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STUDIES OF TRICYCLO[3.2.0.0²,⁴]HEPT-5-ENE
and
TRICYCLO[3.2.0.0²,⁴]HEPTANE 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

Louis Malcolm Leichter, B.S.

The Ohio State University
1972

Approved by

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Department of Chemistry
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DEDICATION

To Mom, Dad, Grandma, Leslie, and

of course Jan!
ACKNOWLEDGMENTS

The author wishes to thank his lab partners, Dr. Constantine Camarasu, Dr. Osvaldo Cox, Mr. Kenneth Fuhr, Dr. Stanley Lang, Jr., Dr. George Meehan, Mr. John Schwartz, and Dr. Michael Short for teaching him and for putting up with his tastes in radio and other punishments; the Paquette Group for making life enjoyable; and Professor Leo A. Paquette for The Privilege.

The author gratefully acknowledges the financial support of the National Institutes of Health for maintaining his solvent(cy).
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PUBLICATIONS


FIELDS OF STUDY

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INTRODUCTION

During the past 15 years, the chemistry of acyclic molecules, especially highly strained polyunsaturated systems has become a useful testing ground of theoretical and practical concepts important to many facets of organic chemistry. The use of polycyclic azo compounds as precursors has been one of the best methods for the preparation of a variety of highly strained hydrocarbons.

Theoretically speaking, azo decomposition could result in the operation of four competitive pathways:

1. The radical centers thus formed may couple to form a σ bond.

2. A strained proximate bond may cleave to form a diene.

3. Hydrogen shifts to the radical centers may take place, or,

4. Insertion into a remote double bond may occur.

The result of azo decomposition is, of course, a function of the molecule in question and the options open to it.

In 1957, Criegee and Rimmelin reported that pyrolysis of 2,3-diazabicyclo[2.2.1]hept-2-ene (1) at 160° for 48 hr led to the formation of bicyclo[2.1.0]pentane (3) in 94% yield. Subsequently, Cohen, Zand, and Steel studied the decomposition of azo compound 1 in the gas phase and established that the loss of nitrogen occurs in an uncatalyzed, homogeneous, first order reaction. The activation energy attending

1
the conversion of 1 to 3 (37 kcal mole$^{-1}$) has been found to be lower than that associated with the decomposition of such monocyclic pyrazolines as 4, 5, and 6 (41-42 kcal mole$^{-1}$). These data have been interpreted to mean that intermediate 1,3-diradicals such as 2 intervene in the formation of three-membered rings. The lower activation energy for 1 suggests that strain is relieved in the transition state, since if the process were concerted and 3 were formed directly, a higher activation energy would be expected.

The thermal decomposition of 2,3-diazabicyclo[2.2.2]oct-2-ene (7) requires temperatures above 200°C. At 240°C, the sole product was identified as 1,5-hexadiene (9). However, because bicyclo[2.2.0]hexane (10) is known to be rapidly converted to 2 at 230°C, 6,7 the unique isolation of 2 does not itself preclude the formation of 10 as the initial product.
arising from diradical coupling. Azo compound $\mathcal{I}$ is more stable than $1$, the difference in reactivity being due to a less favorable activation energy for nitrogen loss in $\mathcal{I}$ ($44.6$ kcal mole$^{-1}$). Significantly, the entropies of activation of both $1$ and $\mathcal{I}$ are sufficiently high ($8.7$ and $10.5$ eu, respectively) to suggest that both C-N bonds are breaking simultaneously in the transition state.

A situation similar to $\mathcal{I}$ occurs in the pyrolysis of $6,7$-diazaquadricyclononane,$^{3,8}$ $6,2,1.1$ non-6-ene ($\mathcal{I}I$). When heated at $140^\circ$ for $14$ hr, $\mathcal{I}I$ afforded norbornadiene ($\mathcal{I}3$). Morarity noted that this result did not necessarily preclude the intermediate formation of quadracyclane ($\mathcal{I}4$), since this hydrocarbon rearranges to norbornadiene under the reaction conditions. Interestingly, ultraviolet irradiation of $\mathcal{I}I$ gave quadracyclane in $35\%$ yield.

As noted above, the participation of a proximate bond can cause the azo compound to undergo simultaneous extrusion of nitrogen and rearrangement to a diene. Thus, in 1965, Askani noted with considerable
dismay that attempts to prepare 2,3-diazabicyclo[2.2.2]octa-2,5-diene (16), even under the mildest conditions, led only to the production of 1,3-cyclohexadiene (17). More recently, this reaction has been reinvestigated by Lemal who estimated that the half-life of 16 at -78° is approximately one minute.

Replacement of the double bond in 15 by a cyclopropane ring as in 18 results in added thermal stability. Thus, Martin and Roth have observed that solutions of 18 at 25° are slowly converted to 1,4-cycloheptadiene 19 and nitrogen. In analogous fashion, azo compound 20
has been found to undergo loss of nitrogen at 25° to give 1,4-cyclhexadiene \((21)\).

More recently, Trost and Cory have found that thermolysis of \((22)\) occurs at 100° to give benzene exclusively. \(^{14}\) Of the two possible path-
ways, these authors favored the novel eight electron process (Path B) based on the lack of formation of Dewar benzene (23) and the poor initial overlap between the C$_2$-C$_3$ and C$_4$-C$_5$ bonds which could account for the high temperatures required.

A similarly positioned cyclobutane ring as in 24 provides less acceleration to the loss of nitrogen than a cyclopropane ring.

Recent examples of compounds which provide unequivocal demonstration of the fact that cleavage of a cyclopropyl bond is kinetically favored over that of an internal σ bond in a four membered ring are 25 and 27, photolysis of which provide 26 and 28 respectively. In this
case, because the small rings are exo fused, the bent bonds are not favorably oriented for overlap as C-N cleavage begins. Accordingly, concerted loss of nitrogen is not possible. Nevertheless, the results require that production of the transient 1,4-diradicals from 25 and 27 be followed by cleavage of that adjacent C-C linkage endowed with the greatest "bent bond" character, i.e., cyclopropyl.

From a theoretical standpoint, the conversions of 1 to 3 and 1 to 2 may be considered as retrograde homo- and bis-homo-1,2-cycloadditions, processes which are forbidden to be concerted from orbital symmetry considerations. As a result, pyrolytic decompositions of 2,3-diazabicyclo[2.2.1]hept-2-enes and 2,3-diazabicyclo[2.2.2]oct-2-enes very likely require the intermediacy of diradicals of type 2 and 8. The thermal lability of 15, however, is readily understood to be the result of an allowed (σ2a+σ2a+π2s) concerted thermal reaction. The internal cyclopropyl bonds of 18 and 20 have sufficient π character to cause thermally allowed (σ2s+σ2s+σ2s) concerted conversions to 18 and 21 to occur readily.

Initially, it was suggested that relief of steric interactions between the bridgehead atoms in 16 and 20 was partially responsible
for the ease of nitrogen loss observed for these compounds. On the basis of his further studies with 11, 29, and 30, Allred has now shown that such factors contribute little if anything to the enhanced reactivity. Thus, because 20 and 30 have essentially the same order of reactivity and 11 exhibits a lower order of reactivity than 20, relief of strain associated with opening of the cyclopropyl ring cannot be a major factor. Rather, the ease of nitrogen extrusion is considered to be electronic in origin. The greater the amount of \( p \) character overlap possible between the bond to be cleaved and the breaking C-H bond, the more facile the reaction; the concerted transition state of 20 is depicted in 31. In 11, 29, and possibly also 22, the "bent" cyclopropyl
bonds are geometrically constrained so as to be almost perpendicular to the orbitals of the C-N bonds, so that cyclopropyl participation contributes little to the transition state. In 18, 20, and 30, good overlap is possible, while in 15, the overlap is excellent.

The fourth alternative mentioned above, intramolecular insertion into a remote double bond, was unknown until the present work. The only related examples were the trapping 1,3-diradicals from 3H-indazoles on an intermolecular basis with olefins such as butadiene and the insertion of the non-azo derived 1,3-diradical from 32 into the π bond to give 33.

\[
\begin{array}{c}
\text{C}_6\text{H}_5 \\
\text{C}_6\text{H}_5
\end{array}
\xrightarrow{\Delta}
\begin{array}{c}
\text{C}_6\text{H}_5 \\
\text{C}_6\text{H}_5
\end{array}
\]

The 7,8-diazatricyclo[4.2.1.0^2,5]non-3,7-diene and tricyclo-
[3.2.0.0^2,4]hept-6-ene systems (34 and 35 respectively) were selected as the objects of this study since the diradical available to the first system (36) theoretically possesses all of the above mentioned options. This work describes the preparation of substituted derivatives of 34 and 35 and the investigation of the conditions conducive to the operation of each of these pathways.
PART I

THE TRICYCLO[3.2.0.0^2,4]HEPT-6-ENE SYSTEM

Background

At the inception of this study, examples of the tricyclo[3.2.0.0^2,4]-hept-6-ene system were virtually unknown. The lone examples were 37^21 and 38^22. Unfortunately, the method of preparation, which involved carbenoid addition to hexamethyl (Dewarbenzene), was neither conducive to variation of substituent groups nor to the stereoselective placement of these groups. Additionally, ease of structural assignment and
spectral interpretation as well as "chemical elegance" dictated that
the molecule be as simple as possible.

Of the several possible methods to gain entry into the tricyclo-
heptene system, the one ultimately employed involved cycloaddition of
cyclobutadiene to an isopyrazole. Photolysis or thermolysis of the
resultant azo compound would then lead to appropriate tricycloheptenes.
There were several advantages to this route. The synthesis of cyclo-
butadiene, though tedious, is relatively painless. Isopyrazoles
are of relatively recent origin, and are quite easily prepared
via dialkylation of a 1,3-diketone in dimethyl sulfoxide, followed
by treatment with hydrazine and removal of water. Furthermore, by
employing various diketones, a diversity of isopyrazoles and hence
tricycloheptenes could be made. It should be noted that substitution
at the 3-position is necessary to prevent rearrangement to the isomeric
pyrazoles. The isopyrazoles employed in this study, \(41a\), \(41b\), and \(41c\)
are shown below.

\[
\begin{align*}
&\text{R1} \quad \text{R2} \\
&\text{1) NaH} \\
&\text{2) CH3I} \\
&\text{3) NaH (excess) DMSO} \\
&\text{4) CH3I (excess)} \\
&\text{H2NNH2 (-H2O)} \\
39 \\
\end{align*}
\]

\[
\begin{align*}
\text{a: } R1 &= C6H5; R2 = C6H5 \\
\text{b: } R1 &= C6H5; R2 = CH3 \\
\text{c: } R1 &= CH3; R2 = CH3 \\
\end{align*}
\]
Results

The Dimethyldiphenyl Case. Exposure of isopyrazole $4_{1a}$ to cyclobutadiene ($h_2$), generated in situ by ceric ion oxidation of cyclobutadieneiron tricarbonyl, furnished tricyclic azo compound $h_3$ in 68% yield (Scheme I). The ultraviolet spectrum of $h_3$ in isooctane displays weak maxima at 346 (e 67) and 357 nm (94) as expected for the azo chromophore. Its nmr spectrum (in CDCl$_3$) reveals three proton singlets at $\delta$ 0.28 and 1.04 (1- and 2-CH$_3$ respectively), two-proton singlets at 3.88 (allyl) and 6.05 (olefinic), and a multiplet (10 H) in the aromatic region (7.32-7.80). The endo stereochemistry of the cyclobutene ring and the spatial relationship of the two methyl groups were established by application of nuclear Overhauser effects. Thus of the two methyl groups, that labeled 1-CH$_3$ is sufficiently distant from the allylic and olefinic hydrogens that it should not contribute to the relaxation of either proton type. In line with this consideration and an awareness that 1-CH$_3$ should experience a substantial upfield shift because of its location above and hence in the shielding region of the azo chromophore, double irradiation of the $\delta$ 0.28 singlet did not result in any significant intensity change of the remaining signals. Saturation of the $\delta$ 1.04 absorption, however, reproducibly gave evidence of a 10% intensity enhancement in the 3.88 peak. Accordingly, the 2-CH$_3$ group and the allylic hydrogens must be proximal, an observation which requires the spatial relationship embodied uniquely in the endo isomer.
Scheme I

\[ \text{CH}_3 \wedge \text{CH}_3 \]

\[ \text{C}_6\text{H}_5 \]

\[ \text{N} \wedge \text{N} \]

\[ \text{CH}_3 \wedge \text{CH}_3 \]

\[ \text{C}_6\text{H}_5 \]

\[ \text{CH}_3 \wedge \text{CH}_3 \]

\[ \text{C}_6\text{H}_5 \]

\[ \text{hv} \]

\[ \text{C}_6\text{H}_5 \]

\[ \text{CH}_3 \wedge \text{CH}_3 \]

\[ \text{C}_6\text{H}_5 \]

\[ -135^\circ \]

\[ \text{hv} \]

\[ 100^\circ \]

\[ 175^\circ \]

\[ \Delta \]

\[ \text{O}_3 \]

\[ \text{O} \]

\[ \text{C}_6\text{H}_5 \]

\[ \text{CH}_3 \wedge \text{CH}_3 \]

\[ \text{C}_6\text{H}_5 \]

\[ \text{hv} \]
Irradiation of \( \frac{1}{2} \) in ether solution with a 200-W Hanovia lamp (Pyrex optics) for 3 hr gave rise to \( \frac{3}{4} \) in quantitative yield. The structural assignment follows chiefly from the nmr spectrum which shows (in CDCl\(_3\)) two methyl singlets at \( \delta 0.88 \) and 1.44, doublets (\( /J/=1.5\) Hz) at 3.36 (allylic) and 6.41 (olefinic), and a ten-proton aryl multiplet centered at 7.22. The anti stereochemistry of \( \frac{3}{4} \) was likewise established by an NOE experiment. Upon saturation of the 1.44 methyl singlet, a 78% enhancement of the 3.36 absorption was noted. The relatively small NOE effects in both \( \frac{1}{2} \) and \( \frac{3}{4} \) are likely attributable to the mutual relaxation of the two allylic hydrogens such that the 2-CH\(_3\) protons contribute less by comparison. The \(^{13}\)C magnetic resonance spectrum of \( \frac{3}{4} \) has also been determined (see Experimental Section).

Clearly, nitrogen elimination from \( \frac{1}{2} \) had proceeded with retention of configuration. In an attempt to gain evidence on the possible intermediacy of the structurally related syn isomer, a degassed methylene chloride solution of \( \frac{1}{2} \) contained in a sealed Pyrex nmr tube was photolyzed at \(-70^\circ\). The progress of the reaction was followed by periodic nmr analysis at \(-60^\circ\). Under these conditions, the decomposition of \( \frac{1}{2} \) was found to be kinetically first order and to afford only \( \frac{3}{4} \). A concerted (\( \sigma^2s+\sigma^2s \)-double retention) process involving synchronous tricyclo:epitene formation and nitrogen departure would lead to such a stereochemical outcome. On the other hand, a step-wise mechanism necessitating the intervention of a planar or rapidly interconverting pyramidal 1,3-diradical intermediate would appear to be precluded since no \( \frac{5}{6} \) was produced (see below). Evidently, the present example affords no syn crossover product (as do a number of
somewhat related structures) because of the excessive strain inherent in this isomer, a situation which could serve to promote still further the exclusivity of the concerted mechanism.

The thermolysis of $\mathbf{44}$ in tetrachloroethylene solution at $100^\circ$ could be conveniently monitored by nmr spectroscopy. After approximately 4 hr, quantitative conversion to quadricyclane $\mathbf{45}$ was observed. Evaporation of the solvent and recrystallization of the residue from ethanol gave $\mathbf{45}$ in 60% isolated yield. This hydrocarbon exhibits moderate ultraviolet absorption (in isooctane) at 234 nm ($\varepsilon$ 8,900) and three singlet nmr absorptions (in CDCl$_3$) at $\delta$ 1.03 (6, methyls), 2.02 (4, cyclopropyls), and 7.29 (10, aryls). Thermal decomposition of $\mathbf{43}$ at $135^\circ$ in Cl$_2$C=CCl$_2$ solution likewise gave rise exclusively to $\mathbf{45}$.

When the thermolysis of this azo compound at different temperatures was monitored by nmr spectroscopy, it was noted that nitrogen evolution and quadricyclane production were slow below $125^\circ$. At $135^\circ$, however, the conversion was complete after 1.5 hr.

Assignment of the quadricyclane structure to $\mathbf{45}$ follows from its ultraviolet absorption and the highly symmetrical nature of its nmr spectrum. In particular, the absence of olefinic protons demands that the molecule be tetracyclic. Chemical substantiation of the quadricyclane formulation was derived by thermal rearrangement of $\mathbf{45}$ in Cl$_2$C=CCl$_2$ solution at $175^\circ$. At this temperature, $\mathbf{45}$ was converted cleanly into the norbornadiene $\mathbf{46}$. Both the uv and nmr spectra of $\mathbf{46}$ reflect the generation of two non-conjugated olefinic linkages in a highly symmetrical setting (see Experimental Section). Not unexpect-
edly, irradiation of 46 in hexane solution through quartz optics resulted in reconversion to 45.

At this point, the unusual substitution pattern in 46 prompted the examination of its thermochemical behavior. Previous studies of norbornadiene and benzonorbornadiene pyrolyses have revealed a marked propensity for skeletal rearrangement to cycloheptatrienes and benzocycloheptatrienes, respectively. These structural changes, in actuality a combination of a 1,3-sigmatropic shift of the bridge carbon atom and subsequent valence isomerization of the resulting norcaradiene, are of considerable current interest. When 46 was heated in an evacuated tube at 200° for 1-2 hr, two isomeric hydrocarbons (47 and 48) were produced. Continued pyrolysis (to 4 hr) gave rise to 48 which was easily isolated as a yellow crystalline substance. Its ultraviolet spectrum in isooctane which showed maxima at 242 (ε 17,600) and 357 nm (14,000), was particularly informative, suggesting the presence of a diphénylnorcaradiene chromophore. The almost identical electronic spectrum of 50 provided supportive evidence for the indicated structure. Also, the presence in the nmr spectrum of 48 of

\[
\begin{align*}
\text{50} & \quad \text{H} \quad \text{C}_{6}\text{H}_{5} \quad \text{C}_{6}\text{H}_{5} \\
\text{51} & \quad \text{H} \quad \text{C}_{6}\text{H}_{5} \quad \text{C}_{6}\text{H}_{5}
\end{align*}
\]
Figure I - 60 MHz NMR Spectrum of 47
two olefinic protons (broadened singlet at δ 6.55) and two low-field
cyclopropyl hydrogens (broadened singlet at 2.38) is consistent with
the norcaradiene formulation and inconsistent with the isomeric cyclo-
heptatriene structure. In ultimate confirmation of the assignment,
ozonolysis of 48 led to cis-1,2-dibenzoyl-3,3-dimethylcyclopropane (49).

Isolation of the kinetically favored pyrolysis product 47 proved
difficult, particularly since conditions were not found which would
cause this isomer to predominate over 46 and 48. The discovery that
photolysis of 48 afforded 47 together with a small amount of p-ter-
phenyl34 did, however, permit its characterization. Significantly,
the ultraviolet spectrum which showed λisoctane \( \lambda_{\text{max}} ^{\text{isoctane}} = 238 (\epsilon 20,800) \) and
303 nm (11,100), was closely similar to that of 51. Additionally,
because the four vinyl protons in 49 appear at widely separated
chemical-shift positions, application of the double resonance technique
permitted detailed analysis of the existing spin-spin interactions:
\( J_{2,3} = 7.5 \) Hz, \( J_{3,5} = 1.7 \) Hz, \( J_{3,e} = 0.7 \) Hz, \( J_{2,5} = 0.5 \) Hz, and \( J_{5,e} \)
11.0 Hz. The nmr spectrum of 47 is reproduced in Fig. I.

That 48 prefers the norcaradiene tautomeric form while 47 prefers
the cycloheptatriene structure is clearly evident. Commentary on the
factors controlling the direction of the various equilibria is deferred
to the Discussion.

Phenyltrimethyl Substitution. Diels-Alder addition of cyclobuta-
diene (42) to 3-phenyl-1,4,5-trimethylisopyrazole (41b), again strictly
controlled by secondary orbital factors, afforded only 52. Facile
conversion to 52 was achieved by photolysis of 52 in ether solution
Controlled pyrolysis of azo compound 52 in CDCl₃ at 152° (sealed tube) for 2 hr proceeded at a satisfactory rate to give five hydrocarbons with no evidence of unreacted starting material. A minor product was 53 (9%) which was seen to rearrange to the four isomeric structures 54-57 if pyrolysis was prolonged. Approximately one-fourth of the mixture consisted of quadricyclane 54 (16%) and norbornadiene 55 (7%). The remaining constituents were bicyclo[3.2.0]heptadiene 56 (15%) and cycloheptatriene 57 (53%). The product distribution was determined by careful quantitative integration of nmr spectra; the mass balance in terms of these five products was essentially quantitative.

As noted above, 53 was equally labile to heat, affording (154°, 2 hr) 54-57 in about the same ratio (18:9:18:46%) together with 9% of unchanged tricycloheptene.

The assignments of structure to the new substances rest on spectroscopic criteria and appropriate chemical transformations. Although 54 and 55 were not readily separated by vpc, their combined nmr spectrum (in CDCl₃) is in excellent agreement with the proposed assignments. The quadricyclane 54 shows the expected pairs of nonequivalent cyclopropyl protons as triplets (/J/=1.7 Hz) centered at δ 1.55 and 1.80. The remaining portion of the spectrum consists of singlets at 0.98 for the bridgehead methyl group and 0.85 for the gem-dimethyl substituents at C₇, together with the aromatic absorption (singlet at 7.18). In the case of 55, the requisite magnetic nonequivalence of the olefinic protons is revealed by two sets of doublets (/J/=5.5 Hz) at δ 6.58 and 6.84; like 54, the norbornadiene shows methyl absorption at 1.28 (3 H)
Scheme II

41b → \text{hv} \quad 52

52 \text{ or } 53 \xrightarrow{\Delta} 54 + 55

51 \xrightarrow{\text{hv}} \xrightarrow{\Delta} 56

56 + 57

51
Scheme II (Continued)

\[ 54 + 55 \xrightarrow{\Delta} \]

or

\[ 58a \]

\[ 58b \]

\[ 57 + \]

\[ 59 \xrightarrow{} \]

\[ 60 \]
and 0.88 (6 H) and the aryl resonance (5 H) at 7.33. Thermal rearrangement of this mixture at more elevated temperatures (175°C) was found to give rise to a new cycloheptatriene (58). Although isomer 58b is preferred on mechanistic grounds (preference given to generation of transient benzylic radical formation), the available evidence does not adequately remove 58a from consideration.

Elucidation of the structural features particular to 56 and 57 was greatly assisted by the finding that these substances could be readily interconverted. At elevated temperatures, for example, 56 was cleanly transformed into 57; conversely, photolysis of 57 gave rise in unexceptional fashion to 56. Although the spectral characteristics of 57 establish its monocyclic nature (see Experimental Section), the exact position of the attachment of the sp²-bound methyl and phenyl groups remained to be confirmed. To this end, 57 was treated with N-phenyltriazolinedione (59) and the thermally labile adduct 60 was isolated. The observation that 60 possesses no cyclopropyl protons, but only olefinic and CH-N nmr absorptions requires that 57 be necessarily formulated as a 1,6,7,7-tetrasubstituted cycloheptatriene.

The formation of 56 from 57 is evidently a highly stereoselective electrocyclic reaction not directly involving the styrene chromophore. The direction of the photochemical bond-forming process is clearly indicated by the nmr spectrum of 56 which displays not only absorptions characteristic of three sp³-bound methyl groups, but also three vinyl protons and a hydrogen attached to a doubly allylic carbon atom. Its ultraviolet spectrum (in isooctane) showed no maximum, but rather a
shoulder at 236 nm (ε 5,100) on the tail of end absorption. The overwhelming selectivity noted in the disrotatory cyclization which produces 56 may be steric in nature, but more likely finds its origin in electronic factors arising from charge polarization in the excited singlet state. The presence in 56 of the styrene functionality which further enhances its stability relative to 61 must also be important.

\[ \text{CH}_3\text{CH}_3\text{CH}_3\text{C}_6\text{H}_5 \]

The Tetramethyl Example. Phenyltrimethyl substitution was seen to result in the operation of several competing radical reactions with quadricyclane formation being less favored (ca 25%) than in the case of 43 and 44. This observation suggested that replacement of the remaining phenyl group by methyl should further decrease the capability of the 1,3-diradical for formation of a tetracyclic structure. In actuality, thermal decomposition of azo compound 62, (200°, 4 hr, neat) or of its photoproduct, tricycloheptane 63, (144°, 12 hr, CDCl₃) led only to mixtures of bicycloheptadiene 64 and cycloheptatriene 65 (Scheme III); no evidence for quadricyclane intervention was obtained.
Scheme III

\[ \text{41c} \xrightarrow{h_2} \text{62} \xrightarrow{hv} \text{63} \]

\[ \text{62 or 63} \xrightarrow{\Delta} \text{64} \]

\[ \text{65} \xrightarrow{hv} \text{65} + \text{64} \]

\[ \text{65} + \text{59} \xrightarrow{} \text{66} \]
For 64, the absence of ultraviolet absorption and the appearance in the nmr spectrum of three vinyl protons, a bridgehead hydrogen, one sp²-bound methyl group, and three high-field methyl singlets suggested that this product was a bicyclo[3.2.0]heptadiene. This conclusion was confirmed by further thermal rearrangement of 64 to 1,6,7,7-tetramethyl-cycloheptatriene (65) whose structure follows unequivocally from spectral data (see Experimental Section) and reaction with 52 to give adduct 66. Further, photolysis of 65 in CDCl₃ through Pyrex resulted in ready isomerization back to 64.

Discussion

In simplest terms, the tricyclo[3.2.0.2,4]hept-6-ene system represents a fusion of the bicyclo[2.1.0]pentane and bicyclo[2.2.0]hex-2-ene systems. Using the strain energies listed in Table I, and making the gross assumption that the strain energies of fused rings are approximately those of the sum of the strain energies of the rings involved, then the strain energy of tricycloheptene is at least 85 kcal mole⁻¹. Furthermore, the energies of activation needed for the cleavage of the central bonds provide some insight into the results discussed herein (Table II). The energy required for rupture of the C₁-C₄ bond in bicyclo[2.1.0]pentane is relatively low (E_{act} \sim 29-35 \text{ kcal mole}^{-1}) while that required for hydrogen migration (E_{act} = 45.5 \text{ kcal mole}^{-1}) and for formation of 1,4-pentadiene (E_{act} = 52.3 \text{ kcal mole}^{-1}) is relatively high. Conversely, the activation energy for the cleavage of the C₁-C₄ and C₂-C₃ bonds in bicyclo[2.2.0]hexane to form 1,5-hexadiene
### Table I. Strain Energies of Some Model Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{\text{str}}^{a}$ (kcal mole$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="triangle.png" alt="Image" /></td>
<td>28.13</td>
<td>44</td>
</tr>
<tr>
<td><img src="square.png" alt="Image" /></td>
<td>54.5</td>
<td>44</td>
</tr>
<tr>
<td><img src="rectangle.png" alt="Image" /></td>
<td>26.90</td>
<td>44</td>
</tr>
<tr>
<td><img src="pentagon.png" alt="Image" /></td>
<td>30.6</td>
<td>44</td>
</tr>
<tr>
<td><img src="hexagon.png" alt="Image" /></td>
<td>57.3</td>
<td>44</td>
</tr>
<tr>
<td><img src="heptagon.png" alt="Image" /></td>
<td>59.2$^b$</td>
<td>45</td>
</tr>
<tr>
<td><img src="octagon.png" alt="Image" /></td>
<td>101.1</td>
<td></td>
</tr>
<tr>
<td><img src="nonagon.png" alt="Image" /></td>
<td>$\geq 85.,^c$</td>
<td></td>
</tr>
<tr>
<td><img src="decagon.png" alt="Image" /></td>
<td>$\geq 85.,^c$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Based on group increments, derived from heats of formation of the cyclic alkanes in completely skew free conformations, unless otherwise noted.

$^b$Based on calculations using MINDO methods.

$^c$Based on ring strain additivities.
**Table II. Activation Energies for Some Model Reactions**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$E_{act}$ (kcal mole$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Reaction 1" /> $\rightarrow$ <img src="image2" alt="Reaction 2" /></td>
<td>45.6</td>
<td>7</td>
</tr>
<tr>
<td><img src="image3" alt="Reaction 3" /> $\rightarrow$ <img src="image4" alt="Reaction 4" /></td>
<td>52.3</td>
<td>7</td>
</tr>
<tr>
<td><img src="image5" alt="Reaction 5" /> $\rightarrow$ <img src="image6" alt="Reaction 6" /></td>
<td>35.8</td>
<td>46</td>
</tr>
<tr>
<td><img src="image7" alt="Reaction 7" /> $\rightarrow$ <img src="image8" alt="Reaction 8" /></td>
<td>32.9</td>
<td>46</td>
</tr>
<tr>
<td><img src="image9" alt="Reaction 9" /> $\rightarrow$ <img src="image10" alt="Reaction 10" /></td>
<td>29.0</td>
<td>47</td>
</tr>
<tr>
<td><img src="image11" alt="Reaction 11" /> $\rightarrow$ <img src="image12" alt="Reaction 12" /></td>
<td>36.0</td>
<td>7</td>
</tr>
</tbody>
</table>
is low by comparison ($E_{\text{act}} = 36.0 \text{ kcal/mole}^{-1}$). The presence of a double bond in a bicyclohexane should lower this energy still further.

When bond lengths are considered, some additional possibilities become apparent. The presence of a double bond in a four-membered ring has been found to lengthen the bond opposite to it.\(^41,42\) Also, the bond lengths in bicyclopentane show a short $C_1-C_4$ bond, and a long $C_2-C_3$ bond. Taken together, this information would tend to predict

\[
\begin{align*}
C-C &= 1.54 \text{ Å} \\
C_1-C_2 &= 1.34 \text{ Å} \\
C_3-C_4 &= 1.57 \text{ Å} \\
C_1-C_4 &= 1.439 \text{ Å} \\
C_2-C_3 &= 1.622 \text{ Å}
\end{align*}
\]

tricycloheptenes to have the distorted structure shown below, and to suffer facile cleavage of the $C_1-C_5$ bond. Indeed, in the absence of other overriding effects, this would appear to be the case.

\[
\text{Quadricyclane Formation. The tricycloheptene-quadricyclane inter-conversion constitutes an example of an overriding effect in that the initial step is cleavage of the $C_2-C_4$ bond. The ability of phenyl}
\]
groups to lower activation energies and alter reaction pathways is well preceded. For example, the cis-trans isomerization of diphenyl cyclopropane has been found to have an activation energy of 33.5 kcal mole\(^{-1}\) while that of dimethylcyclopropane is 59.4 kcal mole\(^{-1}\). In addition, the thermal rearrangement of 32 to 33 occurs at 60\(^\circ\) while that of 67 to 68 requires 200\(^\circ\) and gives a different product. Clearly, the phenyl groups have a pronounced effect on the ultimate course of the rearrangement.

In the present instance, although data for 1,4-diphenylbicyclo-[2.1.0]pentane are lacking, the effects are expected to surely be in the same direction. In actual fact, homolytic rupture of the C\(_2\)-C\(_4\)
bond does give diradical $69a$. The precise geometry of $69a$, although pictured as a planar species with $sp^2$-hybridization in order to achieve maximum stabilization is, of course, not known. The only requirement

![Diagram](image)

$69a$

is that the orbitals initially associated with the $C_2$-$C_4$ bond be intercepted by the cyclobutene $\pi$ system with retention of configuration. Since azo compound $43$ behaves analogously, it would appear that the same intermediate is involved in the thermal reaction which converts it to $45$. Unfortunately, because the decomposition of $43$ requires temperatures ($\sim135^\circ$) in excess of those required for the $44 \to 45$ conversion, no firm conclusion regarding the possible intervention of $44$ can be drawn. However, support for the intermediacy of $44$ (and also of $53$ and $63$) is evidenced by the observation that thermolyses of $83$, $87$, or $92$ (see Part II) occur at similar temperatures to give isolable tricycloheptanes as initial products. In addition, some tricycloheptene was isolated from short term pyrolyses of $43$, $52$, and $62$. If the $[\sigma^2s+\sigma^2s+\pi^2s]$ process required to pass directly from $43$ to $45$ were concerted, one would assume that a more ready fragmentation would be seen. A firm answer must await the synthesis of the exo isomer of $43$,
and a comparison of the two rates of decomposition.

Recently, Gassman postulated the syn isomer of \( \text{I}_1^4 \), \( \text{I}_0 \), as a key intermediate in quadricyclane formation. To bypass the intermediacy of \( \text{I}_9 \), he advanced the notion of rapid flap inversion \( \text{via} \) an intermediate (\( \text{I}_1 \)) in which the bridgehead radicals at \( \text{C}_2 \) and \( \text{C}_4 \) maintained their tetrahedral character. Addition of the olefinic bond to the central bicyclopentane bond of \( \text{I}_1 \) would then lead to quadricyclane. This author believes that Gassman is in error for several reasons. Firstly, the syn isomer would be prohibitively strained; not surpris-
ingly, the search for this entity was not fruitful (vide supra). If formed, Gassman's proposal requires that the \( \pi \) linkage move inward toward the inside of the bicyclopentane flap, a motion which would further increase repulsive non-bonded interactions. This is energetically unrealistic. In contrast, ring opening to diradical 69a would relieve strain and provide maximum stabilization to the diradical intermediate. Secondly, intramolecular cycloaddition of the syn isomer requires approach of a cyclobutene \( p \) orbital to the back lobe of a bent bond which lies substantially out of plane (71). Because this intermediate is, of necessity, highly rigid, the electrons in this instance can partake only of marginal overlap in the transition state. In contrast, the \( p \) orbitals in 69b are seen to be orthogonally aligned, and thus overlap is maximized. Lastly, the demonstrated need for at least one phenyl substituent at \( C_2 \) or \( C_4 \) is most consistent with the above discussed concept that facile rupture of the \( C_2-C_4 \) bond is a necessary prelude to quadricyclane formation. In contrast, the attack of olefins on bent \( \sigma \) bonds has not been shown to exhibit dependence on substitution at the bridgehead sites.

In 43 and 44, intramolecular trapping of diradical 69 occurs to the exclusion of all other possible reactions. When the substitution pattern is altered from dimethyldiphenyl to phenyltrimethyl as in 52 and 53, the capability for quadricyclane formation is substantially reduced (to ca 25\%), while in tetramethyl examples 62 and 63, no analogous intramolecular cycloaddition is seen. Similarly, no quadricyclane formation is observed upon pyrolysis of 21,53 (however, the complexity
of the nmr spectra and the insurgence of competitive [1.5]-sigmatropic hydrogen shifts renders it difficult to exclude completely the possibility of its formation in this instance).

\[\text{CH}_3\text{CH}_3\text{CH}_3\text{CH}_3\rightarrow \text{CH}_3\text{CH}_3\text{CH}_3\text{CH}_3\]

\[\text{2I}\rightarrow \text{72}\]

Inherent in these observations is the realization that the presence of at least one phenyl substituent is necessary to insure some measurable degree of breakage of the C\textsubscript{2}-C\textsubscript{4} bond and subsequent capture by the cyclobutene ring. Otherwise, reactions resulting from cleavage of the C\textsubscript{1}-C\textsubscript{5} bond began to dominate. For \textit{52} and \textit{53}, both the C\textsubscript{2}-C\textsubscript{4} and C\textsubscript{1}-C\textsubscript{5} cleavages compete, while in \textit{62} and \textit{63} (as well as \textit{3I}), only products resulting from cleavage of the bicyclohexene central linkage were seen (see below).

Conversion to Bicyclo[3.2.0]heptadienes and Tropolidenes. The carbon skeletal rearrangement attending the formation of bicycloheptenes \textit{56} and \textit{64} from their respective tricycloheptene precursors, appears unprecedented. Two possible pathways deserve mention. The first process necessitates that the tricycloheptene undergo conrotatory rupture
of the internal bicyclo[2.2.0]hexene σ bond (cf 73), perhaps with concomitant diradical cleavage of the C₂-C₄ bond, to provide a mono-trans-cycloheptatriene (74). The substantial strain in 74 would promote relatively rapid passage to bicycloheptadiene 75 under the reaction conditions. Disrotatory opening, or more probably, diradical cleavage of

![Reaction Scheme](image)

the C₁-C₅ and C₂-C₄ bonds, would lead directly to the observed tropilidene products (76 → 78). Since the bicyclo[3.2.0]heptadienes 56 and 64 are converted only very slowly to cycloheptatrienes 57 and 65, respectively, under the reaction conditions necessary for tricycloheptene rearrangement, the dienes do not serve as precursors to the trienes.
Rather the reactions are kinetically controlled and the two pathways must be competitive. This would require that conrotatory (and presumably symmetry allowed) ring opening be less efficient that nonconcerted disrotatory opening. Although this seems unlikely at first glance, it must be remembered that, in this case, the price of concertedness would be the formation of a highly strained intermediate (74).

Alternatively, the conversion to bicycloheptadienes can occur by means of a formal homo-1,3-sigmatropic carbon rearrangement. Because it is difficult to conceive of a process in which the C1-C7 bond of 72 undergoes total cleavage before appreciable C4-C7 bridging occurs, the favored approach to the transition state is considered to involve a torsional motion in which compression of the C5-C1-C7 bond angle leads to effective overlap of the p orbital at C7 with the free-radical center at C4. Subsequent homolysis of the C1-C7 bond in 80 serves to
complete the transposition to 75. Some degree of credence is lent to this possibility by the observation that the photochemical rearrangement of certain bicyclo[3.2.0]heptadienes to quadricyclanes may involve similar utilization of a cyclobutene double bond. A polar counterpart is perhaps also operative in the unbuffered acetolysis of the bicyclo[4.2.0]oct-7-en-2-ol brosylates. In any event, this mechanistic possibility bears many similarities to the reaction which results in quadricyclane formation where the possible first step is bonding of C7 to C2 instead of C4. In 79, the energy required to twist this intermediate in order that C7 approach C4 can hypothetically be counterbalanced at the transition state by an awareness in the reacting system at that stage (product development control) that the bicycloheptadiene to be formed is significantly less strained than the related quadricyclane.

A drawback to this mechanism is the observation that no "leakage" occurs. If 72 were indeed an intermediate, then one would expect to see some bicycloheptadiene upon pyrolysis of 44, and some quadricyclane upon pyrolysis of 63. In principle, a distinction between the two proposed pathways is available since a skeletal rearrangement is uniquely associated with the second mechanism. The preparation of a suitable mono- or dideuterated tricycloheptene would provide the requisite test of these alternatives.

The Norcaradiene-Cycloheptatriene Equilibria. Cycloheptatriene and the great majority of its derivatives do not contain detectable amounts of their norcaradiene valence tautomers at equilibrium.
Although the interconversion is symmetry allowed, an equilibrium constant favoring the norcaradiene form has been noted most frequently when the substituents at C7 are strongly electron withdrawing or incorporate external π systems geometrically disposed with the correct symmetry for orbital interaction. A theoretical basis for these observations has recently been advanced. Substituents on the cycloheptatriene have also been recognized to effect the position of equilibrium but much less is known about these influences.

Tropolidenes \(49, 51, 57,\) and \(58,\) when compared to norcaradienes \(48\) and \(50,\) provide some revealing information about substituent effects. Thus, the indiscriminate placement of one, two, or even three aryl substituents on the cycloheptatriene ring does not shift the equilibrium toward the bicyclic form. However when two phenyl groups are positioned at C2 and C5 as in \(48\) and \(50,\) stable norcaradienes are obtained. This strong bias very likely finds its origin in the extended conjugation now connecting the two aromatic centers, which stabilizing influence is not available to the monocyclic forms. This effect can be expected to be weakened significantly as the aryl groups are replaced by alkyl residues.

Lastly, the demonstrated interconversion of \(47\) and \(48\) is deserving of comment. As in the previous examples studied by Berson, the basic assumption is that the thermally induced skeletal rearrangement of \(47\) to \(48\) occurs via the corresponding norcaradiene (estimated endothermicity about 11 kcal mole\(^{-1}\)). A 1,5-sigmatropic carbon rearrangement of the gem-dimethyl group (consequently, no stereochemical
information derivable in this case) then leads to $^{48}$. The driving force behind the directionally biased migration depicted in $^{82}$ is presumably the development of extended conjugation associated with the 1,4-

diphenylbutadiene moiety. The interesting photo-1,5-sigmatropic carbon rearrangement of norcaradiene $^{48}$ back to $^{47}$, although preceded particularly in benzonorcaradiene derivatives, represents the first example of a "closed loop reaction sequence" within this series.
PART II
THE TRICYCLO[3.2.0.0²,⁴]HEPTANE SYSTEM

Background

In view of the high degree of strain present in the tricyclo- [3.2.0.0²,⁴]hept-6-ene compounds, and the novel reactions which they were found to undergo, it was decided to investigate their saturated counterparts, the tricyclo[3.2.0.0²,⁴]heptanes. From Table I and again using the crude assumptions made earlier, the strain energy in these compounds should also be ≥ 85 kcal mole⁻¹. Additionally, it was anticipated that much of the chemistry should be fundamentally different, since intramolecular trapping to form quadricyclane products would now be inoperative.

Results

The Dimethyldiphenyl Case. Diimide, generated in solution by neutralization of dipotassium azodicarboxylate with acetic acid, was found to readily reduce 43 to the saturated azo compound 83 (90% yield). Although a large excess (20-100 fold) of azodicarboxylate was necessarily employed to realize maximum yields, no reduction of the azo linkage was observed. Photochemical extrusion of nitrogen (Pyrex optics) was found to result in high conversion (86%) to the corresponding tricycloheptane 84. The anti stereochemistry of 84 was determined by its preparation also from 44 whose anti configuration had
been established earlier (*vide supra*). Spectral data of the diimide product of \( \text{I} \) confirmed that the compounds generated by both methods were identical (Scheme IV).

Thermolysis of a degassed deuteriochloroform solution of \( \text{II} \) could be conveniently monitored by nmr spectroscopy. After 5 hr at 140°, \( \text{II} \) was found to undergo quantitative conversion to \( \text{III} \). Further heating at 210° for 3 hr, caused \( \text{III} \) to experience fragmentation exclusively to 5,5-dimethyl-1,4-diphenylcyclopentadiene (\( \text{V} \)) and ethylene (\( \text{VI} \)).

Indicative of highly extended conjugation, \( \text{V} \) displays a blue fluorescence and an ultraviolet spectrum (in iso-octane) with absorptions at 232 (\( \varepsilon \) 9,000) and 330 nm (15,400). In agreement with formal loss of ethylene, the nmr spectrum (in CDCl\(_3\)) of \( \text{V} \) consists of a multiplet at \( \delta \) 7.50 (10, aryl), a singlet at 6.77 (2, olefinic), and a singlet at 1.65 (6, gem-dimethyl). Comparison with the spectral data reported for 1,4-diphenylcyclopentadiene tended to substantiate the proposed assignment. Finally, complete structural confirmation was derived from ozonolysis which led to diketone \( \text{X} \), a precursor to isopyrazole \( \text{XI} \) utilized earlier in this sequence.

In an attempt to elucidate the mechanistic implications attending the production of ethylene, compounds \( \text{II}b \) and \( \text{III}b \) were prepared. Addition of dideuteriodiimide to \( \text{I} \) gave \( \text{II}b \), photolysis of which provided \( \text{III}b \). The pyrolyses of \( \text{II}b \) and \( \text{III}b \) were performed on neat samples at 210° in sealed tubes. At this temperature, the \( \text{II} \rightarrow \text{III} \) conversion was so rapid that the product mixture was independent of which the two was used as reactant. For analysis, the 1,2-dideuterioethylene produced
Scheme IV

$^{l_3} \xrightarrow{R'=H\text{N}=N\text{H}} \xrightarrow{\text{R}}$

$^{83} \xrightarrow{210^\circ} \xrightarrow{\text{RHC=CHR}} ^{86}$

$^h \xrightarrow{\text{hv}}$

$^84 \xrightarrow{210^\circ} ^{85}$

$\xrightarrow{\text{O}_3}$

$\xrightarrow{40a}$

$\text{a}, \text{ R} = \text{H}; \text{b}, \text{ R} = \text{D}$
Table III. Deuterated Ethylenes from Pyrolysis at 210°

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Reactant</th>
<th>( \text{CH}_2=\text{CHD}^a )</th>
<th>Absolute</th>
<th>Products, % Yield</th>
<th>Relative</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>83b</td>
<td>10.2</td>
<td>82.1</td>
<td>7.7</td>
<td>91.4</td>
</tr>
<tr>
<td>2</td>
<td>83b</td>
<td>11.5</td>
<td>79.0</td>
<td>9.5</td>
<td>89.3</td>
</tr>
<tr>
<td>3</td>
<td>84b</td>
<td>9.8</td>
<td>82.0</td>
<td>8.2</td>
<td>90.9</td>
</tr>
<tr>
<td>4</td>
<td>84b</td>
<td>10.7</td>
<td>81.0</td>
<td>8.3</td>
<td>90.7</td>
</tr>
</tbody>
</table>

\(^a\)Consistently, ca. 10\% monodeuteration was encountered in the DN=ND reduction of 83 (mass spectral analysis of 83b and 84b); no production of 83a and 84a was noted. The ethylene analyses are in full agreement with the mass spectral data. The chemical shift for the protons in CH2=CHD (double irradiation conditions) is found at 535.4 Hz.\(^{69}\)
was transferred on a high vacuum line to an nmr tube containing 0.3 ml of CCl₄/TMS (see Experimental Section). The relative proportions of cis and trans-86b, determined by deuterium decoupled proton nmr spectroscopy, are summarized in Table III.

The relative intensities of the absorptions due to cis- (532.1 Hz) and trans-1,2-dideuterioethylene (532.7 Hz) indicated that 90 ± 1% of the cis isomer was present in the pyrolysis mixtures. Previous studies have shown that cis-trans isomerization of 1,2-dideuterioethylene is negligible at temperatures as high as 450°C under similar conditions. Some minor amount of equilibration in 83b and 84b could not be summarily dismissed; however, nmr monitoring of these pyrolysis reactions indicated that such conversions were not significant if operative.

Phenyltrimethyl Substitution. Treatment of 52 with diimide, generated in situ as before, provided 87 in excellent yield (95%). Facile transformation to 88 was achieved either by photolysis in ether solution or by controlled thermolysis in CDCl₃ (140°C, 3 hr, sealed nmr tube). When either 87 or 88 was pyrolyzed (210°C, 4 hr, neat), cycloreversion to ethylene and cyclopentadiene (89) was again observed. Now, however, this pathway represented only 55% of the total reaction. The remaining 45% consisted of a difficultly separable mixture of 90 (~15%), 91 (~15%), and one other unidentified substance (~15%).

The assignments to structures 89, 90, and 91 were based on spectroscopic criteria and comparison with appropriate model compounds. Elemental analysis and accurate mass determination indicated that 89 resulted from formal loss of ethylene. The nmr spectrum which shows one w-
Scheme V

$$\text{CH}_3\text{CH}_3 \quad \text{N} = \text{N} \quad \text{H} \quad \text{CH}_3 \text{CH}_3 \quad \text{N} = \text{N} \quad \text{H} \quad \text{CH}_3 \text{CH}_3 \quad \begin{array}{c} \text{hv or } \Delta \\ 210^\circ \end{array} \quad \text{CH}_3 \text{CH}_3 \quad \text{CH}_3 \text{CH}_3$$

$$\text{H}_2\text{C} = \text{CH}_2 \quad + \quad \begin{array}{c} \text{CH}_3 \\ \text{C}_6\text{H}_5 \end{array} \quad \begin{array}{c} \text{CH}_3 \\ \text{C}_6\text{H}_5 \end{array} \quad \begin{array}{c} \text{CH}_3 \text{CH}_2 \\ \text{C}_6\text{H}_5 \end{array} \quad \begin{array}{c} \text{CH}_3 \text{CH}_3 \\ \text{C}_6\text{H}_5 \end{array}$$

$$\begin{array}{c} 52 \\ 87 \\ 88 \\ 86 \\ 89 \\ 90 \\ 91 \end{array}$$
phenyl group, two non equivalent olefinic protons at δ 6.60 and 6.00, one sp³-bound methyl at 1.90, and two equivalent sp³-bound methyls at 1.19 is in excellent agreement with the assignment. Finally, comparison of the electronic and nmr spectra of 82 with those of the cyclopentadienes obtained in the dimethyldiphenyl and tetramethyl series (85 and 94) indicated that 82 was a composite of these two.

The combined spectrum of 20 and 21 (in CDCl₃) is likewise in accord with the proposed structures. Compound 20, whose nmr displays a one proton triplet at δ 5.42 (/J/=7.2 Hz, olefinic), broad one-proton singlets at 5.00 and 4.80 (exocyclic methylenes), and the gem-dimethyl singlet at 1.17, compares favorably with that of 25 which has an analogous structure. The assignment of 21 is likewise based on nmr similarities with that of the related hydrocarbon obtained in the tetramethyl series (96). The most relevant absorptions appear at δ 5.92 (m, 1, olefinic), 5.70 (br m, 1, olefinic), 1.78 (br s, 3, =C=CH₃) and 1.14 (s, 6, gem-dimethyl).

The Tetramethyl Example. The above mentioned observation that phenyltrimethyl substitution was seen to result in several competing reactions, in which cyclopentadiene formation was less favored than in the dimethyldiphenyl case, suggested that replacement of the remaining phenyl group by methyl would further decrease the amount of cyclopentadiene produced. To this end, 92 was prepared, again by exposure of its unsaturated congenor (62) to diimide. Thermal decomposition (210°, 1.5 hr, neat) of 92 or of its tricycloheptane photoproduct (93) was found to give a mixture containing four components (Scheme VI).
Scheme VI

\[ \text{Scheme VI} \]

\[ \begin{align*}
\text{CH}_3 & \quad \text{CH} \\
\text{N} & \quad \text{N} \\
\text{CH}_3 & \quad \text{CH}_3 \\
\end{align*} \]

\[ \xrightarrow{\text{H}_2 \text{N} = \text{N} \text{H}^{-}} \]

\[ \begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{N} & \quad \text{N} \\
\text{CH}_3 & \quad \text{CH}_3 \\
\end{align*} \]

\[ \xrightarrow{\text{hv}} \]

\[ \begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\end{align*} \]

\[ \xrightarrow{210^\circ} \]

\[ \begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3 \\
\end{align*} \]

\[ \text{CH}_3 \quad \text{CH}_3 \\
\text{CH}_3 \quad \text{CH}_3 \\
\text{CH}_3 \quad \text{CH}_3 \\
\]

\[ \begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3 \\
\end{align*} \]

\[ \text{CH}_2 = \text{CH}_2 \]

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

\[ 62 \quad 92 \quad 93 \]

\[ 93 \quad 94 \quad 95 \quad 96 \]

\[ 86 \]
The first of these was shown to be $1,1,5,5$-tetramethylcyclopentadiene ($94$). However this now accounted for only a quite small proportion of the mixture ($\leq 2.5\%$). The identification of $94$ was based on a comparison of its observed electronic and nmr spectra with those described in the literature.

The second constituent was determined to be tricycloheptane ($93$). The third component ($95$) was characterized on the basis of its spectral properties. The nmr spectrum reveals one endocyclic olefinic proton at $\delta 5.37$, two exocyclic methylene hydrogens at 4.94 and 4.72, four allyl protons, two aliphatic protons, an $sp^2$-bound methyl, and two $sp^3$-bound methyls. Structural assignment to $95$ was based chiefly on the highly symmetrical nature of its nmr spectrum which indicates the presence of two equivalent allylic hydrogens (br m, 2.15), two $sp^2$-bound methyls (br s, 1.77), and a gem-dimethyl group (s, 1.23).

The Parent System. Because the amount of cyclopentadiene produced seemed to be dependent upon the ability of substituents to weaken the $C_2-C_4$ bond relative to the $C_1-C_5$ bond, it was decided to prepare and pyrolyze the parent hydrocarbon, anti-tricyclo[3.2.0.0$^{2,4}$]heptane ($100$). This compound, recently prepared by Tanida via low temperature photolysis of azo compound $18$, was found by him to afford two products in a 10:1 ratio upon thermolysis. The major of these was characterized as $1,4$-cycloheptadiene. The suspicion that the minor product was cyclopentadiene led to the repetition of their work.

Tricyclo[3.2.0.0$^{2,4}$]heptane was prepared as outlined in Scheme VII. The sequence ultimately employed represented a composite of the
Scheme VII

59 + N=N-C_6H_5 \xrightarrow{\text{acetone, } 0^\circ} 97

\[ \text{92} \]

\[ \text{99} \]

\[ \text{98} \]

\[ \text{18} \]

\[ \text{100} \]

\[ \text{19} \]

1) NaCMe/IMSO
2) HCl
3) CuCl_2

aq NH_3
-20^\circ

ether, -20^\circ

h_\nu

175^\circ, 15 \text{ min}
methods reported by the Tanida and Roth groups for the preparation of \( \text{18} \), with numerous modifications (see Experimental Section).

Cycloaddition of 4-phenyl-1,2,4-triazoline-3,5-dione (59) to cycloheptatriene at \(-40^\circ\) gave a 92% yield of 27. Atmospheric hydrogenation over platinum oxide afforded 28 (89%) which was hydrolyzed by heating with a five-fold excess of sodium methoxide in dimethyl sulfoxide. The resulting hydrazo compound was not isolated, but rather converted immediately to the cuprous chloride complex 22 by treatment with hydrochloric acid and cupric chloride. Because the previous workers had observed that \( \text{18} \) decomposed even at room temperature, the complex was converted to the free azo compound at \(-20^\circ\). This was accomplished through treatment with precooled aqueous ammonia. The azo compound was extracted into precooled ether; the ethereal solution was dried, concentrated under reduced pressure, transferred to a quartz test tube, and photolyzed, all at \(-20^\circ\). A low, but sufficient, yield of 100 (5%) was realized.

Upon pyrolysis (neat, 173° for 15 min), tricyclo[3.2.0.0\(^2\)2,4]heptane gave 1,4-cycloheptadiene (19) as the only product. A minor component (\( \sim 10\% \)) was found to be unreacted tricycloheptane. Both nmr and flame ionization vpc confirmed that these were the only substances present.

Discussion

In Part I, it was argued that the C\(_1\)-C\(_5\) bond was normally the weakest one in the tricycloheptene system. Furthermore, it was assumed
that, except for quadricyclane formation, all reactions involved initial C<sub>1</sub>-C<sub>5</sub> bond scission. It was felt that this was in part due to an increased bond length and a lowered transition state energy, both brought about by the presence of the double bond. In the tricyclo-

\[3.2.0.0^{2,4}\] heptane system, the absence of the \( \pi \) bond at C<sub>6</sub>-C<sub>7</sub> renders the C<sub>1</sub>-C<sub>5</sub> cleavage more difficult. Such a change results in more equitable rates of cleavage of the C<sub>2</sub>-C<sub>4</sub> and C<sub>1</sub>-C<sub>5</sub> bonds than was seen earlier.

Cyclopentadiene and Ethylene Formation. Once again, phenyl substitution is seen to lower the energy required for cleavage of the C<sub>2</sub>-C<sub>4</sub> bond below that necessary for C<sub>1</sub>-C<sub>5</sub> scission. This results in fragmentation to cyclopentadiene and ethylene.

Of the possible mechanistic pathways leading to these products, both concerted \([\sigma^2s + \sigma^2s + \sigma^2s]\) fragmentation, and initial cleavage to a 1,3-diradical are possible. The deuterium labeling studies show that the opening of the anti-tricycloheptane nucleus occurs in highly stereoselective fashion, with a preference for double retention of approximately 9:1. This ratio is substantially greater than the corresponding \([\sigma^2s + \sigma^2s/\sigma^2s + \sigma^2a]\) ratio found with 7,8-cis-exo-dideuterio-cis-bicyclo-

\[4.2.0\] octane (i.e. 0.75). Also, the product distribution appears sufficient to dismiss the intervention of diradical intermediates such as \[101\] and \[102\]. If formed, such species would be expected to undergo extensive bond rotation as there exists no apparent reason why \( k_{\text{rot}} \) (either direction) should not be competitive with \( k_{\text{scis}} \) in the inter-
mediates. This would result in disruption of the stereochemical sense of the fragmentation.

The most probable mechanistic interpretation is that as fragmentation of the C\textsubscript{2}-C\textsubscript{4} bond commences, progressive rehybridization in the \textit{sp}\textsuperscript{2} direction to give maximum stabilization to the developing diradical takes place (103 → 105). Whether the two cyclobutane bonds rupture at

\begin{align*}
\text{103} &\rightarrow \text{104} \\
\text{105}
\end{align*}
intermediate stage 104, where the orbitals of the C₂-C₄ bond have become well canted but not yet completely severed (resulting in a concerted mechanism) or only after diradical 105 is formed (formally now a stepwise process) is not known. The data only require that the two edge bonds in the four membered ring break simultaneously.

Formation of cyclopentadienes and ethylene constitutes the first example in which highly stereoselective cycloreversion of a cyclobutane to olefinic products becomes energetically accessible and possibly concerted due to the suprafacial fragmentation of a third proximate σ bond. If operative, the concerted \([\sigma^2s+\sigma^2s+\sigma^2s]\) process would contrast remarkably with the severe distortions associated with the \([\sigma^2s+\sigma^2a]\) pathway otherwise demanded of concerted cyclobutane fragmentations.

In the phenyltrimethyl, tetramethyl, and perhydro series, a steady decrease in the amount of cyclopentadiene product is seen (55%, 2.5%, 0%, respectively). This reflects the insurgence of reactions resulting probably from initial cleavage of the C₁-C₅ bond (see below).

**Cycloheptadiene Formation.** The formation of cycloheptadienes 19, 21, and 26 is analogous to the bicyclo[2.2.0]hexane \(\rightarrow\) 1,5-hexadiene rearrangement. 7,77-80 Interestingly, it also represents the "high energy" pathway for bicyclo[2.1.0]pentane decomposition 79-82 (Table II). The relatively low temperatures necessary to effect complete reaction of the tricycloheptanes (ca 210°) as compared with bicyclo[2.1.0]-pentanes (ca 270-310°) 7,61,82 and the similarity of these temperatures to those required for bicyclo[2.2.0]hexane decompositions (ca 170°) 7.
suggests that C$_1$-C$_5$ homolytic scission is the initial step.

The formation of 92 and 95 is not well understood at the present time. Conceivably, these dienes could arise from a 1,3-prototropic shift in the diradical initially formed. Bond reorganization would then lead to the observed products (106-109). Some credence is lent to this mechanism by the observations of Evnin and Arnold $^{83,84}$ that 110 is converted to 111 upon heating. It should be noted, however, that 95 cannot arise from 96 (and presumably 92 cannot come from 91) since 96 was found to be stable to the reaction conditions employed.

106

R = C$_6$H$_5$

R = CH$_3$

107

108

109
\[
\begin{align*}
\text{CH}_3 & -\text{CH}_3 & \rightarrow & \Delta \\
(\text{CD}_3)\text{CH}_3 & - & & \\
\text{N} & - & \text{N} & - & \text{C}_6\text{H}_5 \\
\end{align*}
\]
PART III
SILVER(I) CATALYZED REARRANGEMENTS

Background
A field of much current investigation is that dealing with transition metal catalyzed rearrangements of highly strained polycyclic molecules. Transition metals, and in particular silver(I), have been found to cause carbon skeletal rearrangements in a wide variety of molecules. In particular, cubyl and bicyclobutyl systems have been well studied. In view of the high degree of strain present in the tricyclo[3.2.0.0²⁴]heptane skeleton, it was decided to investigate its behavior toward silver(I).

Results
Addition of a few crystals of either silver tetrafluoroborate or silver perchlorate to a deuteriochloroform solution of contained in an nmr tube was found to result in exclusive rearrangement
to 3,4-dimethyl-2,4-diphenylbicyclo[3.2.0]hept-2-ene (112). Although the exact stereochemistry about C4 is presently unknown, only one isomer was formed.

The structure of 112 was assigned on the basis of its spectral properties. In particular, the electronic spectrum (in isooctane) displays absorption at 251 nm (ε 12,200) characteristic of a styrene chromophore. The nmr spectrum (in CDCl₃) reveals a ten proton multiplet at δ 7.32, one allylic proton (br m) at 3.75, one tertiary proton (br m) at 2.80, a four proton envelope from 1.20 to 2.33, an sp²-bound methyl group at 1.82, and a methyl singlet at 1.47. Additionally, the absence of olefinic absorptions demands a tetrasubstituted double bond.

In a similar fashion, 88 was found to rapidly afford 113 under similar conditions. Tentative assignment to 113 was likewise based on its spectral properties. Again the ultraviolet spectrum indicates the presence of a styrene chromophore at 247 nm (ε 5,100). The nmr displays five aryl and one allyl protons (δ 7.25 and 3.58 respectively),
one bridgehead proton (2.63), five aliphatic hydrogens (1.25-2.33),
one sp²-bound methyl (1.73), and two sp³-bound methyls (1.04 and 0.96).

Ultimate confirmation for the structure of 113 (and thus, by
analogy 112) was derived by its synthesis via an unambiguous route
(Scheme VIII). 2-Phenyl-1,5,5-trimethylcyclopentadiene 123 was pre-
pared from d-camphor as described in the literature. Dichloroketene,
generated in situ, added as expected to the least hindered olefinic
bond to give dichlorocyclobutane 124. Dechlorination of 124 with
tri-n-butyltin hydride gave ketone 125 which upon Wolff-Kishner reduc-
tion provided 113. The details of the reaction sequence in Scheme
VIII are described in the Experimental Section.

Discussion

Although hydride shifts are known to occur in silver catalyzed
rearrangements, alkyl migrations appear to be unprecedented. Any
attempt to describe in detail the mechanism of bicycloheptene formation
must explain the following: First, why is only one of the isomers of
112 produced and is that isomer 112a or 112b? and, second in the for-
Scheme VIII (Continued)

\[ 120 \rightarrow 121 \rightarrow 122 \]

\[
\begin{align*}
\text{hv} & \quad C_6H_{12} \\
& \\
\text{Wolff-Kishner} & \\
& \\
123 &
\end{align*}
\]
mation of 113, why is no methyl migration to the benzylic carbon atom (to give 126) observed?

A possible mechanism (127 – 131) which satisfies both of these points involves initial oxidative addition of silver ion to the exo

\[
\begin{align*}
127 & \quad \rightarrow \quad 128 \quad \rightarrow \quad 129 \\
130 & \quad \rightarrow \quad 131
\end{align*}
\]

\[ R = \text{C}_6\text{H}_5 \]
\[ R = \text{CH}_3 \]
side of the bicyclopentane portion of 127 to form 128. Although 128 would be expected to open in two directions, the phenyl groups might tend to promote the formation of carbonium ion 129 because of residual π interaction between Ag⁺ and the benzene π cloud. Alternatively, simultaneous methyl migration and rupture of the carbon-silver bond would provide 130 directly. The possibility that the catalyst initially bonds to the hydrocarbon at one of the tricycloheptane edges should not be discounted. Accordingly, information bearing on the question of chemically-controlled methyl migration is still lacking.

Although precise kinetic data have not been obtained, the phenyltrimethyltricycloheptane rearrangement is recognized to be faster than that of the dimethyldiphenyl analogy. The causative factors underlying this aspect of tricyclo[3.2.0.2,4]heptane chemistry demands further more detailed investigation.
EXPERIMENTAL SECTION

General. Melting points are corrected and boiling points are uncorrected. Elemental analyses were performed by the Scandinavian Micro-analytical Laboratory, Herlev, Denmark. Ultraviolet spectra were recorded with a Cary 14 spectrometer, while nmr spectra were taken with Varian A-60A and HA-100 instruments. Infrared spectra were obtained with a Perkin-Elmer Model 137 Infracord spectrometer and mass spectra were measured with an AEI MS-9 mass spectrometer at an ionizing energy of 70 ev. The NOE experiments were carried out by Dr. Paul Demarco, Eli Lilly and Co., Indianapolis, Indiana. The dideu-terioethylene determinations were performed by Professor Gerhard Closs, University of Chicago, and the C13 nmr spectrum was obtained through the courtesy of Professor Ernest Wenkert, Indiana University.
EXPERIMENTAL PART IA

Preparation of Isopyrazoles

2,2-Dimethyl-1,3-diphenyl-1,3-propanedione (40a). Into a 1-l 3-necked round bottom flask equipped with stirrer and nitrogen inlet were added 300 ml of anhydrous dimethyl sulfoxide and 9.57 g (0.223 mol) of sodium hydride (56%, mineral oil dispersion). An addition funnel containing 50 g (0.223 mol) of 1,3-diphenyl-1,3-propanedione (22a) in 250 ml of dimethyl sulfoxide was attached and the contents were added over 1.5 hr. Methyl iodide (31.9 g, 0.223 mol) was added over 1.5 hr and the reaction stirred for 1 hr after which time another 9.57 g of sodium hydride was carefully added. This was followed 0.5 hr later by another 31.9 g of methyl iodide added over 0.5 hr. After stirring for 3 hr an additional 31.9 g of methyl iodide was added. After the solution had stirred overnight, it was poured into 600 ml of ether and the mixture was filtered to remove precipitated salts. The salts were washed with ether (3 x 250 ml) and the combined ether solution was washed with water (3 x 250 ml) and dried. Filtration and solvent removal followed by recrystallization from ethanol gave 30 g (53%) of the desired compound, mp 95-98°C (lit. mp 95-97°C); ir (CHCl₃) 6
2882, 1653, 1595, 1577, 1453, 1443, 952, and 943 cm⁻¹; δCDCl₃ 7.07-8.00 (m, 10, aryl) and 1.67 (s, 6, gem-dimethyl).

4,4-Dimethyl-3,5-diphenylisopyrazole (h1a). Into a flask equipped with magnetic stirrer were added 30 g (0.119 mol) of 2,2-dimethyl-1,3-diphenyl-1,3-propanedione (40a), 7.85 g (0.238 mol) of anhydrous hydrazine (97%), and 200 ml of carbon tetrachloride. A condenser was attached and the solution was refluxed for 12 hr. Upon cooling, the reaction mixture was washed with water (2 x 250 ml) and dried. Filtration, solvent removal, and recrystallization from carbon tetrachloride gave 21.9 g (74%) of off-white needles, mp 125-127°C (lit mp 127-128°C); IR (CHCl₃) 2874, 1504, 1486, 1453, 1433, 1340, 1003, 830, and 689 cm⁻¹; δCDCl₃ 7.25-8.17 (m, 10, aryl) and 1.68 (s, 6, gem-dimethyl).

2,2-Dimethyl-1-phenyl-1,3-butanedione (40b). Into a 1-l 3-necked flask equipped with stirrer and nitrogen inlet were added 300 ml of anhydrous dimethyl sulfoxide and 12.7 g (0.308 mol) of sodium hydride (57%, mineral oil dispersion). An addition funnel containing 50 g (0.308 mol) of 1-phenyl-1,3-butanedione (39b) in 250 ml of dimethyl sulfoxide was attached and the contents added over 1.5
hr. Methyl iodide (44 g, 0.308 mol) was added over 1.5 hr and the reaction stirred for 1 hr after which time another 12.7 g of sodium hydride was carefully added. This was followed 0.5 hr later by another 44 g of methyl iodide added over 0.5 hr. After stirring for 3 hr an additional 44 g of methyl iodide was added. After stirring overnight the solution was poured into 600 ml of ether and the mixture filtered to remove precipitated salts. The salts were washed with ether (3 x 250 ml) and the combined ether solution was washed with water (3 x 250 ml) and dried. Filtration and solvent removal, followed by distillation gave 54.8 g (92%) of a slightly colored liquid, bp 69-70° at 0.3 mm (lit bp 68° at 4 mm); ir (neat) 1706, 1667, 1255, 1120, 919, 876, 802, 775, and 709 cm⁻¹; δ^CDCl₃ 7.25-7.97 (m, 5, aryl), 2.08 (s, 3, methyl), and 1.47 (s, 6, gem-dimethyl).

3-Phenyl-4,4,5-trimethylisopyrazole (4lb). Into a flask equipped with magnetic stirrer were added 54.8 g (0.287 mol) of 1-phenyl-2,2-dimethyl-1,3-butanedione (40b), 9.5 g (0.287 mol) of anhydrous hydrazine (97%), and 200 ml of carbon tetrachloride. A condenser was attached and the solution was refluxed for 1 hr after which time an additional 9.5 g of hydrazine was added and the solution refluxed for an additional 2 hr. Upon cooling, the reaction mixture was washed with water (2 x 250 ml) and dried. Filtration, solvent removal, and fractional recrystallization ad nauseam from ether gave yellow-white
crystals. Recrystallization from ether at -70° gave 34.5 g (64%) of off-white crystals, mp 95-97° (lit mp 94-94.5°); ir (CHCl₃) 2890, 1577, 1458, 1144, 1007, and 833 cm⁻¹; δ<sub>CDCl₃</sub><sub>TMS</sub> 7.34-8.14 (m, 5, aryl), 2.22 (s, 3, methyl), and 1.39 (s, 6, gem-dimethyl).

3,3-Dimethyl-2,4-pentanedione (4Oc). Into a 1-ℓ 3-necked round bottom flask equipped with stirrer and nitrogen inlet were added 300 ml of anhydrous dimethyl sulfoxide and 42 g (1.0 mol) of sodium hydride (57%, mineral oil dispersion). An addition funnel containing 100 g (1.0 mol) of 2,4-pentanedione 32c in 250 ml of dimethyl sulfoxide was attached and the contents added over 1.5 hr. Methyl iodide, 143 g (1.0 mol), was added over 1.5 hr and the reaction mixture stirred for 1 hr after which time another 42 g of sodium hydride was carefully added. This was followed 1.5 hr later by another 143 g of methyl iodide added over 0.5 hr. After stirring for 3 hr an additional 143 g of methyl iodide was added. After the solution had stirred overnight it was poured into 600 ml of ether and the mixture was filtered to remove precipitated salts. The salts were washed with ether (3 x 250 ml) and the combined ether solution was washed with water (3 x 250 ml) and dried. Filtration and solvent removal followed by distillation gave 68 g (53%) of the desired product, bp 54-56° at 10 mm (lit bp 58° at 10 mm); ir (neat) 2950, 1721, 1701, 1353, 1285, 1109, and 961 cm⁻¹; δ<sub>CDCl₃</sub><sub>TMS</sub> 2.14 (s, 6, methyl) and 1.36 (s, 6, gem-dimethyl).
3,4,4,5-Tetramethylisopyrazole ($\text{H} \text{C}$). Into a flask equipped with magnetic stirrer were added 12.8 g (0.10 mol) of 3,3-dimethyl-2,4-pentanedione ($\text{H} \text{C}$), 4.95 g (0.15 mol) of anhydrous hydrazine (97%) and 200 ml of benzene. A condenser was attached and the solution was refluxed for 3 hr. Upon cooling, the water was separated off and the benzene layer dried. Filtration and solvent removal followed by distillation gave 9.74 g (78%) of the isopyrazole, bp 109-114$^\circ$ at 12 mm ($\text{liter}$ bp 109-112$^\circ$ at 12 mm): mp 43$^\circ$; ir (neat) 2933, 1645, 1577, 1458, 1422, and 1379 cm$^{-1}$; $\delta_{\text{CDCl}_3}^{\text{TMS}}$ 2.14 (s, 6, methyl) and 1.14 (s, 6, gem-dimethyl).
EXPERIMENTAL PART IB

The Tricyclo[3.2.0.0\(^{2,4}\)]hept-6-ene System

\[ \text{endo-7,8-Diaza-9,9-dimethyl-1,6-diphenyltricyclo[4.2.1.0\(^{2,5}\)]nona-3,7-diene} \]

To a cold (0\(^\circ\)) magnetically stirred solution of 3,5-diphenyl-4,4-dimethylisopyrazole (41a, 2.48 g, 0.01 mol) and cyclobutadieneiron tricarbonyl (42, 1.92 g, 0.01 mol) in 125 ml of acetone under nitrogen was added 27.4 g (0.05 mol) of ceric ammonium nitrate in portions during 30 min. The resultant slurry was poured into anhydrous ether and the precipitated cerium salts were removed by filtration. The filtrates from two identical runs were evaporated and the combined crude product was chromatographed on silica gel. Elution with ether-hexane (1:9) and recrystallization from hexane gave 4.09 g (68%) of 43 as white crystals, mp 153-154\(^\circ\) dec; ir (CHCl\(_3\)) 2924, 1605, 1495, 1464, 1443, 1389, 1372, 1290, 1030, and 998 cm\(^{-1}\); \(\lambda_{\text{isoctane max}}\) 346 sh (\(\epsilon 67\)) and 357 nm (94); \(\delta_{\text{CDCl}_3}^{\text{TMS}}\) 7.32-7.80 (m, 10, aryl), 6.05 (s, 2, olefinic), 3.88 (s, 2, allyl), 1.04 and 0.28 (s, 3 each, methyls).

Anal. Calcd for C\(_{21}\)H\(_{20}\)N\(_2\): C, 83.96; H, 6.71. Found: C, 83.94; H, 6.78.
anti-3,3-Dimethyl-2,4-diphenyltricyclo[3.2.0.0²⁴]hept-6-ene (44).

A. Photolysis of 43. A solution of 100 mg (0.33 mmol) of 43 in 2 ml of ether contained in a quartz test tube was irradiated with a 200W Hanovia lamp (Pyrex filter) housed in the usual Pyrex cooling jacket. The progress of the reaction, followed by thin layer chromatography, was deduced to be complete in 3 hr. Solvent removal afforded 90 mg (100%) of pure 44, mp 65.5-67.0°C; ir (CHCl₃) 1603, 1488, 1439, 1144, 1093, 1060, 812, 762, 747, 697, and 674 cm⁻¹; δCDCl₃ TMS (m, 10, aryl), 6.14 (d, J=1.5 Hz, 2, olefinic), 3.36 (d, J=1.5 Hz, 2, allyl), 1.44 and 0.88 (s, 3 each, methyls). The C¹3 nmr chemical shifts are in ppm from external CS₂ based on internal CCl₄ (96.5): C₃, 158.0; C₂, 139.2; C₁, 144.5; C₆, 50.9; 1-CH₃, 169.7; 2-CH₃, 176.7; aryl carbon attached directly to the tricycloheptene nucleus, 54.2; α-C, 63.5; η-C, 65.3; η-C, 66.9.


B. Low Temperature Photolysis of 43. Into an nmr tube were placed 30.2 mg (0.10 mmol) of 43, methylene chloride, and tetramethylsilane. After degassing, the tube was sealed. The irradiation was carried out by immersing the sealed nmr tube in an uncoated Pyrex Dewar flask containing Dry-Ice-isopropyl alcohol. The tube was positioned near a wall of the vessel for convenient exposure to the 200W lamp. Low temperature
nmr spectra (-60°) were recorded at various intervals of time: 0.5 hr, ca. 25% conversion to 44; 1.0 hr, ca. 50%; 1.75 hr, ca. 80%; 2.0 hr, ca. 100%. No other products were seen to develop.

7,7-Dimethyl-1,4-diphenylquadricyclane (45). A. Thermal Rearrangement of 44. A solution of 56 mg (0.21 mmol) of 44 in tetrachloroethylene (containing a small amount of TMS) was placed in an nmr tube and sealed in vacuo at -70°. NMR spectra were recorded after the entire tube had been immersed in a preheated furnace for varying periods of time.

After 4 hr at 100°, 44 was found to be transformed completely to quadricyclane 45. The tube was opened and the product (34 mg, 60%) was isolated as long white needles, mp 136.5-138.5°, after recrystallization from ethanol; ir (CHCl3) 1600, 1486, 1458, 1441, 1357, 919, 881, 847, and 814 cm⁻¹; λmaxisoctane 234 nm (ε 8900); δCDCl3TMS 7.29 (br s, 10, aryl), 2.02 (s, 4, cyclopropyl), and 1.03 (s, 6, methyis).


B. Thermal Degradation of 43. A solution of 201 mg (0.67 mmol) of 43 in 1 ml of tetrachloroethylene was sealed into an evacuated 12 mm Pyrex tube at -196°. The sealed tube was then placed in a mineral oil bath which had been preheated to 135°. After 1.5 hr, the tube was cooled, opened, and rinsed of contents. Solvent removal at reduced pressure, followed by two recrystallizations from ethanol gave 44 mg (46.5%) of
quadricyclane \( \text{h}_5 \), mp 136.5-138.5°, which was identical to the material isolated above.

For the purpose of comparing the thermal behavior of \( \frac{1}{2} \) and \( \frac{1}{4} \), ca. 50 mg of each substance in deuteriochloroform solution was sealed into evacuated nmr tubes. These tubes were placed adjacent to each other in the furnace and heated at 99° for 1 hr. The azo compound gave no evidence of conversion to \( \frac{1}{4} \), whereas the tricycloheptene had undergone 37% conversion to this product.

7,7-Dimethyl-1,4-diphenylnorbornadiene (46). Initial studies were performed with a 60 mg sample of \( \frac{1}{2} \) in tetrachloroethylene solution sealed in an evacuated nmr tube. After heating at 135° for up to several hr, only the presence of quadricyclane \( \frac{45}{45} \) was detected. Subsequent heating of the tube at 175° for 3.5 hr revealed essentially complete conversion to \( \frac{46}{46} \). When the experiment was continued at 200° (~30 hr), \( \frac{46}{46} \) was seen to rearrange to \( \frac{47}{47} \) and then \( \frac{48}{48} \).

In a typical preparative scale experiment, 201 mg (0.67 mmol) of \( \frac{43}{43} \) in 1.8 ml of tetrachloroethylene sealed in an evacuated length of 12 mm Pyrex tubing was heated at 175° for 5 hr. After cooling, the solvent was removed under reduced pressure and the residual solid was recrystallized twice from ethanol to afford 102 mg (50%) of \( \frac{46}{46} \) as white crystals, mp 188-190°; ir (CHCl₃) 1603, 1493, 1439, 1377, 1361, 1321, 1004, 972, and 911 cm⁻¹; \( \lambda_{\text{max}} \text{isoctane} \) 253 (ε 670), 258 (695), and 266 nm.
(485); $^1$CDCl$_3$ 7.40 (br s, 10, aryl), 7.07 (s, h, olefinic), and 0.83 (s, 6, methyls).

**Anal.** Calcd for C$_{21}$H$_{20}$: C, 92.60; H, 7.40. Found: C, 92.30; H, 7.56.

Photolysis of 46. A solution of 50 mg (0.184 mmol) of 46 in 15 ml of hexane was irradiated with a 200W Hanovia lamp using quartz optics. After a 1-hr period of irradiation, 33% conversion to 45 had been achieved (nmr analysis). Because continued irradiation resulted in gradual polymer formation, the 1-hr reaction time was considered optimal. The product was identical to quadricyclane 45.

7,7-Dimethyl-2,5-diphenylnorcaradiene (48). As noted above, pilot nmr studies revealed that heating of 46 for several hours at 200° led via 47 to 48. Preparative scale isolation of 48 was achieved by heating 102 mg (0.33 mmol) of 43 in an evacuated tube at 200° for 4 hr.

The residue was recrystallized from ethanol to furnish 33 mg (28%) of 48 as bright yellow crystals, mp 159-161°; ir (CHCl$_3$) 1587, 1481, 1437, 1377, 1364, 894, and 692 cm$^{-1}$; $^1$H-isooctane 242 ($e$ 17,600) and 357 nm (14,000); $^1$CDCl$_3$ 7.20-7.80 (m, 10, aryl), 6.55 (br s, 2, olefinic), 2.38 (br s, 2, cyclopropyl), and 1.12 (s, 6, methyls).

**Anal.** Calcd for C$_{21}$H$_{20}$: C, 92.60; H, 7.40. Found: C, 92.68; H, 7.37.
Ozonolysis of 48. A solution of 85 mg (0.31 mmol) of 48 in 30 ml of absolute methanol was ozonized at -70° using 12.4 meq of ozone. To the resulting solution was then added a mixture of 2 ml of absolute methanol, 0.1 ml of glacial acetic acid, and 0.2 g of sodium iodide. Stirring for 4 hr was followed by dilution with 100 ml of water. Sodium bisulfite was added until the iodine color disappeared and then sodium carbonate was introduced to render the solution alkaline. Extraction with ether (3 x 125 ml) and drying of the combined extracts gave after evaporation a mixture of white crystals in a yellowish cöl. Chromatography on silica gel and recrystallization from carbon tetrachloride afforded 28 mg (33%) of 49 as white crystals, mp 136-137°; ir (CHCl₃) 1672 cm⁻¹; λmax CH₃OH 247 (ε 24,200) and 275 sh nm (4,300); δCDCl₃ 7.38-6.08 (m, 10, aryl), 2.80 (s, 2, cyclopropyl), 1.50 and 1.40 (s, 3 each, methyls).


Photolysis of 48. Into an nmr tube were placed 69 mg (0.25 mmol) of 48 and 0.5 ml of deuteriochloroform/TMS. The solution was irradiated for various periods of time with a 200W Hanovia lamp (Pyrex optics) until the nmr showed that 48 was no longer present (ca. 45 min). The nmr spectrum
of the major product was identical with that observed earlier for the first-formed thermal rearrangement product of \( \text{H}_6 \).

Attempts to obtain \( \text{H}_7 \) sufficiently pure for elemental analysis were not successful; \( \lambda_{\text{max}}\) isoctane 238 (ε 20,800) and 303 nm (11,100);

\[ \delta_{\text{CDCl}_3} 7.12-7.63 (m, 10, aryl), 6.83 (m, /J/_{3,5}=1.7 \text{ Hz}, /J/_{2,3}=7.5 \text{ Hz}, /J/_{3,6}=0.7 \text{ Hz}, 1, H_3), 6.40 (m, /J/_{2,5}=0.5 \text{ Hz}, /J/_{5,6}=11.0 \text{ Hz}, 1, H_8), 6.20 (m, 1, H_2), 5.37 (m, 1, H_6), \text{ and } 1.03 (s, 6, methyls), \text{ with most of the absorptions showing long-range coupling.} \]

A small amount of \( p \)-terphenyl, mp 210-212° (lit mp 213°) was also isolated from the photolysate. The uv, nmr, and ir spectra were identical with those of an authentic sample.

\[ \text{endo-7,8-Diaza-1-phenyl-6,9,9-trimethyltricyclo}[4.2.1.0^{2,5}]\text{nona-3,7-diene (52).} \]

Treatment of a cold (0°) solution of 1.86 g (0.01 mol) of 3-phenyl-4,5,5-trimethylisopyrazole (4lb) and 1.92 g (0.01 mol) of cyclo-butadieneiron tricarbonyl (42) in 125 ml of acetone with 27.4 g (0.05 mol) of ceric ammonium nitrate in portions during 30 min gave rise, after the previously described workup (two identical runs combined at this point), chromatography on silica gel, and recrystallization from
ethanol, to 1.30 g (27.3%) of 52 as white crystals, mp 103-105°C; ir (CHCl₃) 2874, 1603, 1493, 1468, 1447, 1389, 1370, 1356, 1091, and 989 cm⁻¹; λ_max (isoctane) 324 sh (e 31), 347 sh (100), and 356 nm (154); δ(CDCl₃) 7.35-7.83 (m, 5, aryl), 6.07 (m, 2, olefinic), 3.68 (d, /J/=3.5 Hz, 1, allyl), 3.08 (d, /J/=3.5 Hz, 1, allyl), 1.67 (s, 3, bridgehead methyl), 0.93 and 0.42 (s, 3 each, methyls), the latter of which is positioned above the azo linkage.


anti-2-Phenyl-3,3,4-trimethyltricyclo[3.2.0.0²,⁴]hept-6-ene (53). A solution of 200 mg (0.85 mmol) of 52 in 3 ml of ether contained in a quartz test tube was irradiated with a 200W Hanovia lamp source (Pyrex filter). After 2.5 hr, thin-layer chromatography showed the absence of starting material. Solvent removal under reduced pressure gave a quantitative yield of 53. Molecular distillation afforded 150 mg of a colorless liquid, bp 44°C at 0.01 mm; ir (neat) 2865, 1608, 1493, 1445, 1295, 810, 776, 756, and 700 cm⁻¹; δ(CDCl₃) 7.17 (br m, 5, aryl), 6.57 (m, 1, olefinic), 6.27 (m, 1, olefinic), 3.17 (m, 1, allyl), 2.97 (m, 1, allyl), 1.30 (s, 3, bridgehead methyl), 1.23 and 0.78 (s, 3 each, methyls).

Pyrolysis of JG. Pilot nmr experiments revealed the following information: 105°, 1 hr, no decomposition; 132°, 1 hr, partially converted to 53 under way; 158°, 1 hr, no 52, some 53, and four new products; 162°, 20 hr, only the new products (times are cumulative). For preparative purposes, a solution of 238 mg (1.0 mmol) of JG in 1 ml of tetrachloroethylene was heated at 175° for 18 hr (evacuated tube) and the product mixture was subjected to vpc (125°, 5% XE-1150 on Chromosorb G). The first peak (14%) proved to be an inseparable 1:1 mixture of quadricyclane 54 and norbornadiene 55. For 54, \( \delta_{\text{CDCl}_3} \) 7.18 (s, 5, aryl), 1.80 and 1.55 (t, \( J=1.7 \) Hz, 2 each, cyclopropyls), 0.93 (s, 3, bridgehead methyl), and 0.85 (s, 6, methyls), and 0.85 (s, 6, methyls). For 55, \( \delta_{\text{CDCl}_3} \) 7.35 (m, 5, aryl), 6.84 and 6.58 (d, \( J=5.5 \) Hz, 2 each, olefinic), 1.28 (s, 3, bridgehead methyl), and 0.88 (s, 6, bridge methyls).

The second component (69%) was found to be JG; ir (neat) 2825, 1603, 1445, 1420, 1350, 1335, 1328, 830, 762, 735, and 693 cm\(^{-1}\); \( \lambda_{\text{isoctane}}^{\text{max}} \) 225 sh (e 10,800) and 283 nm (5,600); \( \delta_{\text{CDCl}_3} \) 7.00-7.33 (m, 5, aryl), 6.42-6.58 (m, 2, olefinic), 6.05-6.37 (m, 2, olefinic), 1.02 (s with additional small long-range coupling, 3, C1-methyl), and 0.97 (s, 6, C7-methyls).
Anal. Calcd for C_{10}H_{18}: C, 91.37; H, 8.63. Found: C, 91.24; H, 8.69.

The third component (17%) was \textit{g8}; ir (neat) 2950, 1600, 1493, 819, 775, 747, 703, and 694 cm\(^{-1}\); \(\lambda_{\text{isoctane max}}^{\text{max}}\) 237 (e 16,600) and 300 nm (5,600); \(\delta_{\text{CDCl}_3}\) 7.20-7.55 (m, 5, aryl), 6.73 (br d, /J/=7.0 Hz, 1, olefinic), 6.17 (br d, /J/=7.0 Hz, 1, olefinic), 5.28 (d, /J/=10.0 Hz, 1, olefinic), 1.97 (br s, 3, methyl), and 1.05 (s, 6, \textit{gem}-dimethyl).

Anal. Calcd for C_{18}H_{38}: C, 91.37; H, 8.63. Found: C, 91.25; H, 8.55.

A shorter term pyrolysis (2 hr) of \textit{g2} (250 mg, 1.05 mmol) at a lower temperature (152\(^{\circ}\)) and vpc separation of the products gave the following results. The first fraction consisted of \textit{g2} (9.9 mg, 9.1%). The second fraction (37.4 mg, 38%) was a mixture of quadricyclane \textit{g4} (16%), norbornadiene \textit{g5} (7%), and bicyclo[3.2.0]heptadiene \textit{g6} (15%). Although reproducible integrations of adequately separated peaks could be attained on small-sized injections of this mixture into the gas chromatograph, attempts to isolate pure samples were not successful. The third fraction (52.4 mg, 53%) was \textit{g7}.
Photoisomerization of 57. A solution of 48.6 mg (0.23 mmol) of 57 in CDCl₃/TMS contained in an evacuated nmr tube was irradiated (200W Hanovia lamp) until the nmr spectrum revealed the total disappearance of starting material (12 hr). When the lone volatile product was purified by vpc (101°, 5% XF-1150 on Chromosorb G), there was obtained 16.3 mg (33%) of 56 identical with the pyrolysis product of the same structure; ir (neat) 3012, 2950, 1603, 1493, 1472, 1453, 1439, 1379, 1366, 1357, 1285, 894, 856, 840, 765, 747, and 698 cm⁻¹; λisoctane 256 sh nm (ε 5,100); δCDCl₃/ TMS 7.27 (s, 5, aryl), 6.52 (d, /J/=2.5 Hz, 1, olefinic), 6.23 (dd, /J/=2.5 and 1.0 Hz, 1, olefinic), 5.80 (d, /J/=2.5 Hz, 1, olefinic), 3.20 (m, 1, allyl), 1.36, 1.08, and 1.07 (s, 3 each, methyls).


Thermal Rearrangement of 56. A solution of 56 in CDCl₃/TMS sealed in an evacuated nmr tube was heated at various temperatures with the following results: 100°, 1 hr, no reaction; 140°, 1 hr, no reaction; 150° 1.5 hr, no reaction; 160°, 1 hr, no reaction; 170°, 1 hr, approximately 50% conversion to 57.

In addition, heating a sample of 57 under similar conditions at 172° for 60 hr resulted in no reaction.
Thermal Rearrangement of 52. A solution of 52 (25 mg) in CDCl₃/TMS in an evacuated nmr tube was heated at 154°C for 2 hr. Quantitative integration of the nmr spectra gave the following product composition: 54 (18%), 55 (9%), and 57 (46%).

Cycloaddition of 57 and N-Phenyltriazolinenedione (59). A solution of 26.9 mg (0.128 mmol) of 57 and 22.8 mg (0.13 mmol) of 59 in 15 ml of acetone was stirred overnight at room temperature. Evaporation of the solvent and silica gel chromatography (elution with chloroform) gave 60 in high yield (45 mg). This adduct proved to be unstable upon heating or upon standing in solution, being subject to facile retro (4+2) cycloaddition. The nmr spectrum showed no cyclopropyl protons: δCDCl₃/TMS 7.45 (br s, 5, aryl), 7.55 (br s, 5, aryl), 6.43 (m, 2, olefinic), 5.02 (m, 2, bridgehead), 1.44, 1.38, and 0.81 (s, 3 each, methyls).

endo-7,8-Diaza-1,6,9,9-tetramethyltricyclo[4.2.1.0²,5]nona-3,7-diene (62). Portionwise treatment of a cold (0°C) solution of 1.24 g (0.01 mol) of freshly prepared 3,4,4,5-tetramethylisopyrazole (41c) and 1.92 g (0.01 mol) of cyclobutadiene-iron tricarbonyl (42) in 125 ml of acetone with ceric ammonium nitrate was terminated when further addition caused no additional evolution of carbon monoxide. Approxim
mately 20 g of ceric salt was required and the duration of addition caused no additional evolution of carbon monoxide. Approximately 20 g of ceric salt was required and the duration of addition was 30 min. The resultant slurry was poured into 400 ml of ether, filtered to remove precipitated salts, washed with water (3 x 250 ml), dried, filtered, and evaporated to give a mixture of crystals in a red oil. Preparative scale vpc purification (130°, 10% SE-30 on Chromosorb W) afforded 519 mg (29.4%) of 62 as white crystals, mp 57.5-58.5°; ir (CHCl₃) 1466, 1439, 1387, 1372, 1277, 957, 901, and 851 cm⁻¹; λ max isoctane 348 sh (ε 138) and 356 nm (230); δ°CDCl₃ 6.05 (s, 2, olefinic), 2.90 (s, 2, allyl), 1.58 (s, 6, bridgehead methyls), 0.82 and 0.54 (s, 3 each, bridge methyls).

**Anal.** Calcd for C₁₁H₁₆N₂: C, 74.95; H, 9.15. Found: C, 74.85; H, 9.04.

**anti-2,3,3,4-Tetramethyltricyclo[3.2.0.0²₄]hept-6-ene (63).** A solution of 75 mg (0.426 mmol) of 62 in 2 ml of pentane contained in a test tube was irradiated with a 200W Hanovia lamp (Pyrex optics). The progress of the reaction was monitored by vpc and shown to be complete after 1.5 hr. Isolation by preparative scale vpc (95°, 10% SE-30 on Chromosorb W) furnished 25 mg (33%) of 63 as a highly volatile liquid; ir (CHCl₃) 1550, 1445, 1348, 1295, 1285, 1188, and 775 cm⁻¹; δ°CDCl₃ 6.50 (m, 2, olefinic), 2.84 (m, 2, allyl), 1.03 (s, 9, methyls), and 0.93 (s, 3, methyl).
Anal. Calcd for C_{11}H_{16}: C, 89.12; H, 10.88. Found: C, 89.26; H, 10.92.

Pyrolysis of 62. A sealed tube containing 176 mg (1.0 mmol) of 62 was heated in a furnace at 200° for 4 hr. The resulting product mixture was separated into its components by preparative scale vpc (98°, 10% SE-30 on Chromosorb W). The first fraction (15 mg, 13.3%) was found to be 1,2,2,3-tetramethylibicyclo[3.2.0]hepta-3,6-diene (64); ir (neat) 3021, 2941, 1451, 951, 894, 850, 824, 754, and 742 cm^{-1}; \( \lambda_{\text{max}} \) \text{isoctane} end absorption only; \( \delta_{\text{CDCl}_3} \) 6.46 (d, \( /J/=3.0 \text{ Hz}, 1, \text{H}_7 \)), 6.13 (dd, \( /J/=3.0 \text{ and } 1.2 \text{ Hz}, 1, \text{H}_8 \)), 5.45 (br m, \( /J/=2.3 \text{ Hz}, 1, \text{H}_4 \)), 3.01 (br m, 1, \text{H}_5 \), 1.58 (m, \( /J/=1.5 \text{ Hz}, 3, \text{C}_3\)-methyl), 1.29 (s, 3, methyl), and 0.97 (s, 6, methyls).

Anal. Calcd for C_{11}H_{16}: C, 89.12; H, 10.88. Found: C, 89.15; H, 10.85.

The second fraction (78.1 mg, 69.4%) was 1,6,7,7-tetramethylcycloheptatriene (65); ir (neat) 2933, 1443, 1387, 1370, 1355, 829, and 736 cm^{-1}; \( \delta_{\text{CDCl}_3} \) 6.38 (m, 2, \text{H}_3 and \text{H}_4), 6.13 (m, 2, \text{H}_2 and \text{H}_5), 1.95 (br s, 6, =C<CH_3) and 1.03 (s, 6, gem-dimethyl). Double irradiation of the \( \delta \) 1.95 absorption resulted in collapse of the 6.13 multiplet to a pattern identical to that seen at 6.38.

The third fraction (19.4 mg, 17%) was unreacted starting material.

Thermal Rearrangement of 63. A solution of 15 mg of 63 in CDCl₃/TMS contained in an evacuated nmr tube was heated at 144° for varying periods of time. The appearance of 64 and 65 was assessed by integration of the nmr spectra: 2 hr, 64 (38%) and 65 (62%); 6 hr, 64 (62%) and 65 (58%); 12 hr, 64 (43%) and 65 (57%).

In order to assess the thermal stabilities of these two products, the following experiments were conducted. Heating of 64 at 150° for 8 hr (neat) led to no reaction; after 1 hr at 200° (Cl₂C=CCl₂ solution), however, 5% conversion to 65 was seen. In a separate study, a solution of 65 in CDCl₃ was found to be unchanged after 14 hr at 200°.

Photorearrangement of 65. A solution of 40 mg of 65 in CDCl₃/TMS contained in an nmr tube was irradiated at room temperature for various periods of time with a 200W Hanovia lamp until the nmr revealed the absence of starting material (12 hr). At this point, the spectrum was identical to that of 64.
Cycloaddition of 65 and N-Phenyltriazolinodione (52). A solution of 29.6 mg (0.20 mmol) of 65 and 35 mg (0.20 mmol) of 52 in 15 ml of acetone was stirred at room temperature until colorless (2 hr). Evaporation of the solvent and chromatography on silica gel (elution with chloroform) gave 66 in high yield (64 mg). As with 60, this adduct was unstable to heat and upon standing in solution (development of pink color). The nmr spectrum showed no cyclopropyl hydrogens; δ_CDCl_3 7.46 (br m, 5, aryl), 6.32 (m, 2, olefinic), 4.90 (m, 2, bridgehead), 1.28 (s, 6, methyls), 1.20 and 1.05 (s, 3 each, gem-dimethyl).
EXPERIMENTAL PART II

The Tricyclo[3.2.0.0^2,4]heptane System

endo-7,8-Diaza-9,9-dimethyl-1,6-diphenyltricyclo[4.2.1.0^5]nona-7-ene (83). To a magnetically stirred mixture of 12.93 g (66.6 mmol) of potassium azodicarboxylate and a solution of 1.00 g (3.33 mmol) of 4 in 125 ml of absolute methanol in a round bottom flask equipped with drying tube and serum cap was slowly injected 12.02 g (200 mmol) of glacial acetic acid in 2 ml portions over a 2-hr period. Upon disappearance of the yellow color (ca. 1 hr), the reaction mixture was poured into a separatory funnel, 250 ml of water was added, and the precipitated product was extracted into ether by extraction (3 x 200 ml). The combined extracts were neutralized with saturated sodium bicarbonate solution, washed with saturated sodium chloride solution, and dried. Filtration, evaporation, and recrystallization from pentane gave 0.91 g (90%) of 83 as a white powder, m, 101.5-103° dec; ir (CHCl₃) 2999, 1605, 1495, 1468, 1389, 1372, and 1022 cm⁻¹; λₘₐₓ (isoctane, 350 nm (ε 100) and 362 nm (125); δ(CHCl₃) 7.38-8.00 (m, 10, aryl), 3.60 (m, 2, cyclobutanes), 1.82 (m, 4, cyclobutanes), 0.83 and 0.22 (s, 3 each, methyls).

anti-3,3-Dimethyl-2,4-diphenyltricyclo[3.2.0,0²,4]heptane (84). A.

Photolysis of 83. A solution of 302.7 mg (1.001 mmol) of 83 in 2 ml of ether contained in a quartz test tube was irradiated with a 200W Hanovia lamp housed in the usual Pyrex cooling jacket. The progress of the reaction, monitored by thin layer chromatography, was deduced to be complete in 2.5 hr. Solvent removal followed by molecular distillation afforded 237 mg (86%) of 84 as a viscous colorless liquid, bp 75° at 0.1 mm; ir (neat) 2965, 1603, 1490, 1441, 776, 747, and 702 cm⁻¹; δCDCl₃ 7.28 (br s, 10, aryl), 2.89 (m, 2, cyclobutanes), 2.12 (m, 4, cyclobutanes), 1.27 and 0.82 (s, 3 each, methyls).

Anal. Calcd for C₂₁H₂₂: C, 91.92; H, 8.08. Found: C, 91.98; H, 8.11.

B. Diimide Reduction of 44. To a magnetically stirred mixture of 2.13 g (11.0 mmol) of potassium azodicarboxylate and a solution of 150 mg (0.552 mmol) of 44 in 40 ml of absolute methanol in a round bottom flask equipped with a drying tube and serum cap was slowly injected 2.00 g (33.0 mol) of glacial acetic acid in 0.25 ml portions over a 1-hr period. Upon disappearance of the yellow color (ca. 1 hr) the reaction mixture was poured into a separatory funnel, 150 ml of water was added and the product taken into ether by extraction (3 x 200 ml). The combined ether extracts were neutralized with saturated sodium bicarbonate solution, washed with saturated sodium chloride solution
and dried, filtration and evaporation followed by molecular distillation afforded 125 mg (82%) of \( \text{84} \) which was identical to the material isolated above.

5,5-Dimethyl-1,4-diphenylcyclopenta-1,3-diene (85). Initial studies were performed with a 50 mg sample of \( \text{83} \) in deuteriochloroform/TMS solution sealed in an evacuated nmr tube. After heating at 100° for 5 hr, partial conversion to \( \text{84} \) was observed; after heating at 140° for 3 hr, complete conversion to \( \text{84} \) was found. Subsequent heating of the tube at 210° for 3 hr revealed complete conversion to \( \text{85} \) and ethylene (86).

In a typical preparative scale experiment, 100 mg (0.331 mmol) of \( \text{83} \) in 1.5 ml of tetrachloroethylene, sealed in an evacuated length of 12 mm Pyrex tubing was heated at 209° for 7 hr. After cooling, the tube was opened, the solvent was removed at reduced pressure and the residual solid was sublimed, 57° at 0.1 mm, to give 68 mg (84%) of a yellow-white solid. Recrystallization from ether afforded the pure product as long white needles, mp 96-98°; ir (CHCl₃) 1603, 1490, 1460, 1443, 850, and 693 cm⁻¹; \( \lambda_{\text{max}} \) cyclohexane 232 (ε 9,000) and 330 nm (15,400); \( \delta_{\text{TMS}} \) (CDCl₃) 7.50 (m, 10, aryl), 6.77 (s, 2, olefinic), and 1.65 (s, 6, methyls).

Ozonolysis of 85. A solution of 151 mg (0.614 mmol) of 85 in 200 ml of absolute methanol was ozonized at -70° until the uptake of ozone ceased. To the resulting solution was then added a mixture of 4 ml of absolute methanol, 0.2 ml of glacial acetic acid, and 0.45 g of sodium iodide. Stirring for 4 hr was followed by dilution with 500 ml of water. Sodium bisulfite was added until the iodine color disappeared and then sodium carbonate was introduced to render the solution alkaline. Extraction with ether (3 x 250 ml) and drying of the combined extracts gave, after evaporation, 40 mg (26%) of crude ketone. Recrystallization from ethanol gave the pure ketone, mp 95-97°, which was found to be identical to 40a (vide supra).

endo-7,8-Diaza-9,9-dimethyl-1,6-diphenyltricyclo[4,2,1,0^2,5]nona-7-ene-cis,exo-3,4-d_2 (83b). The preparation of the cis,exo-dideuterio compound 83b was accomplished in a manner analogous to that of 83.

Treatment of 1.00 g (0.00333 mol) of 43 in 100 ml of ethanol-0-d with potassium azodicarboxylate and acetic acid-0-d resulted in 80% conversion to product. This mixture was recycled; in all, a 110-fold excess of potassium azodicarboxylate was required. Workup and recrystallization from pentane gave 0.740 g (73%) of product, mp 102-104°; ir (CHCl_3) 2874, 2174, 1603, 1428, 1462, 1441, 1383, 1366, 1300, and 1018 cm^{-1}; _{2}^{6}^1{DCl_TMS} 7.38-8.00 (br m, 10, aryl), 3.57 (m, 2), 1.73 (m, 2), 0.83 and 0.22 (s, 3 each, methyls). Analysis of the mass spectrum indicated
the following: diprotio compound 0%, monodeuterio compound 9%, and dideuterio compound 91%.

\[ \text{anti-3,3-Dimethyl-2,4-diphenyltricyclo[3.2.0.0^{2,4}]heptane-cis,exo-d}_p \] (84b). A solution of 200 mg (0.66 mmol) of 83b in 3 ml of ether contained in a quartz test tube was photolyzed in a manner analogous to the diprotio compound. The reaction was terminated after 2.5 hr. Solvent removal and molecular distillation afforded 144 mg (79%) of 84b, bp 75° at 0.1 mm; ir (neat) 2865, 2174, 1603, 1490, 1441, 753, and 699 cm\(^{-1}\); \(\delta^{\text{CDCl}_3}\) 7.25 (br s, 10, aryl), 2.90 (m, 2), 2.00 (m, 2), 1.27 and 0.80 (s, 3 each, methyls). Analysis of the mass spectrum indicated the following: diprotio compound 0%, monodeuterio compound 9%, and dideuterio compound 91%.

Pyrolyses of 83b and 84b. In a typical experiment, ca. 50 mg of either 83b or 84b was placed in a pyrolysis apparatus designed for this purpose and shown in Figure II. The apparatus was placed on a high vacuum line and the valve closed when the pressure was 0.2 \(\mu\). Placement of the pyrolysis chamber in an oven maintained at 210° for 4 hr was followed by removal, cooling, and addition of 0.3 ml of carbon tetrachloride/10% TMS to the nmr tube. The apparatus was again placed on the high vacuum line, liquid nitrogen was placed under both the nmr tube and the pyrolysis chamber and the whole apparatus again evacuated to 0.2 \(\mu\). Closure of the valve to the manifold, followed
Figure II - Dideuterioethylen Transfer Apparatus
by removal of cooling agent from under the pyrolysis chamber, resulted in speedy transfer of 1,2-dideuterioethylene (66b) to the nmr tube. The nmr tube was then sealed under vacuum and sent for analysis.

endo-7,8-Diaza-1-phenyl-6,9,9-trimethyltricyclo[4.2.1.02,5]nona-7-ene (87). To a magnetically stirred mixture of 19.4 g (0.10 mol) of potassium dicarboxylate and solution of 1.19 g (0.005 mol) of 52 in 250 ml of absolute methanol contained in a round bottom flask equipped with drying tube and serum cap was slowly injected 18.0 g (0.30 mol) of glacial acetic acid in 1 ml portions over a 1-hr period. The reaction mixture was stirred for an additional hour after which time the yellow color had disappeared. The white suspension was poured into a separatory funnel, 250 ml of water was added, and the precipitated product was taken into ether by extraction (2 x 250 ml). The combined extracts were neutralized with saturated sodium bicarbonate solution (2 x 250 ml), washed with saturated sodium chloride solution (2 x 250 ml), and dried. Filtration and solvent removal gave a white solid in a yellow oil. The oil was removed under high vacuum and the solid sublimed (56° at 0.05 mm) to give 1.14 g (95%) of 87 as a white solid. Recrystallization of a small sample from hexane gave the pure compound, mp 72-74°; ir (CHCl₃) 2924, 1605, 1488, 1462, 1441, 1387, 1366, 1130, and 1013 cm⁻¹; λmax (cyclooctane) 352 sh (ε 78) and 363 nm (144); δCDCl₃ 7.30-7.92 (br m, 5, aryl), 3.08-3.63 (br m, 1), 2.53-3.00 (br m, 1), 1.66-1.88
(m, 4), 1.68 (s, 3, bridgehead methyl), 0.73 and 0.36 (s, 3 each, gem-dimethyl).


**anti-2-Phenyl-3,3,4-trimethyltricyclo[3.2.0.0²⁴]heptane (88).** A solution of 140 mg (1.00 mmol) of 87 in 3 ml of ether contained in a quartz test tube was irradiated with a 200W Hanovia lamp (Pyrex optics). After 2.5 hr, thin layer chromatography showed the absence of starting material. Solvent removal followed by molecular distillation afforded 185 mg (87%) of 88 as a colorless liquid, bp ambient temperature at 0.04 mm; ir (neat) 2907, 1603, 1490, 1449, 1381, 1368, 764, and 698 cm⁻¹; δ<sup>CDCl₃</sup><sub>TMS</sub> 7.17 (br s, 5, aryl), 1.57-2.83 (envelope, 6, cyclobutanes), 1.33 (s, 3, bridgehead methyl), 1.06 and 0.79 (s, 3 each, gem-dimethyl).

**Anal. Calcd for C₁₆H₂₀: C, 90.50; H, 9.50. Found: C, 90.70; H, 9.46.**

Pyrolyses of 87 and 88. Pilot nmr experiments performed on 87 provided the following information: 100°, 1 hr, no reaction; 140°, 3 hr, virtually completed conversion to 88; 210°, 3 hr, several new products.

For preparative purposes, a sealed evacuated tube containing 240 mg (1.00 mmol) of 87 was heated at 210° for 4 hr and the resulting product mixture subjected to vpc (150°, 10% SE-30 on Chromosorb W).
The first fraction (80 mg, 55%) was found to be 1-phenyl-4,5,5-trimethylcyclopenta-1,3-diene (89); ir (neat) 3012, 2924, 1595, 1534, 1486, 1453, 1435, 1351, 1020, 826, 757, and 689 cm\(^{-1}\); \(\lambda_{\text{max}}\) isoctane 222 sh (\(\epsilon 6,000\)) and 306 nm (11,200); \(\delta_{\text{CDCl}}\) \(^3\) 7.08-7.65 (br m, 5, aryl), 6.60 (d, \(/J/ = 2.3\) Hz, 1, H\(_2\)), 6.00 (dd, \(/J/ = 1.2\) Hz, 1, H\(_3\)), 1.90 (d, 3, =C–CH\(_3\)), and 1.19 (s, 6, gem-dimethyl).

**Anal.** Calcd for C\(_{14}\)H\(_{18}\): C, 91.25; H, 8.75. Found: C, 91.41; H, 8.72.

The second fraction (67 mg, 45%), obtained as an inseparable mixture, was found to contain 90 (~ 15%). Although separable upon small sized injections, these substances could not be separated when a preparative scale was employed. The combined nmr spectrum (in CDCl\(_3\)) was in excellent agreement with the proposed assignments. For 90; \(\delta_{\text{CDCl}}\) \(^3\) 5.42 (t, \(/J/ = 7.2\) Hz, 1, olefinic), 5.00 (br s, 1, exocyclic methylene), 4.80 (br s, 1, exocyclic methylene), and 1.17 (s, 6, gem-dimethyl). For 91; \(\delta_{\text{CDCl}}\) \(^3\) 5.92 (m, 1, olefinic), 5.70 (br m, 1, olefinic), 1.78 (br s, 3, =C–CH\(_3\)), and 1.14 (s, 6, gem-dimethyl).

In a comparative experiment, nmr pyrolysis of 88 indicated the following: 100\(^\circ\), 1 hr, no reaction; 140\(^\circ\), 3 hr, no reaction; 210\(^\circ\), 3 hr, the same products as above.
endo-7,8-Diaza-1,6,9,9-tetramethyltricyclo[4.2.0.0^{2,5}]nona-7-ene (22).

To a magnetically stirred mixture of 25 g (0.128 mol) of potassium azodicarboxylate and a solution of 1.13 g (0.0064 mol) of crude 62 in 125 ml of absolute methanol in a round bottom flask equipped with drying tube and serum cap, was slowly injected 23.1 g (0.385 mol) of acetic acid in 2 ml portions over a 1-hr period. Upon disappearance of the yellow color, the reaction mixture was poured into a separatory funnel, 125 ml of water was added, and the product taken into ether by extraction (3 x 125 ml). The combined extracts were neutralized with saturated sodium bicarbonate solution (2 x 125 ml), washed with water (2 x 125 ml) and saturated sodium chloride solution (2 x 125 ml), and dried. Filtration, followed by solvent removal by distillation through an efficient column, gave a concentrated ether solution of product. Preparative scale vpc purification (125°, 10% SE-30 on Chromosorb W) gave 606 mg (53%) of 22 as white crystals, mp 33.0-33.5°; ir (CHCl₃) 2890, 1462, 1437, and 1376 cm⁻¹; λ_max ¹isoctane 347 sh (ε 97) and 362 nm (246); δ_CDCl₃ 2.45-2.73 (br m, 2, cyclobutane hydrogens), 1.50-1.83 (br m, 4, cyclobutane hydrogens buried under bridgehead methyls), 1.59 (s, 6, bridgehead methyls), 0.59 and 0.46 (s, 3 each, bridge methyls).

Anal. Calcd for C_{11}H_{18}N₂: C, 74.11; H, 10.18. Found: C, 74.20; H, 10.36.
anti-2,3,3,4-Tetramethyltricyclo[3.2.0.0\(^2,4\)]heptane (\(\text{**2**}\)). A solution of 89 mg (0.50 mmol) of \(\text{**2**}\) in 1 ml of ether contained in a test tube was irradiated with a 200W Hanovia lamp (Pyrex optics). After 3 hr, thin layer chromatography indicated the absence of starting material.

Isolation by preparative scale vpc (100\(^0\), 10% SE-30 on Chromosorb W) furnished 47 mg (62\%) of \(\text{**3**}\) as a highly volatile colorless liquid; ir (neat) 2882, 1447, 1385, 1366, 1245, 1220, 1149, 1111, and 866 cm\(^{-1}\); \(\delta\)\(_{\text{CDCl}_3}\) 1.83-2.50 (envelope, 6, cyclobutane hydrogens), 1.02 (s, 6, bridgehead methyls), 0.94 and 0.87 (s, 3 each, gem-dimethyl).

**Anal.** Calcd for C\(_{11}\)H\(_{18}\): C, 87.92; H, 12.08. Found: C, 87.71; H, 11.96.

**Pyrolysis of \(\text{**2**}\).** A sealed evacuated tube containing 147 mg (0.825 mmol) of \(\text{**2**}\) was heated in a furnace at 210\(^0\) for 1.5 hr. The resulting product mixture was separated into its components by preparative scale vpc (78\(^0\), 10% SE-30 on Chromosorb W).

The first fraction, present in small amounts was found to be 1,4,5,5-tetramethylcyclopenta-1,3-diene (\(\text{**4**}\)) by comparison with the uv and nmr spectra of the known compound; \(\lambda_{\text{max}}\)\(_{\text{CDCl}_3}\) 259; \(\delta\)\(_{\text{TMS}}\) 5.87 (s, 2, olefinic), 1.85 (d, /J/\text{allylic} = 0.6 Hz, 6, =C\(_{\text{CH}_3}\)) and 0.93 (s, 6, C\(_5\)-methyls).
The second fraction (22.4 mg, 29%) was tricycloheptane (93).

The third fraction (16.5 mg, 21%) was 95; ir (neat) 2907, 1634,

\[ \text{CH}_3 \text{-CH}_3 \]

\[ \text{CH}_3 \text{-CH}_2 \]

1451, 1372, 1364, 1351, 1124, 1101, 855, 822, and 705 cm\(^{-1}\); \( \delta^{\text{CDCl}_3} \text{TMS} \) 5.37 (triplet with allylic coupling, \( /J/=7.2 \) and \( /J/=1.2 \) Hz, 1, olefinic), 4.94 (d, \( /J/=1.2 \) Hz, 1, exocyclic methylene), 4.72 (d, \( /J/=1.2 \) Hz, 1, exocyclic methylene), 1.37-2.50 (br m, 6, ring protons), 1.71 (d, 3, \( =\text{C}\text{-CH}_3 \)), and 1.18 (s, 6, gem-dimethyl).

Anal. Calcd for \( \text{C}_{11}\text{H}_{18} \): C, 87.92; H, 12.08. Found: C, 88.05; H, 12.18.

The fourth fraction (38.3 mg, 50% was 2,3,3,4-tetramethylocyclohepta-1,4-diene (96); ir (neat) 2924, 1445, 1385, 1370, 1351, 1114, 1088, and 824 cm\(^{-1}\); \( \delta^{\text{CDCl}_3} \text{TMS} \) 5.68 (br m, 2, olefinic), 2.15 (br m, 4, allylic), 1.77 (br s, 6, \( =\text{C}\text{-CH}_3 \)), and 1.23 (s, 6, gem-dimethyl).


Pyrolysis of 95. A sealed evacuated tube containing 97.8 mg (0.651 mmol) of 95 was heated in a furnace at 210° for 1.5 hr. The resulting product mixture was separated into its components by preparative scale vpc (78°, 10% SE-30 on Chromosorb W) and the product distribution was
determined by planimetry of the vpc trace.

The first fraction (≤ 2.5%) was found to be 94. The second fraction (≤ 0.8%) was not identifiable. The third fraction (≤ 8.4%) was unreacted starting material and the fourth fraction (≤ 2.0%) was 95. The last fraction (≥ 86.4%) was 96.

**Thermal Stability of 96.** In order to assess the thermal stability of 96, a tetrachloroethylene solution of 96 contained in a sealed nmr tube was heated at 208° for 5 hr. No further rearrangement was observed.

4-Phenyl-2,4,6-triazapentacyclodecane-11-ene-3,5-dione (97). Into a 1-l 3-necked flask equipped with magnetic stirrer, drying tube, and addition funnel were added 17.51 g (0.10 mol) of N-phenyltriazolinedione (54) and 500 ml of acetone. The solution was cooled to −40° and 11.0 g (0.12 mol) of cycloheptatriene was added over 5 min. The deep red color disappeared after 0.5 hr and stirring was continued for an additional 1 hr. Solvent removal at reduced pressure followed by recrystallization from ethyl acetate gave 24.6 g (92%) of cycloadduct, mp 188-189° (lit. 182 mp 186-188°); ir (CHCl₃) 1761, 1706, 1493, 1397, 1258, 1133, 1053, 958, 915, and 868 cm⁻¹; δ_CDCl₃ 7.42 (br s, 5, aryl), 6.09 (t, /J/=3.6 Hz, 2, olefinic), 5.21 (m, 2, bridgehead), 1.62 (m, 2, cyclopropyl), 0.70 and 0.35 (AB of ABM₂, /J_AB/=6.8 Hz, /J_AB'/=6.0 Hz, /J_BM/3.2 Hz, 1 each, cyclopropyl methylene).
4-Phenyl-2,4,6-triazacyclo[5,3.2.0^2,6.0^8,10]quadricyclododecane-3,5-dione (98). To a magnetically stirred solution of 6.10 g (0.0228 mol) of 97 in 600 ml of anhydrous tetrahydrofuran was added 0.700 g of platinum oxide and the mixture was hydrogenated at atmospheric pressure until the uptake of hydrogen ceased.

Filtration through Celite to remove catalyst, followed by solvent removal and recrystallization from acetone, gave 5.4 g (89%) of the desired compound, mp 147.5-149 °C (lit 138-139 °C); ir (CHCl_3) 2911, 1757, 1695, 1401, 1274, 1126, 961, and 876 cm^{-1}; {^1}H NMR 7.27-7.75 (br m, 5, aryl), 4.61 (m, 2, bridgehead), 1.33-2.17 (br m, 6), and 0.73 (m, 2, cyclopropyl methylene).

anti-6,7-Diazabicyclo[3.2.2.0^2,4]nona-6-ene Cuprous Chloride (99).

To a magnetically stirred solution of 2.00 g (0.00743 mol) of triazolidinedione (98) in 30 ml of anhydrous dimethyl sulfoxide and under nitrogen was slowly added 4.012 g (0.0743 mol) of sodium methoxide and the reaction mixture was heated at 87 °C for 14 hr. Upon cooling, the dark brown solution was slowly acidified to pH 4 with 1:1 hydrochloric acid (ca. 20 ml). A solution of cupric chloride dihydrate (5.0 g), water (100 ml), and 1:1 hydrochloric acid (2.0 ml) was then added over a 30-min period. The solution slowly turned dark red and stirring was continued for an additional 1.5 hr. Filtration, followed by wash-
ing with 30 ml each of water, acetone, and chloroform gave 1.28 g (78%) of the red complex, mp 124° (dec (lit mp 120° dec).

**anti-Tricyclo[3.2.0.0²,⁴]heptane (100).** To a flask containing 500 mg (2.26 mmol) of 99 in a bath maintained at -20° was added 30 ml of pre-cooled (-20°) aqueous ammonia and the resultant mixture was swirled for 5 min. The liberated azo compound (18) was taken into cold ether (-20°) by extraction (5 x 5 ml) and dried. Filtration, followed by solvent removal by distillation through a short path column at reduced pressure and temperature (-20°), gave a concentrated ethereal solution of azo compound. Immediate low temperature (-20°) irradiation of this solution with a 450W Hanovia lamp (Pyrex optics) for 3 hr followed by preparative scale vpc (75°, 10% SF-96 on Chromosorb G) gave 10.2 mg (5%) of the desired tricycloheptane (100); δ<sub>CDCl<sub>3</sub></sub> 2.38 (m, 4, hydrogens at C<sub>6</sub> and C<sub>7</sub>), 2.08 (m, /J/₁,₃<sub>exo</sub>=1.0 Hz, 2, hydrogens at C<sub>1</sub> and C<sub>5</sub>), 1.63 (doublet of triplets, /J/₂,₃<sub>exo</sub>=5.5 Hz, /J/₁,₃<sub>endo</sub>=1.8 Hz, 2, hydrogens at C<sub>2</sub> and C<sub>4</sub>), 0.70 (dd, /J/₃<sub>exo</sub>,₃<sub>endo</sub>=4.2 Hz, 1, exo-hydrogen at C<sub>3</sub>), and 0.28 (doublet of triplets, 1, endo-hydrogen at C<sub>3</sub>).

The second component of the photolysis mixture, 44.0 mg (21%), was found to be 1,4-cycloheptadiene (19), ir (neat) 2985, 2882, 2885, 1658, 1433, 824, and 682 cm⁻¹; δ<sub>CDCl<sub>3</sub></sub> 5.68 (m, 4, olefinic), 2.87 (m, 2, doubly allylic hydrogens),
and 2.27 (m, 2, allylic hydrogens).

Pyrolysis of 100. An nmr tube containing 6 mg (0.064 mmol) of 100 which had been sealed in vacuo at -196° was placed in an oven maintained at 173° for 15 min. After the tube had been removed from the oven and allowed to cool, it was opened, deuteriochloroform/TMS was added, and the nmr spectrum was immediately recorded. Only cycloheptadiene (19) and a small amount of unreacted tricycloheptane (100) were found to be present (ratio of approximately 8:1). Flame ionization vpc confirmed that these were the only components.
EXPERIMENTAL PART III

Silver(I) Catalyzed Rearrangements

3,4-Dimethyl-2,4-diphenylbicyclo[3.2.0]hept-2-ene (112).

A. Silver Tetrafluoroborate. To a deuteriochloroform/TMS solution of 106.7 mg (0.389 mmol) of 84 contained in an nmr tube were added several crystals of silver tetrafluoroborate. The tube was placed in a constant temperature bath maintained to 40°C and the nmr spectrum was recorded periodically. The reaction was deduced to be 85% complete after 8 hr. After 24 hr, the contents of the tube was poured into 20 ml of saturated sodium chloride solution, stirred for 10 min to precipitate silver salts, extracted with ether (3 x 20 ml), and dried. Filtration, solvent removal, and molecular distillation afforded 70.4 mg (66%) of 112 as a viscous colorless liquid, bp 90°C at 0.08 mm; ir (neat) 2924, 1603, 1488, 1439, 1364, 1062, 1029, 763, 717, and 695 cm⁻¹; λ<sub>max</sub><sub>isoctane</sub> 251 nm (ε 12,200); δ<sub>CDCl₃</sub><sub>TMS</sub> 7.32 (m, 10, aryl), 3.75 (br m, 1, H₁), 2.80 (br m, 1, H₅), 1.20-2.33 (envelope, 4, hydrogens on C₆ and C₇), 1.82 (d, /J/₁,CH₃ = 1.7Hz, 3, =C-CH₃), and 1.47 (s, 3, methyl).


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D. Silver Perchlorate: A deuteriochloroform/TMS solution of $^{84}$ contained in an nmr tube was treated with several crystals of silver perchlorate. The nmr spectrum, recorded after 44 hr at 40° indicated 35% conversion to $^{112}$.

2-Phenyl-3,4,4-trimethylbicyclo[3.2.0]hept-2-ene (113). A deuteriochloroform/TMS solution of $^{88}$ (99.1 mg, 0.471 mmol) contained in an nmr tube was treated with several crystals of silver tetrafluoroborate. The nmr spectra, recorded continuously, indicated the reaction to be complete within 0.5 hr (at probe temperature, $\sim 40^\circ$). The contents of the tube were poured into 20 ml of saturated sodium chloride solution, stirred for 10 min, extracted with ether (3 x 20 ml), and dried. Filtration, solvent removal, and molecular distillation afforded 78 mg (79%) of 113, bp 42° at 0.1 mm; ir (neat) 2915, 1603, 1490, 1456, 1435, 1370, 1353, 1125, 1098, 1064, 1030, 769, 751, 722, and 695 cm$^{-1}$; $\lambda_{\text{max}}$ 247 nm ($\epsilon$ 5,100); $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 7.25 (br s, 5, aryl), 3.58 (br m, 1, H$_1$), 2.63 (br m, 1, H$_5$), 1.25-2.33 (envelope, 4, hydrogens on C$_6$ and C$_7$), 1.73 (d, $\delta/1/CH_3 = 1.8$Hz, 3, $=CCH_3$), 1.04 and 0.96 (s, 3 each, methyls).

Anal. Calcd for C$_{16}$H$_{20}$: C, 90.50; H, 9.50. Found: C, 89.91; H, 9.42.
Camphorquinone (115). A mixture of camphor $\dfrac{114}{114}$ (100 g, 0.66 mol), selenium dioxide (125 g, 1.14 mol), and acetic anhydride (150 ml) was refluxed for 5 hr. Upon cooling, the mixture was filtered, the selenium washed with acetic acid, and the orange-yellow filtrate carefully neutralized with potassium hydroxide solution. The precipitated quinone was taken into ether by extraction (5 x 250 ml), washed with saturated sodium bicarbonate solution, and dried. Filtration, solvent removal at reduced pressure, and recrystallization from hexane gave 86.8 g (86%) of yellow crystals. The nmr spectrum indicated that only about 50% reaction had occurred. The impure product was recycled, this time using 250 g (2.28 mol) of selenium dioxide. Workup as above gave 70 g (64%) of camphorquinone, mp 194-196° (lit mp 198°).

Camphorquinone 3-Tosylhydrazone (116). A solution of 69 g (0.415 mol) of camphorquinone and 89 g (0.478 mol) of p-toluenesulfonylhydrazine in 500 ml of absolute methanol was refluxed for 3 hr. Upon cooling, the solution was diluted with water (500 ml), and the thick yellow oil which separated was taken up in methylene chloride (500 ml). The organic layer was washed with water (2 x 250 ml) and dried.
Solvent removal at reduced pressure gave a faintly yellow oil which was used in the next step, without further purification.

3-Diazocamphor (117). A solution of the crude tosylhydrazone in 250 ml of 2 N sodium hydroxide was covered with 500 ml of pentane and the mixture stirred for 12 hr. The organic layer was decanted, dried, and the solvent removed at reduced pressure. The resulting bright yellow solid was sublimed at 50° at 0.03 mm to give 58.0 g (78% based on 115) of 3-diazocamphor, mp 73-75° (lit mp 75°).

Pericyclocamphanone (118). To a stirred boiling suspension of freshly activated copper bronze (50 g) in 250 ml of dry benzene was added 300 ml of a solution of 3-diazocamphor (31.7 g, 0.173 mol) in 750 ml of benzene. The evolution of nitrogen was quite fast. The remainder of the solution was slowly added over 30 min, and the reaction mixture refluxed for an additional 1.5 hr. Upon cooling, the catalyst was filtered off, and the solvent removed under reduced pressure. The crude product was sublimed at 95° at 10 mm to give 23.7 g (89% of pericyclocamphanone. Recrystallization of a small sample from hexane afforded white crystals, mp 165-168° (lit mp 170°).
3-Phenyl-4,7,7-trimethyltricyclo[2.2.1.0²,⁶]heptan-3-ol (119). Into a 2-l 3-necked flask equipped with condenser, mechanical stirrer, and under nitrogen were added 300 ml of dry ether and 13.0 g (1.878 mol) of lithium wire. A small amount of a solution of bromobenzene (147.4 g, 0.939 mol) in 200 ml of ether was added and the mixture refluxed for 5 min to initiate phenyllithium formation. Cooling to 0° was followed by dropwise addition of the remaining bromobenzene over 2 hr. The mixture was then allowed to warm to room temperature and stirred for an additional 4 hr. The phenyllithium solution was then brought to reflux and a solution of pericyclocamphane (118; 43.66 g, 0.291 mol) in 200 ml of ether-tetrahydrofuran was added over 1 hr. Refluxing was continued for 18 hr after which time the reaction was allowed to cool, ice water was slowly added, and the crude alcohol taken into ether by extraction (4 x 250 ml). The combined extracts were washed with water and dried. Filtration followed by solvent removal at reduced pressure gave an oil which was immediately used in the next step without isolation of the alcohol.

5-exo-Acetoxy-2-phenylbornene (120). A solution of the crude alcohol (112) from above in acetic anhydride (300 ml) was heated under reflux for 12 hr. Most of the acetic anhydride was removed in vacuo. The residue
was diluted with 500 ml of water, stirred overnight, neutralized with potassium carbonate and extracted into ether (3 x 250 ml). The combined ether layers were washed with water (2 x 125 ml) and dried. Filtration and solvent removal gave an oil which solidified upon standing, and was used in the next step without further purification.

5-exo-Hydroxy-2-phenylbornene (121). A solution of the crude acetate (120) from above in 500 ml of ethanol containing 30 g of potassium hydroxide was heated under reflux for 2 hr. Upon cooling, the mixture was diluted with water (500 ml) and the alcohol was taken into ether by extraction (4 x 250 ml) and dried. Filtration, solvent removal, and recrystallization gave 35 g (53\% based on 118) of 121, mp 84-85° (lit 97 mp 86-87°).

2-Phenylbornen-5-one (122). A mixture of 11.4 g (0.05 mol) of 121 and 129 g (0.50 mol) of dipyridine-chromium (VI) oxide complex in 750 ml of methylene chloride was allowed to stir for 24 hr. After this time, the mixture was filtered, the precipitate washed copiously with water (4 x 250 ml), and dried. Solvent removal at reduced pressure followed by chromatography on silica gel and elution with hexane-ether (9:1) gave 9.3 g (83\%) of the desired ketone (122) as a colorless oil. The
ir spectrum (neat) which shows absorptions at 2924, 1743, 761, and 696 cm\(^{-1}\) and the nmr spectrum which exhibits intensities at \(\delta_{\text{CDCl}_3}^{\text{TMS}} 7.28\) (br s, 5, aryl), 5.92 (d, /J/3,4 = 3.7Hz, 1, olefinic), 2.78 (d, 1, bridgehead), 2.11 (s, 2), 1.17, 1.08, and 1.03 (s, 3 each, methyls) are in excellent agreement with the values cited in the literature.

2-Phenyl-1,5,5-trimethylcyclopenta-1,3-diene (123). A solution of 6.0 \(g (0.027 \text{ mol})\) of 122 in 300 ml of cyclohexane and under nitrogen was irradiated with a 200 W Hanovia lamp (Pyrex optics). The reaction, continuously monitored by TLC was deduced to be complete in 7 hr. Solvent removal at reduced pressure followed by chromatography on silica gel and elution with hexane gave 2.0 \(g (41\%)\) of 123 as a colorless oil.

The ir spectrum (neat) which exhibits absorptions at 2924, 763, 737, and 694 cm\(^{-1}\) and the nmr spectrum which shows intensities at \(\delta_{\text{CDCl}_3}^{\text{TMS}} 7.34\) (m, 5, aryl), 6.47 (d, /J/3,4 = 5.4Hz, 1, olefinic), 6.28 (d, 1, olefinic), 1.93 (s, 3, =C\(\text{CH}_3\)), and 1.12 (s, 6, gem-dimethyl) are in excellent agreement with the values cited in the literature. The cyclopentadiene was used in the next step without further purification.
7,7-Dichloro-2-phenyl-3,4,4-trimethylbicyclo[3.2.0]hept-2-ene-6-one (124). To a stirred solution of 553 mg (3.0 mmol) of 123 and 576 mg (3.0 mmol) of dichloroacetyl bromide in 40 ml of hexane and under nitrogen, was slowly added 304 mg (3.0 mmol) of triethylamine. A copious white precipitate immediately formed and stirring was continued for an additional 6 hr after which time an additional 25 ml of hexane was added. The mixture was poured into a separatory funnel, washed with water (2 x 10 ml), 5% hydrochloric acid solution (2 x 20 ml), 5% sodium bicarbonate solution, and dried. Filtration followed by solvent removal at reduced pressure gave 838 mg (75%) of the dichloroketone; \( \text{IR (neat)} 2950, 1805, 779, 762, \text{and} 694 \text{ cm}^{-1}; \text{\( ^{1}J_{\text{H}}\text{CDCl}_3\text{TMS} 7.35 \text{ (br s, 5, aryl), 4.48 (dd, /J/_{1,5} = 7.7 \text{ and} /J/_{1,\text{CH}_3} = 1.5Hz, 1, H_1), 3.89 (d, 1, H_3), 1.79 (d, 3, =C<\text{CH}_3), 1.31 \text{ and} 1.13 \text{ (s, 3 each, methyls). This compound was used immediately in the next step without further purification.}} \)

2-Phenyl-3,4,4-trimethylbicyclo[3.2.0]hept-2-ene-6-one (125). To a solution of 0.812 g (0.00275 mol) of 124 and 1.65 g (0.00566 mol) of tri-n-butyltin hydride in 25 ml of hexane and under nitrogen, was added ca. 15 mg of azobisisobutyronitrile (AIBN). The solution was refluxed

\[ \text{formula} \]
for 12 hr, and upon cooling, solvent was removed at reduced pressure. Chromatography on silica gel and elution with pentane gave a fraction containing 0.403 g (65%) of the desired ketone; bp 50° at 0.1 mm; ir (neat) 2915, 1773, 1488, 1458, 1437, 768, 752, and 697 cm⁻¹; δ<sub>CDCl₃</sub> <sub>TMS</sub> 7.32 (br s, 5, aryl), 3.75 (m, 1), 3.45 (m, 1), 3.08 (m, 1), 2.65 (m, 1), 1.72 (d, /J/1,CH₃ = 1.3Hz, 3, =<sup>C</sup>-<sup>CH₃</sup>), 1.27 and 1.09 (s, 3 each, methyls).


2-Phenyl-3,4,4-trimethylbicyclo[3.2.0]hept-2-ene (113). To 150 mg (0.663 mmol) of 125 was added 5 ml of a solution containing 0.685 g of potassium hydroxide and 0.50 ml of hydrazine hydrate in 20 ml of ethylene glycol. The reaction mixture was placed in a bath maintained at 200° and allowed to reflux for 3 hr. Upon cooling, the apparatus was washed with pentane (20 ml) and poured into a separatory funnel. Water (40 ml) was added, and the aqueous layer extracted with pentane (2 x 20 ml). The combined pentane solutions were washed with water (2 x 20 ml) and dried. Filtration, solvent removal at reduced pressure followed by preparative scale vpc (140°, 10% SE-30 on Chromosorb W) gave 51.3 mg (36%) of 113 which was identical to the material isolated above.
REFERENCES


29. See for example: (a) S. J. Cristol and R. L. Snell, ibid., 80, 1950 (1958); (b) G. S. Hammond, N. J. Turro, and A. Fischer, J. Amer. Chem. Soc., 83, 4674 (1961); (c) P. G. Gassman, D. H. Aue, and D. S. Patton, ibid., 90, 7271 (1968); (d) J. R. Edman, ibid., 91, 7103 (1969), and pertinent references cited in these papers.


32. \( \lambda_{\text{max}} ^{\text{cyclohexane}} = 245 \text{ (} \epsilon 28,800) \) and 364 nm (10,700); see ref 33.


34. The formation of p-terphenyl could plausibly occur by the expulsion of dimethylcarbene from the excited state of \( ^{4} \delta \). No attempts have been made in this study to trap the reactive fragment or to establish conclusively its generation under these conditions.

35. \( \lambda_{\text{max}} ^{\text{CH}_3\text{OH}} = 244 \text{ (} \epsilon 20,000) \) and 325 nm (15,100); see ref 36.


37. Such effects are recognized to be particularly influential when cyclobutadiene (\( ^{4} \delta \)) is forced to function as the diene component. Apparently, the strong preference for endo stereochemistry also operates when \( ^{4} \delta \) plays the dienophile role in such (\( 4+2 \)) cycloadditions.

38. Compare the nmr spectrum of bornadiene: \( ^{6} \text{CCl}_4 \text{C}_{\text{TMS}} \) 1 6.55 \( (\text{dd,} /j/ = 3.0 \) and 1.6 Hz, 2, vinyl), 6.27 \( (\text{dd,} /j/ = 3.0 \) and 1 Hz, 2, vinyl), 3.01 \( (\text{m,} 1, \text{bridgehead proton}) \), 1.20 \( (\text{s,} 3, \text{bridgehead methyl}) \), and 1.03 \( (\text{s,} 6, \text{C7-methyl}) \). The author wishes to thank Professor M. R. Willett, III for a copy of this spectrum.


53. L. M. Leichter, present work.


57. This subject has been recently reviewed: G. Maier, Angew. Chem., 87, 446 (1967).


59. E. Ciganek, ibid., 93, 2207 (1971); 89, 1454 (1967); 87, 652 (1965).


66. \( \lambda_{\text{max}} \) of ethanol 232 (\( \varepsilon \) 12,300) and 346 nm (22,900); \( \delta_{\text{TMS}} \) 7.27-7.77 (m, 15, aryl), 6.93 (br s, 2, olefinic), and 3.75 (br s, 2, methylenes); see reference 67.


68. This method of analysis was suggested by Professor G. Closs, whom the author also wishes to thank for the spectral determinations cited herein.

69. Downfield from TMS at 100 MHz.


71. \( \lambda_{\text{max}} \) of cyclohexane 259 nm (\( \varepsilon \) 5,170); \( \delta \) 5.81 (s, 2, olefinic), 1.81 (d, \( J_{\text{ally}} = 1.1 \) Hz, 6, =\( \text{C}-\text{CH}_3 \)), and 0.92 (s, 6, gem-dimethyl); see reference 72.


89. For other metal catalyzed rearrangements of bicyclobutane systems see: (a) P. C. Gassman and T. Nakai, *ibid.*, 23, 5897 (1971); (b) R. Noyori, T. Suzuki, Y. Kumagai, and H. Takaya, *ibid.*, 23, 5894 (1971); (c) P. C. Gassman and T. J. Atkins, *ibid.*, 93, 4597 (1971); (d) P. C. Gassman, T. J. Atkins, and F. J. Williams, *ibid.*, 93, 1812 (1971); (e) P. C. Gassman and T. J. Atkins, *ibid.*, 93, 1042 (1971); (f) P. C. Gassman, G. R. Meyers, and F. J. Williams, *Chem. Commun.*, 842 (1971); (g) M. Sakai, H.


91. (a) $\lambda_{\text{max}}^\text{CHCl}_3$ 279 nm ($\epsilon$ 27,800); see A. E. Gillam and D. H. Hey, *J. Chem. Soc.*, 1170 (1939); (b) Varian Catalog, 2, no. 671; (c) Sadtler Standard Infrared Spectra, no. 9568.


