporator, four products were observed by vapor-phase chromatography. These were, in the order of their elution (relative percentages shown in brackets): endo-tricyclo[4.3.1.0$^{1,6}$]decan-7-ol ($8_{3}$, 8%), exo-tricyclo[4.3.1.0$^{1,6}$]decan-1-ol ($8_{2}$, 8%), bicyclo[4.3.1]dec-6-en-1-ol ($10_{6}$, 52%), and bicyclo[4.4.0]dec-1, (6)-en-3-ol ($10_{7}$, 33%). Preparative vpc on a 10' x 3/8'' 15% Carbowax 1500 3% KOH on 60/80 Chrom G column at $185^\circ$ allowed isolation of the two major products, $10_{6}$ and $10_{7}$.

Compound $10_{7}$, initially collected as a liquid, $n_D^{23}$ 1.5173 [lit. $n_D^{27}$ 1.5180], eventually solidified to give white crystals, mp 42.43\(^{\circ}\). This compound was identical by ir, nmr, mass spectra, and vpc retention times, to an independently synthesized sample of $10_{7}$.

Compound $10_{6}$ was collected as a white solid, mp 73.5-74\(^{\circ}\).

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118. A 10' x 3/8'' 10% Carbowax 20M KOH on 60/80 Chrom W column at 190\(^{\circ}\) was used for this purpose.
An ir spectrum (CCl₄) gave absorptions at 2.82µ (free OH str), 2.9 (H bonded OH), 3.27µ (olefinic CH str), 6.05µ (olefinic CH bend), and 9.46µ (CO str); an nmr spectrum showed absorptions at 6°TMS 5.5 (br t, J = 5.5 Hz, 1H), 1.87-2.34 (m, 7H, with a strong absorption at 2.05, and another, s, 1H, at 2.11 which is variable and readily exchanges with deuterium oxide), and 1.09-1.87 (m, 6H); a mass spectrum gave m/z 152. An analytical sample, mp 73.5-74°C, was collected by a second preparative vpc collection on the aforementioned column.

Anal. Calcd for C₁₀H₁₆O: C, 78.89; H, 10.59. Found: C, 78.79; H, 10.50.

When 8₄ was subjected to the solvolysis conditions at 85°C for 400 sec (approximately 10% reaction), vpc showed after preparative thin layer chromatography indicated ca, 4, 25, 70, and 1% of 8₂, 8₂, 106, and 107, respectively. When 8₄ was subjected to the solvolysis conditions for 45,200 sec (10 half-lives, ~100% reaction), vpc showed 8₂, 8₂, 106, and 107 present in the amounts of 7, 5, 59, and 20%, respectively, as determined against biphenyl as an internal standard.

Products from Solvolysis of endo-1,3,1,0-Tricyclo[4.3.1.0₁₈]decan-7-ol p-Nitrobenzoate (8₅). Into 20 ml of 70% aqueous acetone was placed 226 mg (0.75 mmol) of 8₅ in a Carius tube. After sealing under argon, the tube was allowed to stand at 85°C for two days. After
workup (same as for $8_4$), vpc$^{118}$ showed ca. 5, 7, 56, and 32% of $8_3$, $8_2$, 106, and 107, respectively. Preparative vapor phase chromatography on a $10' \times \frac{3}{8}'$ 15% Carbowax 1500 3% KOH on 60/80 Chrom G column at 185° allowed isolation of 106 and 107. These were in all respects identical to the products of the exo isomer, $8_4$. When $8_5$ was subjected to the solvolysis conditions at 85° for 800 sec (approximately 10% reaction), vpc$^{118}$ after preparative thin layer chromatography indicated ca. <1, 30, 68, and 0% of $8_3$, $8_2$, 106, and 107, respectively. When $8_5$ was subjected to the solvolysis conditions for 87,800 sec (10 half-lives, ~100% reaction), vpc$^{118}$ showed $8_3$, $8_2$, 106, and 107 present in the amounts of 6, 8, 63, and 14, respectively, as determined against biphenyl as an internal standard.

Stability of exo and endo-Tricyclo[4.3.1.0$^{1,8}$]decan-7-ol ($8_2$ and $8_3$) to Solvolysis Conditions. Into a Carium tube flushed with argon was placed 6.9 mg of $8_2$, 7.1 mg of p-nitrobenzoic acid, and 1.2 mg of 70% aqueous acetone. After sealing under argon, the tube was heated to 85° for 24 hours. After cooling, the contents were poured into 5 ml of ether and were washed with saturated sodium bicarbonate solution and saturated sodium chloride solution. Vapor phase chromatography$^{118}$ showed ca. 8, 12, 71, and 10% of $8_3$, $8_2$, 106, and 107, respectively.

When 6.0 mg of $8_3$, 6.2 mg of p-nitrobenzoic acid and 1.2 ml
of 70% aqueous acetone were treated as above for 24 hours, vpc\textsuperscript{118} showed ca. 15, 15, 55, and 15% of 82, 82, 106, and 107, respectively.

Hydrogenation of Bicyclo[4.3.1]dec-6-en-1-ol (106). To 30.6 mg (0.201 mmol) of 106 in 20 ml of anhydrous ether was added 10 mg of platinum oxide. After hydrogenation at one atmosphere pressure for two hours, the solution was filtered through Celite, concentrated on a rotary evaporator, and vacuum transferred to give a white solid, mp 113-119°. This was sublimed at 70° (15 mm) to give 24.4 mg (79%) of bicyclo[4.3.1]decan-1-ol (138) as a fine white powder, mp 120-126° (lit.\textsuperscript{92} mp 140°). Neither column chromatography on neutral alumina, re-sublimation, recrystallization from pentane, or preparative vpc on a 10' x 3/8' Carbowax 1500 3% KOH on 60/80 Chrom G column at 185° served to raise or sharpen the melting point of 138. Compound 138 was completely homogeneous by vapor phase chromatography on both a 10' x 1/8' 10% Carbowax 20M KOH on 60/80 Chrom W column at 190° and a 10' x 1/8' 10% SE-30 on Diaport S column at 150°. An ir spectrum (CCl\textsubscript{4}) was very simple, giving rise to only five major absorptions: 2.72μ (free OH str), 2.91μ (br, H bonded OH str), 3.45μ (br, CH bend), 6.85μ (m, methylene CH scissor), and 9.63μ (s, CO str) [lit.\textsuperscript{92} (film) 2.95μ (br) and 9.61μ]. An nmr spectrum gave \textsuperscript{CDCl\textsubscript{3}}\textsuperscript{\textsubscript{1HMS}} 1.30-1.70 (m, with sh s at 1.49 which readily exchanges with deuterium
oxide) [lit. 6\textsuperscript{32}\textsuperscript{6} \text{CDCl}_3 1.3-1.7]. In addition, two small, broad absorptions, perhaps due to an impurity, were observed at 81.91 and 2.03.

**Anal.** Exact mass molecular weight, Calcd for C\textsubscript{10}H\textsubscript{18}O: 154.1358. Found: 154.1359.

\text{Bicyclo[4.4.0]dec-1(6)-en-3-ol (107)\textsuperscript{90}} \quad \text{Bicyclo[4.4.0]dec-1(6)-en-3-one (80) (1.00 g, 6.67 mmol), and lithium aluminum hydride, (0.125 g, 3.33 mmol), were reacted in 20 mL of anhydrous ether to yield after workup, 0.82 g (82\%) of a very viscous clear oil, bp 79-81\textsuperscript{0} (0.17 mm) [lit.\textsuperscript{80} bp 81-86\textsuperscript{0} (0.2-0.5 mm)] which solidified on standing to give waxy white crystals, mp 39-41\textsuperscript{0}. The \textit{ir} (\textit{CCl}_4) and \textit{nmr} (\textit{CCl}_4-TMS) were as reported.\textsuperscript{90}

8-Hydroxymethylenetricyclo[4.3.1.0\textsuperscript{2,6}]decan-7-one (139). In a 1-L, three-necked, round-bottomed flask, equipped with a mechanical stirrer, reflux condenser, and argon inlet was placed 8.42 g (0.200 mol) of a 57\% sodium hydride suspension in mineral oil. After washing the sodium hydride under argon with three 20-mL portions of anhydrous ether, 100 mL of anhydrous ether was added. To this mixture was added with stirring a solution of 20.00 g (0.133 mol) of tricyclo[4.3.1.0\textsuperscript{2,6}]decan-7-one, 24.80 g (0.336 mol) of ethyl formate, and 250 mL of anhydrous ether by means of an addition funnel over a period of 15 hr (drop rate of 8-10 drops per min). After stirring an additional 24 hr, 3 mL of ethanol was added.
cautiously and the solution was stirred ½ hr. The solution was
extracted with one 600-ml portion, then four 200-ml portions of
0.025% sodium carbonate solution. The combined extracts were
acidified to pH 4 with a 10% hydrochloric acid solution and
immediately extracted, first with one 600-ml portion, and then
two 400-ml portions of methylene chloride. Concentration on a
rotary evaporator followed by a molecular distillation (pot
temperature ~80° at 0.01 mm) gave 17.41 g (73%) of a yellow liquid
which slowly crystallized on standing. The yellow amorphous crys-
tals thus obtained were identical by ir, nmr and chemical pro-
properties to white, amorphous crystals which could be obtained by
very slow and tedious sublimation. An ir spectrum (CCl₄) showed
absorptions at 5.74µ (aldehyde C = 0 str), 5.81µ (ketone C = 0
str), 5.96µ (conjugated ketone C = 0 str), and 6.18µ (conjugated
C = C str); an nmr spectrum showed δ(CCl₄) 11.02 (0.75 H, m, enol
CH proton), 9.67 (0.25 H, d, J = 11 Hz, aldehyde proton), 6.94
(0.75 H, m, vinyl proton of enol), and 0.80-3.50 (12.25 H, m).
An analytical sample was obtained from a re-sublimed sample
(softening point at 65°, mp 77-79°).

Anal. Calcd for C₁₁H₁₄O₂: C, 74.13; H, 7.92. Found:
C, 74.18; H, 7.88.

8-Diazotricyclo[4.3.1.0₁⁴]decan-7-one (57). In a typical ex-
periment, ¹⁷¹⁸ 1.42 g (0.0336 mol) of a 57% sodium hydride suspen-
sion in mineral oil was placed in a 250-ml, three-necked, round-bottomed flask equipped with a reflux condenser, mechanical stirrer and argon inlet. The mineral oil was removed by washing with several portions of anhydrous ether. To the washed sodium hydride was added 80 ml of anhydrous ether and the mixture was cooled to 0° in an ice bath. With stirring, 4.00 g (0.0224 mol) of 8-hydroxymethylenetricyclo[4.3.1.0\(^1\).0\(^1\).8]decan-7-one was added at such a rate as to maintain gentle hydrogen evolution. After the addition was complete, the reaction mixture was allowed to warm to room temperature until the gas evolution ceased (10-15 min). After cooling again to 0°, 4.44 g (0.0224 mol) of p-toluenesulfonyl azide in 40 ml of anhydrous ether was added dropwise in diffuse light. The reaction was subsequently stirred at room temperature in the dark. The progress of the reaction was followed by ir, noting the disappearance of the azide band at 4.65μ and the appearance of the diazo band at 4.75μ. After 5 days, the reaction was complete. The solution was filtered through Celite, taking care to keep active sodium hydride covered at all times with anhydrous ether. The filtrate was placed on a rotary evaporator and the solvent was removed to yield a yellow crystalline solid, 3.45 g (87.5%), mp 63.5-66.5°. Sublimation behind a safety shield (pot temperature 55° at 0.01 mm) of a few crystals gave yellow needles, mp 67-68.5°. An ir (CCl\(_4\)) showed absorptions at 4.75μ (≥CN\(_2\), str), and 5.9μ (C = O, str); an nmr showed δ\(_{\text{TMS}}\) 2.68-3.36 (2H, m
centered at 3.02), and 0.82-2.68 (10H, br, m with two superimposed cyclopropyl proton doublets at 0.94 and 1.04, J = 5 Hz). The yields from several runs ranged between 87 and 100\%. The diazo-ketone was used for irradiation without further purification or characterization.

**Irradiation of 8-Diazotricyclo[4.3.1.0^1,8]decan-7-one (57).** Into a 1-l photolysis vessel equipped with a water cooled pyrex immersion well, nitrogen inlet, reflux condenser and magnetic stirring bar was placed 6.93 g (0.0394 mol) of 8-diazotricyclo[4.3.1.0^1,8]-decan-7-one in one liter of methanol, which has been freshly distilled from magnesium methoxide. Nitrogen was bubbled through the solution for 15 minutes and the irradiation was begun. The reaction was monitored by following nitrogen evolution. After 17.5 hr, nitrogen evolution ceased, after 690 ml had been collected. The irradiation was stopped and the methanol removed on a rotary evaporator. Distillation of the residue yielded 3.67 g (52\%), bp 70-78° (0.50 mm) of a clear liquid. Vapor phase chromatography on a 10' x 1/8" 10% SE-30 on Diaport S column at 160° indicated two major products, in a ratio of approximately 25:75, corresponding to endo-7-carbomethoxytricyclo[4.2.1.0^1,8]nonane and exo-7-carbomethoxytricyclo[4.2.1.0^1,8]nonane, respectively. In addition, two minor components were present in the amount of about 5% each. Preparative vapor phase chromatography on an 8' x 1/4" 20% DC
Silicone on 60/80 Chrom P at 160° allowed isolation of pure exo-7-carbamethoxytricyclo[4.2.1.0^1,6]nonane (95), and the longer retention time impurity (110). Pure endo-7-carbamethoxytricyclo- [4.2.1.0^1,6]nonane (108) and the shorter retention time impurity (140) could not be separated from each other. An infrared spectrum of 95 (neat) gave a characteristic absorbance at 5.73 μ (C = 0 str); an nmr spectrum showed δ_{TMS}^{CCl_4} 3.55 (s, 3H), 2.72 to 3.08 (m, 1H), 0.89 to 2.12 (br, m, 11H), and 0.36 (doublet, J = 5.5 Hz, further split into complex multiplets, 1H). Additionally, a doublet, J = 5.5 Hz, at 1.008, was clearly superimposed on other proton absorptions.

An infrared spectrum (CCl₄) of 110 gave an absorption at 5.80 μ (C = 0 str); and nmr showed δ_{TMS}^{CCl_4} 3.29 (s, 3H), 3.17 (d of d, 1H), 0.75 to 2.55 (br m, 12H). This spectral evidence suggests endo-8-methoxytricyclo[4.3.1.0^3,8]decan-7-one.

Anal. Exact mass molecular weight, Calcd for C₁₁H₁₆O₂:
180.1150. Found: 180.1152.

An nmr of the distilled mixture gave a singlet at δ_{TMS}^{CCl_4} 3.65 in addition to those reported for 95 and 100. The nmr also showed additional absorptions between 60.50 and 0.90, indicating the presence of 108. Integration of the areas indicated a ratio of 108:95 of about 25:75.
exo and endo-Tricyclo[4.2.1.01</ref>6]nonane-7-carboxylic Acid (109).

Into 135 ml of 75% aqueous methanol (75:25 methanol:water) containing 4.10 g (0.0730 mol) of potassium hydroxide was placed 6.56 g (0.0365 mol) of an impure mixture of 95 and 108 from the photolysis of 8-diazotricyclo[4.3.1.01</ref>6]decan-7-one. The mixture was stirred one hour and then refluxed gently for 45 min. After the addition of 110 ml of water, the methanol was distilled off. The remaining aqueous layer was washed with three 60-ml portions of pentane. To the aqueous layer was added approximately 9.91 g (0.0730 mol) of potassium bisulfate in 65 ml of water until the solution reached pH 5. The solution was extracted with four 100-ml portions of ether and the combined ethereal extracts were dried over anhydrous sodium sulfate. After filtration, the ether was removed on a rotary evaporator with a bath temperature less than 25°C to give 5.46 g (90%) of a colorless oil which would solidify to give a white amorphous solid on standing at -5°C, mp 38-55°C (dec).

An ir spectrum (neat) showed absorptions at 2.7-4.3μ (OH str, carboxylic acid) and 5.85μ (C = O str); an nmr spectrum showed the material to be rather pure and gave δCDCl3 10.54 (s, 1H), 3.08 (m, 0.7 H), 2.77 (t, 0.3 H), and 0.40-2.48 (m, 12H) including super-imposed cyclopropyl protons for the major exo isomer at 1.07 (d, J = 4.5 Hz) and 0.51 (d, J = 4.5 Hz, further split into multiplets). This labile acid was used without further purification.
exo and endo-7-Carbomethoxytricyclo[4.2.1.0^1,8]ncnane (95 and 108).

The crude acid 102, made from 8.96 g (0.0498 mol) of crude ester was taken up in 100 ml of ether and an ethereal diazomethane solution added dropwise until gas evolution ceased and the solution remained yellow. Removal of the ether on a rotary evaporator followed by distillation gave 6.64 g (74% from crude ester) of a

sweet smelling colorless liquid, bp 59-62° (0.30 mm). A vpc of this mixture on a 10' x 1/8'' 10% SE-30 on Diaport S column at 170° showed the presence of only two components, 95 and 108, as confirmed by spectral data. An ir spectrum (neat) showed absorptions at 3.23µ (CH str of cyclopropane) and 5.73µ (C = O str); an nmr spectrum gave δCDCl3 3.63 (s, 0.3 H), 3.55 (s, 0.7 H), 2.97 (m, 0.7 H), 2.62 (t, 0.3 H), and 0.42-2.17 (br m, 11H). An analytical sample was prepared by preparative vapor phase chromatography on a 9' x 1/4'' 10% SE-30 on 60/80 Chrom W at 160°, nD 1.4838.

Anal. Calcd for C11H18O2: C, 73.30; H, 8.95. Found: C, 73.19
H, 8.88.

Attempted Equilibration of 95 and 108. Into a solution of 4 ml of dry methanol containing 10 mg of sodium methoxide was placed 40 mg of the epimeric ester mixture. After 27 hr at reflux, no change in relative composition of the mixture was observed by vapor phase chromatography on a 10' x 1/8'' 10% DC Silicone on Diaport S column at 170°.
exo and endo-Tricyclo[4.2.1.0\(^3\)\(^1\)]nonane-7-methanol (89 and 90).

To 65 ml of anhydrous ether containing 1.36 g (0.0357 mol) of lithium aluminum hydride was added dropwise with ice cooling 6.44 g (0.0357 mol) of the purified mixture of esters 95 and 108. The solution was subsequently refluxed gently overnight, cooled, and 5.44 g of 10% sodium hydroxide solution was added dropwise with ice cooling. After stirring for 5 hr at room temperature, the solution was filtered and the lithium salts were washed generously with ether. The ether from the filtrate was subsequently removed on a rotary evaporator and the residue distilled to yield 5.20 g (98%) of a colorless liquid, bp 71-74\(^\circ\) (0.27 mm). This material was estimated to be about a 70:30 mixture of exo-tricyclo[4.2.1.0\(^3\)\(^1\)]nonane-7-methanol (89) and endo-tricyclo[4.2.1.0\(^3\)\(^1\)]nonane-7-methanol (90), respectively, by vpc on a 5\(^\prime\) x 1/8\(^\prime\) 3% FFAP on 45/60 Chrom G column at 120\(^\circ\). The two epimers were separated by preparative vapor phase chromatography using a 12\(^\prime\) x 1/4\(^\prime\) 15% FFAP on 60/80 Chrom W column at 180\(^\circ\).

An ir spectrum (neat) of 90 showed absorbances at 2.97\(\mu\) (OH str) and 3.24\(\mu\) (CH str of cyclopropane); an nmr spectrum gave $\delta_{\text{CDCl}_3}$ 3.80 (m, 2H), 1.04-2.16 (m, 12H), 0.82 (d, J = 5 Hz, 1H), and 0.62 (d of d, J = 5 Hz and J = 2 Hz, 1H). An analytical sample was collected by preparative vpc on a 12\(^\prime\) x 1/4\(^\prime\) 15% FFAP on 60/80 Chrom W column at 180\(^\circ\), $n_D^{19}$ 1.5024.

Anal. Calcd for C\(_{10}\)H\(_{16}\)O: C, 78.89; H, 10.59. Found: C, 78.57.
An ir spectrum (neat) of 89 showed absorption at 2.97μ (CH str) and 3.24μ (CH str of cyclopropane); an nmr spectrum gave 

\[
\delta_{\text{CHCl}_3} = 3.44 \text{ (m, 2H)}, 2.21-2.73 \text{ (br m, 1H)}, 1.00-2.21 \text{ (m, 9H)}, 0.96 \text{ (d, J = 5 Hz, 1H)}, \text{ and } 0.41 \text{ (d, J = 5 Hz, further split into a multiplet)}. 
\]

An analytical sample was collected by vapor phase chromatography on a 10' x 3/8' 15% Carbowax 1500 3% KOH on Chrom G column at 195°, \(n_D^{19} = 1.4964\).

Anal. Calcd for C_{10}H_{16}O: C, 78.89; H, 10.59. Found: C, 78.76; H, 10.58.

**exo-Tricyclo[4.2.1.0^{1,8}]nonane-7-methanol p-Toluenesulfonate (91).**

To 931 mg (4.89 mmol) of p-toluenesulfonyl chloride in 9 ml of anhydrous pyridine was added dropwise with ice cooling a solution of 743 mg (4.89 mmol) of **exo-tricyclo[4.2.1.0^{1,8}]nonane-7-methanol** in 6 ml of anhydrous pyridine. After standing in a refrigerator for three days, the mixture was poured into 50 ml of pentane and washed first with three 50-ml portions of water, then with 50 ml of brine. After drying over anhydrous sodium sulfate, the solution was filtered and the solvent was removed on a rotary evaporator. The residue was evacuated via a vacuum pump overnight (0.01 mm) to yield 1.246 g (83%) of 91 as a white crystalline solid, mp 40-41.5°.

An ir spectrum (melt) showed absorptions at 3.24μ (CH str), 6.25μ (C = C str), and at 7.34, 8.40, and 8.49μ (SO₂ str). An nmr spectrum
showed no impurities and gave $\delta_{\text{CDCl}_3}$ 7.80 (d, J = 9 Hz, 1H), 7.35 (d, J = 9 Hz, 1H), 3.94 (m, 2H), 2.57 (s, 1H), 0.98-2.88 (m, 13H), 0.89 (d, J = 5 Hz, 1H), and 0.51 (d, J = 5 Hz, further split into a multiplet, 1H). An analytical sample was prepared by recrystallization from 95:5 hexane:ether to give 91 as white needles, mp 45.0-45.5°.

Anal. Calcd for C$_{17}$H$_{23}$O$_3$S: C, 66.65; H, 7.24; S, 10.44. Found: C, 66.49; H, 7.30; S, 10.44.

**endo-Tricyclo[4.2.1.0$^{1.6}$]nonane-7-methanol p-Toluenesulfonate (92).**

In a procedure similar to that used for 91, 240 mg (1.59 mmol) of *endo*-tricyclo[4.2.1.0$^{1.6}$]nonane-7-methanol was reacted with 301 mg (1.59 mmol) of p-toluenesulfonyl chloride in 5 ml of anhydrous pyridine. A colorless oil, 415 mg (86%), was obtained which crystallized upon standing at -5° for three days, mp 36.5-38.0°. Spectral data indicated the material was quite pure. An ir spectrum (melt) showed absorptions at 3.21μ (CH str), 6.21μ (C = C str), and at 7.30, 8.39, and 8.46μ (SO$_2$ str). An nmr spectrum showed $\delta_{\text{CDCl}_3}$ 7.62 (d, J = 8 Hz, 1H), 7.17 (d, J = 8 Hz, 1H), 4.05 (d, J = 7 Hz, 2H), 2.40 (s, 3H), 0.96-2.18 (m, 11H), 0.74 (d, J = 5 Hz, 1H), and 0.54 (d, J = 5 Hz, further split into a multiplet, 1H). Recrystallization from hexane gave an analytical sample as white needles, mp 40.5-41.0°.
Anal. Calcd for C_{17}H_{22}O_{3}S: C, 66.65; H, 7.24; S, 10.44.
Found: C, 66.84; H, 7.33; S, 10.45.

Kinetics for 91 and 92

Reagents. A stock solution of 1.6764g (0.0157 molar) of commercial 2,6-lutidine (Eastman) in one liter of 90:10 (vol/vol) acetone-water was used as solvent. Baker reagent grade acetone was used.

Procedure. Approximately 32 mg of the tosylate (about 0.01 molar) was dissolved in the buffered 90% aqueous acetone in a 10 ml volumetric flask. Aliquots of 1.25 ml were transferred to glass ampoules which had previously been flushed with argon. The sealed ampoules were placed in a constant temperature bath and remove after 0.25, 0.5, 0.75, 1.0, 1.5, 2.0, 2.5 and 10.0 half-lives. They were immediately quenched in an ice-water bath. After warming to room temperature, the ampoules were opened and exactly 1 ml withdrawn with a constant volume automatic pipette. This was diluted to 10 ml with distilled water and titrated with a Metrohm Herisan potentiograph, Model E 426, using 0.0087 N hydrochloric acid solution as titrant. The endpoint was taken to be at pH 4.75, also the inflection point of the titration curve. Measured infinity titers were used and all runs gave linear pseudo first-order plots through 2.5 half-lives. Rate constants were calculated using a Wang Electronic Calculator, Model 360 K.
Product Analysis of the Solvolysis of exo-Tricyclo[4.2.1.0<sup>13</sup>6]-nonane-7-methanol p-Toluenesulfonate (91). Into 25 ml of unbuffered 90% aqueous acetone was placed 250 mg (0.75 mmol) of 91 in a Carius tube previously flushed with argon. The sealed tube was heated to 100° for 50 min. The cooled solution was poured into 50 ml of water and extracted with an 80-ml portion of ether, then with two 20-ml portions of ether. The combined ethereal extracts were washed with two 75-ml portions of saturated sodium bicarbonate solution, 75 ml of saturated salt solution, and dried over anhydrous sodium sulfate. After removal of solvent on a rotary evaporator, two products were observed by vpc on a 10 x 1/8? 5% XF 1150 on 45/60 Chrom W column at 110° in a ratio of approximately 45:55. When either of these isomers was subjected to these reaction conditions, the same ratio was obtained. Preparative vapor phase chromatography using a 15' x 1/4? 5% XF 1150 on 60/80 Chrom W column at 105° allowed collection of the two isomers. The lesser isomer was a white crystalline solid, mp 66.0-67.5° [lit.119,120,98 59-62°, 61-68°]. The ir<sup>98</sup> and nmr<sup>119</sup> spectra were identical to those reported for exo-tricyclo[4.3.1.0<sup>13</sup>6]decan-8-ol (96). The

major isomer was a white crystalline solid which had a softening point at 84°, and mp 89.5-92° [lit\textsuperscript{119} 67-80°]. An ir spectrum (\textit{CCl}_4) gave absorbances at 2.70\textmu (free OH str), 2.92\textmu (hydrogen bonded OH str), and 2.24\textmu (CH str of cyclopropane). An nmr spectrum gave no other absorptions besides a myriad of peaks between \textit{CDCl}_3 \( \delta \text{CHCl}_3 0.37 \) and 2.39, as reported for the expected tricyclo[4.3.1.0\textsuperscript{1,8}]decan-6-ol \textsuperscript{119}. A near infrared spectrum (\textit{CCl}_4) of the tertiary alcohol showed an absorption at 1.651\mu (\( \epsilon 0.248 \)), confirming the presence of the cyclopropyl group \textsuperscript{39} and therefore \textsuperscript{11}.

Anal. Exact mass molecular weight, Calcd for C\textsubscript{10}H\textsubscript{16}O:
\[ \text{152.1201. Found: 152.1204.} \]

When the tosylate was solvolyzed in buffered 90% aqueous acetone at 80° for 10 half-lives, the yields of 96 and 111 were 5% and 91%, respectively, as determined on a 10' x 1/8'' 7% XF 1150 on 60/80 Chrom W column at 110°, using diphenylmethane as an internal standard.

Product Analysis of the Solvolysis of endo-Tricyclo[4.2.1.0\textsuperscript{1,8}]-nonane-7-methanol p-Toluenesulfonate (92). In a Carius tube was sealed under argon 15.4 mg of endo-tricyclo[4.2.1.0\textsuperscript{1,8}]nonane-7-methanol p-toluenesulfonate in 2.0 ml of unbuffered 90% aqueous acetone. After heating at 120° for 45 min, the cooled reaction mixture was poured into 10 ml of water and extracted with three
10-ml portions of ether. The combined ethereal extracts were then washed with 10 ml of saturated sodium bicarbonate, 10 ml of saturated salt solution, and dried over anhydrous sodium sulfate. The solution was then filtered and concentrated on a rotary evaporator. The residue showed only one major component by vpc on a 10' x 1/8'' 5% XF 1150 on 60/80 Chrom W column at 105°. Preparative vpc on a 15' x 1/4'' 5% XF 1150 on 60/80 Chrom W column at 135° allowed isolation of a white solid which was identical in all respects to an authentic sample of bicyclo[4.4.0]dec-1(6)-en-3-ol\textsuperscript{90} (107). When the tosylate was solvolyzed in buffered 90% aqueous acetone for 10 half-lives at 80°, the four expected isomeric alcohols were obtained. These were, in order of elution, endo-tricyclo[4.3.1.0\textsuperscript{1,8}]decan-7-ol (83), exo-tricyclo[4.3.1.0\textsuperscript{1,8}]decan-7-ol (82), bicyclo-[4.3.1]decan-6, (7)-en-1-ol (106), and 107, in yields of 12, 12, 56, and 11\%, respectively, as determined on a 10' x 1/8'' 10% Carbowax 20M KOH on 60/80 Chrom W column at 160° using biphenyl as an internal standard. When the tosylate was solvolyzed at 80° for 1430 sec (approximately 10% reaction), vpc as below after preparative thin layer chromatography indicated ca. 4, 20, 74, and 1% of 83, 82, 106, and 107, respectively. The retention times of the four products were identical to those of authentic samples on three different vpc columns of widely differing polarities. These columns were a 10' x 1/8'' 10% Carbowax 20M KOH on 60/80 Chrom W column at 160°, a 10' x 1/8'' 5% XF 1150 on 45/60 Chrom W column
at 105°, and a 10' x 1/8'' 10% SE-30 on Diaport S column at 160°.

Stability of exo and endo-Tricyclo[4.2.1.0^{18}]nonane-7-methanol to

**Solvolytic Conditions.** Into 6 ml of 90% aqueous acetone which was
0.0156 molar in 2,6-lutidine was placed 10 mg of p-toluenesulfonic
acid and 9 mg of a mixture of the alcohols 89 and 90. These were
sealed in an ampoule under argon and heated to 80° for a period of
26 hr. Vapor phase chromatography of the reaction mixture on three
different columns indicated only the presence of the starting
alcohols. The columns were a 5'x 1/8'' 3% FFAP on 45/60 Chrom G
column at 120°, a 10' x 1/8'' 5% XF 1150 on 60/80 Chrom W column
at 140°, and a 10' x 1/8'' 10% Carbowax 20M KOH on 60/80 Chrom W
column at 190°.

exo and endo-Tricyclo[4.2.1.0^{18}]nonane-7-methyl Ketone (93 and 94).

Into a 250 ml round bottomed flask equipped with a reflux condenser,
argon inlet, rubber septum, and magnetic stirring bar was placed
3.00 g (0.0181 mol) of exo and endo-tricyclo[4.2.1.0^{18}]nonane-7-
carboxylic acid in 150 ml of anhydrous ether (distilled from
lithium aluminum hydride). Under argon, 23.5 ml (0.0434 mol) of
1.85 M methyllithium in ether was added dropwise with ice cooling.
After the addition was complete, the reaction was allowed to stir
an additional 12 hr at room temperature. (An earlier run which was
allowed to stir only one hour resulted in a 55% recovery of the
acid). To the solution was then added, under ice cooling, 5 ml
of acetone. After stirring an additional 0.5 hr, the solution was poured onto 50 g of cracked ice in 50 ml of water. The ether layer was separated and the aqueous layer extracted with two 75-ml portions of ether. The combined ethereal extracts were washed with 150 ml of a saturated salt solution and dried over anhydrous sodium sulfate. After filtration, the ether was removed on a rotary evaporator and the residue distilled to give 2.41 g (81%) of a colorless liquid, bp 69-72° (0.70 mm). An ir spectrum (neat) showed absorptions at 3.22 µ (CH str of cyclopropane) and 5.81 µ (C = O str); an nmr spectrum gave δ<sub>CDCl₃</sub> 3.06 (m, 0.7 H), 2.73 (m, 0.3 H), 0.95-2.30 (m, 10H, with a methyl singlet at 2.19), 0.83 (m, 1H, with superimposed doublet for exo isomer, J = 5 Hz, at 0.83) and 0.55 (m, 1H, with superimposed doublet for exo isomer, J = 5 Hz, at 0.55). A near infrared spectrum (CCl₄) indicated the continued presence of the cyclopropane ring with an absorption at 1.651 µ (ε 0.242). An analytical sample was prepared by preparative vapor phase chromatography on a 9' x 1/₄'' 10% SE-30 on 60/80 Chrom W column at 150°, n<sub>D</sub> 1.4875.


Reaction of 23 and 24 with Peracetic Acid. To 500 mg (3.05 mmol) of a 70:30 mixture of exo and endo-tricyclo[4.2.1.0<sup>1,8</sup>]nonane-7-methyl ketone in 30 ml of methylene chloride containing 8.35 g (78.6 mmol)
of anhydrous sodium carbonate was added dropwise 1.70 g (9.15 mmol of peracid) of 40% peracetic acid with vigorous stirring over a period of 30 min. After stirring an additional 30 min, the solution was poured into 150 ml of pentane. This solution was washed with two 100-ml portions of 10% sodium thiosulfate solution, 100 ml of saturated sodium carbonate solution, 100 ml of saturated sodium chloride solution, and was dried over anhydrous sodium sulfate. After filtration, the material was distilled to give 0.460 g (77%) of a colorless liquid, bp 72-73°C (0.15 mm). Vapor phase chromatography on a 10' x 1/8" 10% SE-30 on Diaport S column at 170°C showed just two products, the starting endo-methyl ketone (94) and a much longer retention time product, 1-acetoxy-7-oxatricyclo-[4.3.1.0^3.8]decane (117). These were isolated by preparative vapor phase chromatography on a 9' x 1/8" 10% SE-30 on 60/80 Chrom W column at 150°C to give 39.3 mg (8% recovery) of 94, n_D 1.4876 and 201.4 mg (34%) of 117, n_D 1.4989.

Compound 94 gave an ir spectrum (CCl_4) which absorbed at 3.21μ (CH str of cyclopropane) and 5.80μ (C = O str); an nmr spectrum showed δ_1HCHCl_3 2.85 (m, 1H), 0.91-2.42 (m, 13H, with a methyl singlet at 2.13), 0.84 (d, J = 4 Hz, 1H), and 0.66 (m, 1H).

Compound 117 gave an ir spectrum (neat) with absorptions at 5.73μ (C = O str) and 8.06μ (C-O str of acetate); an nmr spectrum gave δ_1HCHCl_3 2.92 (d, J = 4 Hz, 1H) and 0.97-2.63 (br m, 15H, with a methyl singlet at 1.96); a near infrared spectrum showed
the lack of a cyclopropyl ring by the lack of any absorptions between 1.600 and 1.675 μ; a mass spectrum, while not giving a parent peak, gave a base peak at m/e 136, corresponding to a loss of acetic acid.

When the reaction was repeated using only 1.2 moles of peracid per mole of starting ketone, incomplete reaction was observed. Only the starting endo-ketone, approximately 50% of the starting exo ketone, and the product 117 were observed by vpc. No other products were observed.


Reduction of 117 with Lithium Aluminum Hydride. Into 5 ml of anhydrous ether (distilled from lithium aluminum hydride) containing 50 mg of lithium aluminum hydride was added dropwise 50 mg of 117 in 1 ml of ether. The solution was stirred 1 hr, cooled in an ice bath, and 200 mg of 10% sodium hydroxide solution added dropwise. After stirring for two hours, the solution was filtered and the solvent removed on a rotary evaporator to give just one product by vpc on a 10' x 1/8' 10% SE-30 on Diaport S column at 170°. Preparative vpc on a 9' x 1/4' 10% SE-30 on 60/80 Chrom W column at 150° gave 21.0 mg (54%) of 7-oxytricyclo[4.3.1.0^8.7]decan-1-ol (129) as a white solid, mp 158-159.5°. An ir spectrum (CCl₄) gave absorptions at 2.71 μ (free OH str) and 2.88 μ (H-bonded OH str); an nmr spectrum gave δ<sub>CCl₄</sub> 3.17 (br s, 1H, variable in
position and disappears in deuterium oxide), 2.84 (m, 1H), and 0.86-2.56 (br m, 12H).

Anal. Exact mass molecular weight, Calcd for C_{11}H_{16}O_2: 304.0994. Found: 304.0997.

In a similar reduction, 100 mg of acetate and 60 mg of lithium aluminum hydride in 15 ml of dry tetrahydrofuran (distilled from lithium aluminum hydride) were refluxed for 12 hr. Workup as before gave only 129 with no traces of bicyclo[4.2.1]nonane-1,6-diol (130).

Reduction of 129 with Lithium in Ethyl Amine. Under argon, 10 cm of \(1/8\)" diameter lithium wire (423 mg) was cut into small pieces and added to 25 ml of ethyl amine in a three necked, round-bottomed flask equipped with a Hershberg stirrer, dry-ice condenser, and argon inlet. After the solution turned deep blue, 60 mg (0.390 mmol) of alcohol was added in 1 ml of ether dropwise under dry-ice:acetone cooling. The solution was then refluxed (17 °) for 4 hr, cooled in an ice bath, and 3.20 g of ammonium chloride added cautiously. To the solution was then added 50 ml of water. After the excess lithium was gone, the solution was extracted with three 25-ml portions of ether and the combined ethereal extracts were washed with 50 ml of saturated sodium chloride solution and dried over anhydrous sodium sulfate. After filtration and removal of solvent on a rotary evaporator, very little product was observed (< 5 mg).
Hence, the combined aqueous washes were continuously extracted with ether and the solvent subsequently removed on a rotary evaporator. Vapor phase chromatography on a 10' x 1/8' 10% SE-30 on Diaport S column at 170° showed the presence of just one component. Preparative vpc on a 9' x 1/4' 10% SE-30 on 60/80 Chrom W column at 150° allowed isolation of 29.6 mg (49%) of bicyclo[4.2.1]nonane-1,6-diol (130), mp 185-187° (sublimes). An ir spectrum (CHCl₃) gave absorbances at 2.74µ (free OH str) and 2.91µ (H-bonded OH str); an nmr spectrum gave δ(TMS) 3.08 (very br m, 2H readily exchanges with deuterium oxide) and 1.14-2.36 (m, 14H). The diol was not soluble in carbon tetrachloride, and was only slightly soluble in chloroform. The diol was soluble in acetone and in water.

**Anal.** Calcd for C₉H₁₆O₂: C, 69.19; H, 10.32. Found: C, 69.18; H, 10.40.

4,5,6,7-Tetrahydro-2-indanol (141). From 4.00 g (0.0298 mol) of 2-indanol and 2.17 g (0.312 mol) of lithium wire (51.3 cm of 1/8'' diameter), in 130 ml of freshly distilled n-propyl amine, 141 was prepared according to the method of Starr and Eastman in 89% yield, nD 1.5092, bp 95-97°, (1.5 mm), [lit 83° (5 mm)]. The alcohol readily took up bromine in carbon tetrachloride and gave an ir spectrum (neat) absorption at 2.95 (OH str); an nmr spectrum showed δ(CCl₄) 4.30 (m, 1H) and 1.20-2.73 (m, 13H).
4,5,6,7-Tetrahydro-2-indanol Acetate (121). To 3.0 g (0.0217 mol) of 141 in 30 ml of anhydrous pyridine was added dropwise with ice cooling, 4.43 g (0.0434 mol) of acetic anhydride. After standing at 5° overnight, the solution was poured into 250 ml of pentane and washed with three 100-ml portions of water and then with 100 ml of saturated sodium chloride solution. After drying over anhydrous magnesium sulfate, the solution was filtered and distilled to yield 3.62 g (92%) of a sweet smelling, colorless liquid, bp 68-68.5° (0.30 mm), which decolorized a bromine-carbon tetrachloride solution. An ir spectrum (neat) of 121 showed absorptions at 5.72μ (C = 0 str) and 8.02μ (-CO₂- str of acetate); an nmr gave δ₃CCl₄ 5.16 (m, 1H) and 1.48-2.81 (m, 15H, with a methyl single at 1.91). An analytical sample was prepared by preparative vapor phase chromatography on a 9' x 1/4'' 10% SE-30 on 60/80 Chrom W column at 140°, nD²⁵ 1.4854.

Anal. Calcd for C₁₁H₁₈O₂: C, 73.30; H, 8.95. Found: C, 73.23; H, 8.97.

exo and endo-8-Acetoxy-10-oxatricyclo[4.3.1.0₁⁷]decane (126 and 122). To 5.12 g (48.3 mmol) of anhydrous sodium carbonate and 0.500 g (2.78 mmol) of 121 in 30 ml of methylene chloride was added dropwise with ice cooling and vigorous stirring, 1.06 g (5.56 mmol of peracid) of 40% peracetic acid over a period of 30 min. After stirring an additional 20 min at room temperature, the reaction
mixture was poured into 150 ml of pentane and was washed with two 100-ml portions of 10% sodium thiosulfate solution, 100 ml of saturated sodium bicarbonate solution, 100 ml of saturated sodium chloride solution, and was dried over anhydrous sodium sulfate. After filtered, the solution was distilled to give 0.500 g (92%) of a colorless liquid, bp 67-69° (0.10 mm). An infrared spectrum (neat) gave absorptions at 5.71 μ (C = 0 str) and 8.02 μ (CCO2-CCl4 str of acetate); an nmr spectrum showed absorptions at δ1MS 5.04 (m, 0.4 H, exo acetate), 4.68 (m, 0.6 H, endo acetate), 2.53 (m, 2H), and 1.10-2.07 (m, 13H). A center cut, bp 69° (0.10 mm) was sent for analysis, nD 1.4729.

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23. For a discussion, see ref. 16c, p. 196.


37. P.E. Eaton and G.H. Temme, III, Abstract of papers, 165th National Meeting of the American Chemical Society, Dallas, Texas, April 8-13, 1973, p. 59. Note: The structure in the aforementioned abstract should be that of tricyclo[2.2.2.0^1,4]-octane and not bicyclo[2.2.0]octane.
47. This is probably a free radical reaction, and not an electrophilic addition as in the case of 7 and 13.


57. An authentic sample of methylcycloheptane was purchased from Chemical Samples Co., Columbus, Ohio.


62. For a recent discussion on the relative importance of each resonance contributor in a similar case, see: R. Noyori, *Tetrahedron Lett.*, 1691 (1973), and references therein.

64. The author wishes to thank Dr. T. Atkins for providing the 1-deuteriocyclopentene used in this experiment.


68. The author wishes to thank Badische Anilin and Soda-Fabrik for a generous gift of 49.


76. This lack of reaction was observed by another laboratory, J.J. Bloomfield, private communication.

(a) E. Vogel and H.D. Roth, Angew. Chem., 76, 145 (1964);

A 450 watt high pressure Hanovia lamp was used for this purpose.


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The change in chemical shifts, $\Delta \delta$, was chosen as a better judge of the effects of steric compression rather than the absolute values of $\delta$. This was done because some of the spectra were recorded vs TMS as internal standard and others were recorded vs chloroform as internal standard. The difference, $\Delta \delta$, of less than 1 ppm should be less subject to drift in the nmr signal than the absolute values. Note also that $\Delta \Delta \delta$ is most informative, since the effects of
exo and endo substitution on H\textsubscript{a} and H\textsubscript{b} work in opposite
directions.


91. The position and coupling constant for this absorption were
very similar to those reported for bicyclo[3.3.1]non-1-ene.
(1970) reports \( \delta 5.62 \) (t, \( J = 7 \) Hz). J.A. Marshall and H.
Faulb, ibid., 92, 948 (1970) reports \( \delta 5.52 \) (t, \( J = 3.5 \) Hz).
The isolation and identification of the bicyclo[4.2.1]non-
1(8)-ene system [J.R. Wiseman, H.-F. Chan, and C.J. Ahola,
ibid., 91, 2812 (1969)] indicates that 106, which should be
less highly strained, may not be very destabilized as a result
of the bridgehead double bond.


93. Unlike the extensively studied cyclopropylcarbinyl cation
system, very little information exists concerning the cyclo-
butylcarbinyl cation. The solvolysis of parent compound,
as well as of some bridged derivatives, is discussed by K.B.
(1966); see also, W.G. Dauben and J.L. Chitwood, ibid., 90,
3835 (1968) and C.F. Wilcox, Jr., and M.E. Mesirov, ibid.,
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94. For recent reviews on this subject see: H.G. Richey, Jr.,
1972, pp. 1201-1294; see also K.B. Wiberg, B.A. Hess, Jr.,

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96. Acetone-water was used as the solvolytic media rather than
the more common buffered acetic acid because the highly
strained tricyclic ring system was susceptible to acetic acid
addition.
97. It was demonstrated that the carbinols 89 and 90 were stable to the reaction conditions and were not responsible for the production of the observed products from solvolysis of 91 and 92.


100. In unbuffered 90:10 v/v acetone:water, only 107 was obtained. It was demonstrated that 106, 82, and 83 were readily converted into 107 in the presence of acid.

101. P.G. Gassman, work in progress.


106. The author wishes to thank Dr. R. Stepple for working out the synthesis of 50: R. Stepple and P.G. Gassman, unpublished results.


108. Care was taken to base wash all glassware in this experiment in order to avoid any acidic surfaces which could polymerize the products.

109. A bank of eight 15-watt Sylvania 'Blacklite' fluorescent tubes was used for this purpose.


116. The amount of time necessary to achieve a certain isomer ratio varied with the dryness of the solvent and the activity of the catalyst. In general, however, about 12 to 15 hr was necessary to achieve 50% conversion.


118. A 10' x 1/8" Carbowax 20M KOH on 60/80 Chrom W column at 190° was used for this purpose.
