REACTIVITY IN THE TRICYCLO [4.1.0.0^2,4] HEPTAN-5-YLIDENE AND THE TRICYCLO [5.1.0.0^3,5] OCTAN-2-YLIDENE SERIES

By

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Abstract of Dissertation Presented to the Graduate Council of the University of Florida in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

REACTIVITY IN THE TRICYCLO [4.1.0.0^{2,4}] HEPTAN-5-YLIDENE AND THE TRICYCLO [5.1.0.0^{3,5}] OCTAN-2-YLIDENE SERIES

By

Oscar Trinidad Garza

August, 1975

Chairman: William R. Dolbier, Jr.
Major Department: Chemistry

The thermal conversions of the p-toluenesulfonylhydrazone sodium salts of (a) the syn- and anti-tricyclo [4.1.0.0^{2,4}] heptan-5-ones as well as those of (b) the syn- and anti-tricyclo [5.1.0.0^{3,5}] octan-2-ones were investigated. The chemistry resulting from the generation and subsequent reaction of the respective carbenes for each series proved most interesting for the case of the tricyclic heptanyldienes.

Three methods were developed for the required synthesis of the syn- and anti-tricyclo [4.1.0.0^{2,4}] heptan-5-ones, the first two methods affording nearly equimolar mixtures of the isomeric ketones while the third method afforded a syn-anti mixture in the ratio 2:98. The novel syn tricyclic heptanone proved exceedingly labile in comparison with the anti isomer.
Carbene product distributions for both isomers in a given series proved similar thereby demonstrating that the cyclopropane orientation differences within an isomeric set afforded no readily identifiable differences in reactivity. Although the observed products for each series studied could be explained largely by the established ethylenic-acetylenic fragmentation process common to cyclopropyl carbones, the case for the isomeric tricyclic heptanylidenes was subjected to further scrutiny because of the plausible operation of a novel six-electron pericyclic process involving the highly-strained species 1,2,5-cycloheptatriene as the primary product derived from either tricyclic heptanylidene.

Three C$_7$H$_8$ monomers and one C$_7$H$_8$ dimer were obtained from the tricyclic heptanylidenes while two C$_8$H$_{10}$ monomers were isolated from the tricyclic octanylidenes. The novel C$_7$H$_8$ monomer cis-1-ethynyl-2-vinyl cyclopropane afforded unusual reactivity, undergoing ostensibly a Cope rearrangement with an approximate half-life, assuming a unimolecular rate-determining step, of two to three hours maximum at 25°C. It remains the subject of ongoing studies, having proved to be the most interesting carbene product isolated from the studies of both tricyclic carbene systems.
CHAPTER I
INTRODUCTION AND BACKGROUND

The question of a quasiaromatic structure as a valid picture of the electronic makeup of certain suitably-designed carbenes has received considerable attention in the past decade.\(^1\) Although cyclopropenylidene (1) has eluded study thus far, cyclopentadienylidene (2) and cycloheptatrienylidene (3) have been studied in detail.\(^1,2\)

\[\begin{array}{c}
\text{1} \\
\text{\(\text{\textbullet \textbullet\textbullet}\)} \\
\text{\(\text{\textbullet\textbullet\textbullet}\)}
\end{array}\quad \begin{array}{c}
\text{2} \\
\text{\(\text{\textbullet \textbullet\textbullet}\)} \\
\text{\(\text{\textbullet\textbullet\textbullet}\)}
\end{array}\quad \begin{array}{c}
\text{3} \\
\text{\(\text{\textbullet \textbullet\textbullet}\)} \\
\text{\(\text{\textbullet\textbullet\textbullet}\)}
\end{array}\]

Assignment of structures such as 4 and 5 to 2 and 3, respectively, has found substantial experimental verification as the result of work by two research groups\(^3,4\) supplemented with extended Hückel calculations performed by Gleiter and Hoffman.\(^5\)
The EHT calculations indicate that the nucleophilic or electrophilic character ought to alternate in the series 1 - 3. The nucleophilic character of 1 and 3, with the \( \sigma^2 \) singlet of each lower than the \( p^2 \) singlet on the potential energy profile, was predicted from calculations of the total charge residing on the respective methylene carbons of 1 and 3: -0.68 and -0.86. Experimental evidence was in turn provided by W.M. Jones and coworkers in the case of 3. A Hammett study was performed in which cycloheptatrienylidene was generated in the presence of an eight-to-tenfold excess of an equimolar mixture of styrene and 3- or 4-substituted styrene. The \( p \) value of +1.05 ± 0.05 obtained from this study provided the first quantitative assessment of the nucleophilicity of a carbocyclic aromatic carbene.\(^4\)

Cyclopentadienylidene, on the other hand, did not readily lend itself to the proposition of electrophilicity based strictly on the extended Hückel treatment. Cyclopentadienylidene showed a very small splitting of the
bishomoaromatic carbene. In the case of 6 the vigorous reaction resulting in extrusion of carbon atoms may preclude the existence of a bishomoaromatic carbene (9). Without Hammett studies and suitable trapping reactions employing both electron-rich and electron-poor olefins, which might afford information concerning the
electrophilicity or nucleophilicity of 6 and 7, no evidence for bishomoaromaticity in 6 and 7 would appear to be forthcoming. Even the isolation of stable forms, dimers and/or oligomers, of 10 and 11, derived from 6 and 7, respectively, while perhaps suggesting a special intermediate as their precursor, would not demonstrate bishomoaromaticity as an operative force in these systems.

The discussion of bishomoaromaticity in the case of 7, fortunately, can be extended due to the supportive work performed by Bergman and Rajadhyaksha included in the same paper. Treatment of 3-bromo-bicyclo [3.2.1] octa-2,6-diene (12) with potassium t-butoxide in DMSO at 25° afforded 8 in 29% yield. Further work demonstrated that (a) carbon-halogen bond cleavage occurred in the
rate-determining step of the reaction, and (b) rapid, reversible deprotonation-reprotonation of 12 occurred at a rate greater than that of rearrangement. The scheme postulated by Bergman envisioned a homoconjugated anion (13)

giving way to a homoconjugated neutral intermediate (14) which subsequently underwent cleavage in the manner typical of cyclopropylcarbenes. Since 7 and 13 both afforded identical product (8), it was logical that a common intermediate (14) should be invoked, the final result being the pictorial representation (15) which corresponds to the $p^2$ configuration of the singlet carbene. In summary
it can be stated that the isolation of 8 via generation of 7 from the tosylhydrazone sodium salt does not appear to be merely a simple case of a cyclopropylcarbene undergoing the well-documented ethylene-acetylene fragmentation process\textsuperscript{1,2} but is, in fact, a case of a stabilized carbene giving said product (8). Although further argument concerning the mechanistic origin of 8 may prove ethereal, it is conceivable that 8 could also arise from allene (11) by a Cope process.\textsuperscript{11}
Consideration of the 1,3-bishomocyclopentadienide species (16), of which 15 would be the σ cation, allows further insight into the postulated existence of 15. HMO calculations predict appreciable bonding interactions between the allylic anionic and olefinic systems in 16. The resonance integral $\beta_{27}$ (or $\beta_{46}$) is approximately equal to $0.3 \beta_0$ where $\beta_0$ is assigned a value of 18 kcal/mole, a value normally used for benzenoid systems. Charge density is greatest at C-2 and C-4 (0.426), considerably less at C-6 and C-7 (0.064), and least at C-3 (0.021). Interestingly enough, the tetracyclic hydrocarbon (18) is obtained as one of three products upon equilibration of 17 employing Streitweiser's catalyst-solvent system, CsNHC$_6$H$_{11}$ in C$_6$H$_{11}$NH$_2$. In order to further test the hypothesis of bishomoaromaticity in the realm of carbene chemistry, it was
deemed necessary to investigate this question from the viewpoint of bishomocyclopentadienyldiene, a species which could possess two isomeric forms; i.e., *syn* and *anti* configurations of the fused cyclopropane rings should be possible. The bishomocyclopentadienyldienes, *syn-* and *anti-*tricyclo [4.1.0.0^{2,4}] heptan-5-ylidenes, 19-\textit{s} and 19-\textit{a} devoid of the molecular constraints as encountered in

![Diagrams of 19-\textit{s} and 19-\textit{a}](image)

6 and 7, would be capable of generating the novel cyclic allene 1,2,5-cycloheptatriene (20), whose structural deformation would place it in the same class with the known 1,2-cycloheptadiene (21) and 1,2-cyclohexadiene (22) species.\textsuperscript{14a,b} Monomers 21 and 22 have been shown to be

![Structures of 20, 21, and 22](image)
transient intermediates as evidenced by the isolation of their dimeric and tetrameric products. In the case of 22 the monomer has also been trapped employing both styrene and 1,3-diphenyl-benzo [c]-furan. The observation of possible dimeric and/or tetrameric products resulting from 20 would lend credence to the concept of a bishomoaromatic carbene although such an observation, by itself, constitutes a unique multiple-bond fragmentation process for a new carbene rather than the actual generation of a particular pseudo-π stabilized carbene.

Other interesting features of the bishomocyclopentadienyldiene investigation would lie in the isolation of the monomeric species, cis-1-ethynyl-2-vinyl-cyclopropane (23) and tetracyclo [4.1.0.2,4.0.3,5] heptane (24). The cyclopropane (23) presents an interesting problem since it might possibly arise from 20 via a Cope process or simply originate as the primary product from the ethylene-acetylene fragmentation process common to cyclopropylcarbenes. Superimposed on the mechanistic alternatives would be the questions of the inherent stability and reactivity of the unknown 23. Tetracyclic heptane (24), synthesized and pyrolyzed by Christl and Brüntrup, converted to cycloheptatriene at 150°C with a reaction half-life of ca. five hours. Despite a strain energy of approximately 100 kcal/mole, it appears that 24 is thermally stable,
suggesting that suitably-generated 19-s or 19-a might give rise to 24 via C-H insertion.

Further speculation about the reactivity of 19-s and 19-a only served to increase the demand for the actual experimental work. The work described in this dissertation was performed principally on the syn- and anti-tricyclo [4.1.0.0²,⁴] heptan-5-ylidenes in order to determine the basic reactivity of these systems and thereby add to the discussion of homoaromaticity in alicyclic carbenes. Further elaboration of the working hypothesis was provided by inspection of the syn- and anti-tricyclo [5.1.0.0³,⁵] octan-2-ylidenes, 25-s and 25-a, which provided a severe test for operational homoaromaticity in carbene systems possessing favorable geometries.
CHAPTER II
SYNTHETIC METHODS

Synthetic entry into both the tricyclo [4.1.0.0²⁴] heptan-5-ylidene and the tricyclo [5.1.0.0³⁵] octan-2-ylidene series was provided by the synthesis of the corresponding syn and anti ketones for each series. Conversion of the ketones to the corresponding p-toluenesulfonylhydrazones (tosylhydrazones) was desirous since tosylhydrazone lithium, sodium, or potassium salts are normally stable precursors which can be subsequently pyrolyzed or photolyzed in solution¹,² or pyrolyzed in the solid state a la Schecter.¹⁷

Three synthetic methods were developed for the synthesis of syn- and anti-tricyclo [4.1.0.0²⁴] heptan-5-ones, 26-s and 26-a, respectively. The first two methods (methods A and B) both afforded a nearly even mixture of the syn and anti ketones while the third method (method C) afforded the ketones in a syn-anti ratio of 2:98.

Method A (Scheme I) began with the known conversion of isobutyric acid to the corresponding acid chloride followed by treatment with triethylamine to afford the dimethylketene dimer, tetramethyl-1,3-cyclobutanedione (27).¹⁸ Treatment of 27, in the known manner,¹⁹ with allyl Grignard
afforded the C14 keto-alcohol, 5-allyl-5-hydroxy-2,4,4-trimethyl-7-octen-3-one (28), which was subsequently converted to diallyl ketone (29) by base-catalyzed cleavage with barium hydroxide. Diallyl ketone (29) was converted to its ethylene ketal (30) which was treated with iodo benzene dichloride. The crude mixture of cis- and trans-7,8-bis (chloromethyl)-1,4-dioxaspiro [4.4] nonanes (31), the product of addition of one mole of chlorine concomitant with radical cyclization to generate the five-membered carbo cyclic structure, was subjected to acid-catalyzed hydrolysis resulting in restoration of the ketone moiety. The resulting mixture of cis- and trans-3,4-bis (chloromethyl)-cyclopentanones (32) was treated with 50% sodium hydroxide whereby an α,γ loss of two moles of HCl was effected resulting in the isolation of two ketonic products which nmr, ir, uv, mass spectral, and elemental analyses indicated to be C7H8O isomers.

The isolation of the two ketonic products, which proved to be the desired tricyclic heptanones, 26-s and 26-a, proved initially troublesome when attempting the separation work employing typical glpc methods. An injection of the isomeric mixture of ketones onto various Carbowax 20 M columns (column temperatures: 130°C-160°C) typically resulted in the isolation of three isomeric ketones: (a) anti-tricyclo [4.1.0.0^2.4] heptan-5-one, (b) 3,5-cycloheptadienone, and (c) 2,4-cycloheptadienone. The
Scheme I

1. (CH₃)₂CHCO₂H → SOCl₂ → NEt₃ → \( \sim \) → 1) CH₂ = CH-CH₂MgBr
2) NH₄Cl

3. (CH₃)CH - C - C(CH₃)₂OH → Ba(OH)₂ → \( \sim \) → 29

4. \((\text{CH}_2\text{OH})_2 \xrightarrow{\text{H}^+} \) → \( \sim \) → 30
5. \( \xrightarrow{\text{ICl}_2/\text{CHCl}_3} \) → \( \sim \) → 31
6. \( \xrightarrow{\text{H}^+ \text{H}_2\text{O}, \text{EtOH}} \) → \( \sim \)

7. CH₂Cl → CH₂Cl → \( \sim \) → 32
8. \( \xrightarrow{50\% \text{NaOH, steam dist.}} \) → \( \sim \) → 26-a
9. \( \sim \) → 26-s

syn:anti 52:48
Scheme I - continued

\[ 26-a \quad \rightarrow \quad 26-s \]

\[
\begin{align*}
N-\text{NH-Tos} \\
33-a \\
\Downarrow \\
\text{Na}^+ \\
\text{Tos} - N - N \\
34-a
\end{align*}
\]

\[
\begin{align*}
N-\text{NH-Tos} \\
33-s \\
\Downarrow \\
\text{Na}^+ \\
N - N - \text{Tos} \\
34-s
\end{align*}
\]
anti-tricyclic ketone was identified by comparison of its nmr (100 MHz) with that reported by Gajewski and Shih (1970). The outstanding feature of the nmr of 26-a is the unsymmetrical quartet (J = 3.5 Hz) with a two-proton integration at δ 0.85. The remainder of the nmr spectrum showed three multiplets of two-proton integration each located at δ 1.25, 1.56, and 2.08. The ir (1720 cm⁻¹), uv (λ max 287 nm, ε 28), and mass spectrum (M⁺ 108) were also confirmative of the anti isomer; however, elemental analysis did not prove satisfactory, a situation which persisted until the glpc methods were rectified.

The 2,4 and 3,5-cycloheptadienones, recognizable due to (a) the four-proton multiplet in the region δ 2.17-2.83 for the 2,4 isomer and (b) the four-proton doublet (J = 5.8 Hz) centered at δ 3.00 for the 3,5 isomer, were accounted for by an acid-promoted rearrangement which destroyed the entire fraction of the syn-tricyclic ketone (26-s) and only a portion of the anti fraction (26-a). Previous work by Borg and Kloosterziel had shown that the cycloheptadienones were interconvertible in the temperature range 60°-100° via a facile 1,5 hydrogen shift, resulting in an equilibrium mixture dominated by the 2,4 isomer. This equilibrium explained the observation that the cycloheptadienones eluted from the glpc column as a mixture (two overlapping peaks) while residual 26-a eluted as a distinct component.
Isolation of analytically pure syn- and anti-tricyclic heptanones was accomplished by the use of an alkaline column (10% Carbowax 20 M) employing 3.5% potassium hydroxide to effectively remove active sites from the inert support, typically Chromasorb P-Regular. Whereas liberal injections of ammonia vapor had not prevented destruction of the ketones in the initial glpc work, the potassium hydroxide-coated column allowed for almost quantitative (96% with cycloheptanone as internal standard) separation and isolation of \(26-s\) and \(26-a\) in the temperature range 130°-165°C. It was noted, however, that column temperatures in the range 185°-196° led again to the almost complete destruction of \(26-s\) (4% recovery) suggesting that perhaps the syn isomer was thermally labile.

The novel syn-tricyclo \([4.1.0.0^{2,4}\] heptanone \(26-s\) afforded four complex multiplets in its 100 MHz nmr spectrum, each multiplet of two-proton magnitude. The multiplets were located at \(\delta 0.76, 1.50, 1.78, \) and 2.18.
The multiplets at 1.50 and 1.78 were overlapping, a feature which readily distinguishes 26-s from 26-a. The ir (1700 cm\(^{-1}\)), uv (\(\lambda_{\text{max}}\) 283, \(\epsilon\) 70), and mass spectrum (M\(^+\) 108) also confirmed the structure of this C\(_7\)H\(_8\)O ketone isomer. Elemental analysis of 26-s proved satisfactory.

Silica gel chromatography conveniently afforded separation of 26-s and 26-a of sufficient purity to allow for subsequent conversion to the corresponding tosylhydrazones, 33-s and 33-a, respectively. Whereas 33-s was observed to have been formed in 83% yield, 33-a, unfortunately, was obtained in only 31% yield. Conversion of 33-s and 33-a to the corresponding sodium salts, 34-s and 34-a, was quantitatively achieved employing sodium hydride (1.2 equivalents) with tetrahydrofuran solvent. Potassium salts of 33-s and 33-a were made by treatment of the tosylhydrazones with potassium tert-butoxide, again using tetrahydrofuran solvent.

Method B (Scheme II) employed a synthetic sequence which appeared to be a more convenient synthetic route than method A. Drawing on the analogy provided by workers such as Doering\(^{23}\) and Gutsche\(^{24}\) in performing intramolecular trapping of intermediates of the copper-ketocarbene type by a remote double bond, a sequence of steps was devised which would utilize \(\textit{cis}\)-ethyl-2-vinyl-cyclopropanecarboxylate (35-c) as the point of entry into the synthetic sequence. Although no stereospecific synthesis of 35-c has
Scheme II

\[
\text{+ } \text{N}_2\text{CHCO}_2\text{Et} \xrightarrow{110^\circ} \text{35} \text{CO}_2\text{Et}
\]

\[
\text{KOH} \xrightarrow{\text{H}_2\text{O-MeOH}} \text{36} \xrightarrow{\text{SOCl}_2} \text{37} \xrightarrow{\text{CH}_2\text{N}_2\text{Et}_2\text{O}}
\]

\[
\text{38} \xrightarrow{\text{CuSO}_4} \text{26-a} \text{syn:anti 47:53} \text{26-s}
\]
been reported to date, a convenient synthesis of cis- and trans-ethyl-2-vinyl-cyclopropanecarboxylates (35) was supplied by Vogel and coworkers. The cis-trans ratio of 35 was determined to be 40:60. Saponification of cis- and trans-35 afforded the corresponding mixture of cis- and trans-cyclopropanecarboxylic acids (36). Treatment of 36 with thionyl chloride afforded a 38:62 mixture of the cis- and trans-cyclopropanecarbonyl chlorides (37). Up to this point the synthetic work was essentially a duplication of Vogel's work which had been concerned with the synthesis and reactivity cis- and trans-2-vinyl-cyclopropylisocyanates. Treatment of 37 with ethereal diazomethane afforded a crude mixture of cis- and trans-1-diazomethylketo-2-vinyl-cyclopropanes (38) as evidenced by the strong ir band at 2100 cm⁻¹ and the diazomethyl singlet at δ 5.31 in the nmr. Copper-catalyzed decomposition of 38 in refluxing cyclohexane afforded the desired isomeric tricyclic heptanones, 26-s and 26-a, in the syn-anti ratio of 47:53; the yield was 32% based upon the cis acid chloride (37).

Method C, while not providing a satisfactory synthesis for 26-s, did provide an interesting route to 26-a. The starting point for the synthetic sequence, as outlined in Scheme III, began with bicyclo [3.1.0] hexan-2-one (39) which could be conveniently synthesized from either 4-tosyloxy cyclohexanone 26 or 2-cyclopentenone.
Initially employing the basic procedure for the synthesis of bicyclo [3.1.0] hex-3-en-2-one (42) outlined by Russel and Stevenson, conversion of 39 to the crude bromoketal (40) was accomplished only after allowing the bromination to proceed at 25°-38°C in ethylene glycol instead of at 0°C. Further modification of the basic procedure was found necessary in the subsequent step for which reverse addition (pinchwise addition of sodium methoxide to a DMSO solution of 40) appeared to be a necessary condition for obtaining a respectable yield, 29% from 39, of the ethylene ketal (41) of bicyclo [3.1.0] hex-3-en-2-one (42). Deketalization of 41 was accomplished with 3%
H₂SO₄ affording 42 in 58% yield. Subsequent treatment of 42 with trimethylsulfoxonium ylide afforded 26-a and 26-s in 66% yield; however, the syn-anti ratio proved to be 2:98, a result which was not totally unexpected.

The synthesis of 42, a monohomocyclopentadienone, catalyzed an attempt at the preparation of the corresponding tosylhydrazone from which the carbene of 42 could ultimately be generated. The attempt met with failure because p-tosylhydrazone destroyed the carbon-carbon double bond in Michael addition fashion. This result agreed with similar results reported by Kirmse who observed that various cyclopentenones and cyclohexenones underwent addition as well as condensation in reactions with p-tosylhydrazone.²⁹

The synthesis of syn and anti tricyclo [5.1.0.0³,5] octan-2-ones, 49-s and 49-a, outlined in Scheme IV, represents the synthetic sequence developed by Lambert, Koeng, and Hamersa.³⁰ Although Lambert had removed a substantial fraction of the cis, cis-tricyclo [5.1.0.0³,5] octyl-2-carboxylic acid (46) from the mixture of cis, cis and cis, trans acids (46) by fractional crystallization, no attempt was made in this work to separate isomeric tricyclic octyl species until arrival at the ketone stage. Birch reduction of benzoic acid afforded 1,4-dihydrobenzoic acid (43) which was treated with ethereal diazomethane. Methyl-1,4-dihydrobenzoate (44), product of methylation with
Scheme IV

1. Benzene $\text{CO}_2\text{H}$ reacts with Na/NH$_3$ in EtOH to form 43.
2. 43 reacts with CH$_2$N$_2$ in Et$_2$O to form 44.
3. 44 reacts with CH$_2$I$_2$ in the presence of Zn - Cu (3 runs) to form 45.
4. 45 reacts with 10% NaOH to form 46.
5. 46 reacts with Pb(OAc)$_4$ to form 47.
6. 47 reacts with LiAlH$_4$ in Et$_2$O to form 48.
7. 48 reacts with CrO$_3$ in H$_2$SO$_4$ - H$_2$O to form 49.
Scheme IV - continued

TosNHNH₂ EtOH

N-NH-Tos

NaH THF

Tos-N-N

N-N-Tos

syn:anti

77:23
diazomethane, was cyclopropanated twice by three-fold treatment with methylene iodide and a zinc-copper couple. The product mixture, largely cis, cis and cis, trans-methyl-tricyclo [5.1.0.0^{3,5}] octyl-2-carboxylates (45), was converted to the corresponding mixture of acids (46) with 10% sodium hydroxide solution. Decarboxylation of 46 with lead tetraacetate afforded the isomeric tricyclic octyl acetates (47) which were subsequently reduced with lithium aluminum hydride to a crude mixture of the alcohols (48). Oxidation of 48 with the Jones reagent provided the tricyclic octanones 49-s and 49-a, which were separated and purified by four consecutive short-path distillations. The syn-anti ratio of the ketones was determined to be 77:23 from this sequence.

Conversion of 49-s and 49-a to the corresponding tosylhydrazones was accomplished although the yields were not good. Syn-tricyclo [5.1.0.0^{3,5}] octan-2-one tosylhydrazone (50-s) was obtained in 42% yield while the anti tosylhydrazone (50-a) was obtained in only 34% yield. Subsequent conversion of 50-s and 50-a to the sodium salts, 51-s and 51-a, was accomplished in the manner identical to that of the tricyclic heptanone tosylhydrazones, 33-s and 33-a.

The concluding facet of work connected with synthetic methods derives from an attempt to assign the various proton absorptions in both the 60 and 100 MHz of the
tricyclic heptanones 26-s and 26-a. Employing Eu (fod)_3, tris (1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanедione) Europium (III), lanthanide-induced shifts produced some rather interesting spectral changes, the most interesting of which demonstrated that the two protons adjacent to the carbonyl function (α-methine cyclopropyl protons) in both 26-s and 26-a were not located farthest downfield in the normal nmr spectra. It appeared that the protons most de-shielded in these systems were the two protons located at C-1 and C-2, the β-methine cyclopropyl protons. Further, rough calculations of the agreement factor R^31a-c for the four types of protons present afforded values of 0.16 and 0.23 for systems 26-s and 26-a, respectively. It was also of interest to note that endo protons at C-3 and C-7 in 26-a lay 0.65 ppm farther upfield than the endo protons of 26-s. It appeared that in 26-a the opposing banana bonds of the cyclopropane rings were exerting a shielding effect on the opposing endo protons while the geometry of 26-s excluded this effect.

These nmr observations of 26-s and 26-a brought to mind the case of bicyclo [3.1.0] hex-3-en-2-one (42) where nmr work by Hasty has shown that the α-methine cyclopropyl proton absorbed at δ 2.01 and the β-methine cyclopropyl proton at 2.38. Further, the C-6-endo proton, as might be suspected, absorbed at higher field (1.12) than the exo proton (1.32) due to the shielding influence of the pi cloud
of the suitably disposed double bond. Since (42) has a resonance form (42-r) which places a positive charge adjacent to the β-methine proton, it may be unfair to use (42) as a model for analogy with regard to 26-s and 26-a. Nevertheless, the observed effects in the nmr of 26-s and 26-a serve to create speculation about the possible contribution of a species which possesses finite partial charge separation as in 26-r. The extreme case, of course, would be contribution from the anti-homoaromatic species 26-aa.

The nmr spectra on the following pages demonstrate the "leap-frog" effects which occurred upon the addition of Eu(fod)₃ to either 26-s or 26-a.
Figure 1. $^1$H 60 MHz nmr of syn-tricyclo [4.1.0$^2$,4] heptan-5-one (26-s).
Figure 2. Nmr or Eu(fod)$_3$/26-s: Molar ratio, 0.13.
Figure 4. Nmr of Eu(fod)$_3$/26-s: Molar ratio, 0.38.
Figure 5. Nmr of Eu(fod)$_3$/26-s: Molar ratio, 0.50.
Figure 6. 60 MHz nmr of \textit{anti}-tricyclo [4.1.0.0^{2,4}] heptan-5-one (26-a).
Figure 8. Nmr of Eu(fod)$_3$/26-a: Molar ratio, 0.20.
Figure 10. Molar ratio, 0.40.
CHAPTER III
PYROLYSIS OF p-TOLUENESULFONYLHYDRAZONE SODIUM SALTS

Simple speculation concerning the probable products to be obtained from both the tricyclo [4.1.0.0^2,4] heptan-5-ylidenes and the tricyclo [5.1.0.0^3,5] octan-2-ylidenes led to the conclusion that moderately volatile products were distinct possibilities. With this in mind it was concluded that pyrolytic techniques which avoided solution work and hence separation problems would be preferred. The method of choice appeared to be high-vacuum pyrolysis of the neat salts. The sodium salts were, for the most part, pyrolyzed according to one of three selected procedures. The foremost technique, an extrapolation of the static technique commonly employed by workers such as Schecter,\(^{17,33}\) was designated the drop-static (D-S) technique in which controlled dropping of the sodium salt onto a heated glass surface under high vacuum (7 \times 10^{-5} - 3 \times 10^{-3} \text{ mm}) was accomplished employing virtually a one-piece vacuum unit (Figure 11), which allowed for pyrolysis, trapping, and transferral (of products) in an all-in-one type of operation. The second technique was the flow (F) technique,
Figure 11. High-vacuum pyrolysis system

A - Coil Trap (Removable)
B - Back-up Traps
C - Transfer Area
D - McLeod Gauge
E - Mercury Manometer
F - Thermocouple Vacuum Gauge
P - Pyrolysis Vessel or Hot Tube
V - Vacuum Pumps (Mechanical and Diffusion)
commonly referred to as the "hot tube" technique. This technique, in comparison with the D-S technique, allowed for longer contact times thereby increasing the chances for further rearrangement of initially-formed carbene products. The final technique was simply the infrequently-used static (S) technique which did find one important application resulting in the isolation of an elusive compound (54-c). The only solution work performed involved several trapping reactions involving the syn-tricyclo [4.1.0.0^2,4] heptan-5-ylidene species and styrene or dimethyl maleate.

The majority of pyrolysis work, involving the sodium salts 34-s, 34-a, 51-s and 51-a, was performed on 34-s and 34-a. Although it was hoped that the different disposition of cyclopropane rings might serve to alter the product chemistry in going from the syn to the anti carbene in each series, this did not prove to be the case. In fact, it appeared that the syn-anti reactivity for each series was the same.

Drop-static (D-S) and simple static (S) pyrolyses of 34-s and 34-a in the range 160°-500°C afforded a white, waxy material, melting sharply at 46°-47°, which was conveniently trapped out on the cold finger (0°-10°) of the modified sublimators used in the D-S and S pyrolyses. The waxy solid exhibited a penetrating odor which always served to announce its presence in the pyrolysate. The solid
discolored upon exposure to air, assuming a yellow-brown coloration within one hour. The thermal stability of the solid appeared suspect since attempted sublimation under high vacuum of impure material led to tarring. Heating the solid in benzene or toluene at temperatures $> 50^\circ$ even under argon or nitrogen also had a deleterious effect.

The structure of the solid was established by spectroscopic evidence and analysis. Infrared bands at 3020, 1650, and 650 cm$^{-1}$ indicated the necessary double bond feature. The nmr spectrum, perhaps the most confirmative piece of spectroscopic evidence, showed a four-proton multiplet at $\delta 2.33$, a two-proton multiplet at 2.35-2.90, a four-proton multiplet at 3.02, and a six-proton multiplet at 5.55. The two-proton multiplet was overlapped on each end by the adjacent four-proton multiplets. The uv spectrum showed a $\lambda_{\text{max}}$ at 254 ($\varepsilon 8120$). The uv absorption maximum corresponded rather well with that reported for tricyclo [9.7.0.0$^{2,10}$] octadeca-5,9,11,15-tetraene (53). Mass spectral analysis showed the parent peak to be m/e 184. Elemental analysis proved satisfactory for a C$_{14}$H$_{16}$ olefinic hydrocarbon. The structure therefore assigned to this unique product was tricyclo [7.5.0.0$^{2,8}$] tetradeca-4,7,9,12-tetraene (52).
Hydrogenation of 52 resulted in the uptake of four moles of hydrogen, the hydrogenated product clearly possessing the parent peak of m/e 192. Attempts to form Diels-Adler adducts with maleic anhydride, dimethyl acetylene-dicarboxylate, and tetracyanoethylene failed, resulting in the tarring of dimeric 52. This failure to form a suitable Diels-Alder adduct was disappointing due to the effort spent in trying to achieve the desired result; nevertheless, it may very well be distortions of the molecular framework in the vicinity of the butadiene moiety are prohibiting the 2 + 4 cycloaddition.

An interesting facet of the isolation and characterization work of 52, formally the dimer of 1,2,5-cycloheptatriene (20), is that the dimer is the major product under all pyrolytic conditions, irregardless of technique and temperature. In light of this fact, the monomeric species 20 would deserve consideration as the primary product resulting from collapse of both tricyclic heptylidenes via a unique six-electron pericyclic reaction (vide infra).
Volatile products isolated from the D-S and S pyrolysies of 34-s and 34-a included toluene (57), cycloheptatriene (56), and two much more interesting products, \textit{trans-ethynyl-2-vinyl-cyclopropane} (54-t) and 4-ethynyl-cyclopentene (55). GLPC analysis employing a column temperature of 68°-70°C provided analytical samples of 54-t and 55. The cyclopropane was isolated in 1.0-11.8% yields in the temperature range 160°-400° with the cyclopentene appearing only at 500° in 3.8% yield. Comparison of the nmr spectrum of the crude volatile pyrolysate prior to GLPC with the nmr spectrum of purified 54-t on several occasions indicated that certain peaks in the cyclopropyl and vinyl regions of the nmr spectrum of the pyrolysate were missing in the nmr of purified 54-t. This observation led to the conjecture that under the GLPC conditions the \textit{cis-1-ethynyl-2-vinyl-cyclopropane} (54-c), if present in the pyrolysate,
was being destroyed. In fact, until the actual isolation of 54-c, the assignment of *trans* stereochemistry to the glpc-purified cyclopropane hinged upon this observation as well as the known instability of both *cis*-1,2-divinyl-cyclopropane (68)\(^\text{35}\) and *cis*-1,2-diethynyl-cyclopropane (69)\(^\text{36}\).

The ir spectrum of 54-t showed the necessary mono-substituted-acetylene bands at 3320 and 2120 cm\(^{-1}\) with the vinyl absorptions displayed at 1635, 980, and 905 cm\(^{-1}\). The 100 MHz nmr spectrum at high field showed a three-proton multiplet at 6 0.80-1.40 (H\(_6\), H\(_7\), and H\(_8\)), an acetylenic doublet at 1.85 (H\(_5\)), and an allylic multiplet at 1.58-1.94 (H\(_4\)). The olefinic regions displayed an ABX pattern with multiplets centered at 4.96 (H\(_3\)), 5.12 (H\(_2\)), and 5.40 (H\(_1\)). Coupling constants afforded by first order analysis are given below:

\[
\begin{align*}
J_{1,2} &= 16.8 \text{ Hz} \\
J_{1,3} &= 9.5 \\
J_{1,4} &= 7.5 \\
J_{2,3} &= 2.5 \\
J_{5,6} &= 2.0
\end{align*}
\]
Mass spectral analysis of 54-t demonstrated the parent peak to be m/e 92, the parent peak also being the base peak. Elemental analysis in turn proved satisfactory for the C$_7$H$_8$ olefinic hydrocarbon.

The assignment of the 4-ethynyl-cyclopentene (55) structure resulted from comparisons with the reported spectroscopic data of 55 which was isolated by Cristl and Harrington as the major product from the pyrolysis of nortricyclenone p-tosylhydrazone sodium salt (58). The ir spectrum of 55 displayed bands at 3325 and 2125 cm$^{-1}$, indicative of a monosubstituted acetylene. The cis nature of the carbon-carbon double bond was supplied by peaks at 1620 and 690 cm$^{-1}$. The 60 MHz nmr spectrum showed an acetylenic doublet at $\delta$ 2.04, a five-proton multiplet region at 2.20-3.20, and an olefinic singlet of two-proton magnitude at 5.68. Mass spectral analysis showed the parent peak, also
the base peak, to be m/e 92. Elemental analysis proved satisfactory thereby confirming the structure of 55. It should be noted that flow (F) pyrolytic work led to increased yields (6.9-25.9%) of 55 in comparison with D-S work.

The fourth and final true carbene product, discounting cycloheptatriene and toluene as bona fide carbene products, to be isolated from pyrolyses of 34-s and 34-a was cis-1-ethynyl-2-vinyl-cyclopropane (54-c) in 17-23% yield. This elusive compound was successfully generated by a simple modification of the basic static technique. Maintaining the sublimator cold finger at -72 to -65°C, twice the normal amount of given sodium salt usually employed was heated from an initial temperature of 140° to 225° over a period of thirty minutes. For the first time, the diazo precursor, syn- or anti-5-diazotricyclo[4.1.0.0^2,4]heptane (59) was observed to have been conveniently generated and trapped (on the cold finger). Coinciding with the observation of the red diazo compound was the successful isolation of 54-c, a species of unusual reactivity. Whereas 54-t proved thermally stable at 169°C in deuterochloroform solution, 54-c underwent complete rearrangement within thirty-six hours in deuterochloroform solution at 25° to afford 52. The implications of this rearrangement upon the nature of the primary product obtained from collapse of the carbene to product are considerable. At this point, although no hard kinetic
Evidence is yet available, it appears that $54-c$ has a half-life in solution of perhaps two to three hours maximum, assuming the unimolecular process, $54-c \rightarrow 20$, to be rate determining.

The syn- and anti-$5$-diazotricyclo [4.1.0.0^{2,4}] heptanes (59) proved extremely unstable, appearing to very slowly lose nitrogen even at the low temperatures employed. This was not surprising since secondary aliphatic diazo compounds had generally been demonstrated to not survive the pyrolysis conditions when generated from the corresponding $p$-tosylhydrazone salts. Moreover, the instability of 59 was in accordance with the reported instability of dicyclopropyldiazomethane (60) which must be kept below $-30^\circ C$ in order to sufficiently retard decomposition.
The ir spectrum of 54-c showed diagnostic absorptions at 3310, 3085, 2120, 1635, and 985 cm\(^{-1}\) although interference from cycloheptatriene and dimer 52 tended to obscure absorptions elsewhere in the spectrum. The 100 MHz nmr spectrum at high field showed two one-proton multiplets at \(\delta 0.78\) (H\(_6\)) and 1.20 (H\(_7\)).* A two-proton multiplet region was observed at 1.48-1.84 (H\(_4\) and H\(_6\)) for the allylic and propargyl protons followed by an acetylenic doublet (H\(_5\)) at 1.88. The olefinic regions displayed an ABX pattern with multiplets centered at 5.10 (H\(_3\)), 5.24 (H\(_2\)), and 5.64 (H\(_1\)). Coupling constants are given below:

\[
\begin{align*}
J_{1,2} &= 15.8 \text{ Hz} \\
J_{1,3} &= 8.5 \text{ Hz} \\
J_{1,4} &= 7.5 \text{ Hz} \\
J_{2,3} &= 2.5 \text{ Hz} \\
J_{5,6} &= 2.0 \text{ Hz}
\end{align*}
\]

*Suitable model compounds for nmr analysis of both 54-t and 54-c as well as 65 were provided by vinyl- and ethylnyl-cyclopropane. \(^{39a,b}\)
In an initial attempt to trap the key reactive intermediate, 1,2,5-cycloheptatriene (20), pyrolysis of 34-s via the D-S technique was effected under high vacuum (9 x 10^{-5} mm: maximum pressure reading) employing a matrix isolation unit, with the matrix window maintained at 6°K as the pyrolysate trap.* Inspection of the uv-visible range 200-500 nm showed the only readily discernible absorption to be due to 52, \( \lambda_{\text{max}} = 254 \). Ir inspection showed principally the presence of the cyclopropane 54 and dimer 52. A peak at 2040 cm^{-1} with a shoulder at 2035 cm^{-1} was of primary interest although without considerably more work in this area it would be extremely premature to assign the absorption to a high-energy allenic stretching mode which would probably be characteristic of 20.

Several attempts to trap the monomer 20 with styrene and dimethyl maleate failed. The products obtained from these reactions were the spiro adducts resulting from trapping of the carbene itself. Heating 34-s in the presence of either styrene or dimethyl maleate in tetraglyme solution afforded the respective adducts 2-phenyl-spiro [cyclopropane-1,5'-syn-tricyclo [4.1.0.0^{2,4}] heptane] (61) and trans-2,3-dicarbomethoxy-spiro [cyclopropane-1,5' syn-tricyclo [4.1.0.0^{2,4}] heptane] (62). Although the yields

*Low-temperature matrix isolation experiments were made possible by the use of matrix isolation equipment available in the laboratories of Dr. William Weltner, Professor of Chemistry, at the University of Florida.
of 61 (34%) and 62 (39%) were not spectacular, they were nevertheless sufficient so as to allow characterization of both species.

The mass spectrum of 61 showed the parent peak to be m/e 196 with elemental analysis proving satisfactory for the C_{15}H_{16} benzenoid hydrocarbon. Peaks at 3070, 3040, 1605, and 700 cm\(^{-1}\) indicated the presence of a monosubstituted mononuclear aromatic structure while an absorption at 3010 cm\(^{-1}\) indicated the cyclopropane structural feature. The nmr of 61 proved most informative since a set of overlapping triplets situated at \(\delta\) 2.15 and 2.30 provided evidence for the presence of an isomeric mixture consisting of \(\text{cis, cis-61}\) and \(\text{trans, trans-61}\). The 60 MHz nmr of isomeric 61
showed two four-proton multiplet regions at δ -0.05 - 0.73 and 0.75 - 1.93. The spiro cyclopropane hydrogens gave rise to (a) one distinguishable doublet at 1.25 and (b) the set of overlapping triplets previously mentioned. The high-field triplet had a coupling constant of 7.5 Hz while the low-field triplet possessed a coupling constant close to 7.0 Hz in magnitude. The uv spectrum displayed B-bands at 262, 267, and 276 nm with a much more intense K-band at 226 nm (ε 7490). The K-band, while 22 nm higher than that of benzene was reasonable since cyclopropylbenzene itself shows a K-band at 219 nm (ε 8900).

The assignment of trans stereochemistry to the spiro dicarboxylate 62 was based on the size of the coupling constant obtained from the AB quartet generated by the spiro cyclopropane hydrogens in the 60 MHz nmr spectrum. The 5.8 Hz splitting observed corresponded well with the 5.6 Hz splitting reported for dimethyl-3,3-dimethylcyclopropane-trans-1,2-dicarboxylate (63). Further the cis and trans cyclopropane dicarboxylates 64-c and 64-t have respective
$J_{AB}$'s of 8.8 and 6.6 Hz, again confirming the trans stereochemistry of spiro adduct 62. The 60 MHz nmr of 62 displayed two four-proton multiplets at $\delta$ 0.52 and 1.70, the two-proton AB quartet with doublets located at 2.42 and 2.65, and two three-proton singlets at 3.72 and 3.76. The mass spectrum showed a very weak parent peak (< 1%) but the base peak at m/e 117, corresponding to $C_9H_9^+$, demonstrated the facile loss of formally two carbomethoxy radicals and one hydrogen atom. The ir spectrum showed particularly strong absorptions at 1740, 1440, 1340, 1290, 1230, and 1165 cm$^{-1}$.

Pyrolyses of syn- and anti-tricyclo [5.1.0.0$^{3,5}$] octa-2-one tosylhydrazone sodium salts, employing the D-S technique, afforded two products in variable total yields ranging from a high of 79.9% to a low of 26.5%. The range of temperatures examined was from 260° to 400°C with product inversion occurring in the vicinity of 400°. The primary product was determined to be $\sigma$-allyl-2-ethynyl-cyclopropane (65) with the 1,5 hydrogen-shifted derivative, octa-1,2,5,7-tetraene (66), growing in yield with corresponding increase in pyrolysis temperature.

The 60 MHz nmr of 65 showed a one-proton multiplet at $\delta$ 0.47 ($H_9$), a complex two-proton multiplet at 1.02 ($H_7$ and $H_8$), and a complex one-proton multiplet at 1.38 ($H_6$). An acetylenic doublet was displayed at 1.81 ($H_5$) followed by a two-proton allylic multiplet at 2.23 ($H_4$).
The vinyl protons gave rise to an ABX pattern with multiplets centered at 5.02 (H₃), 5.10 (H₂), and 5.95 (H₁). Simple first-order analysis supplied the relevant coupling constants:

$$J_{1,2} = 17.6 \text{ Hz}$$
$$J_{1,3} = 9.7 \text{ Hz}$$
$$J_{1,4} = 6.4 \text{ Hz}$$
$$J_{5,6} = 2.0 \text{ Hz}$$

The ir spectrum of 65 showed the necessary acetylenic absorptions at 3320 and 2120 cm⁻¹ with the vinyl contributions displayed at 3080, 1645, 990 and 910 cm⁻¹. The mass spectrum showed the parent peak to be m/e 106 with the base peak located at m/e 91, C₇H₇⁺. Elemental analysis proved satisfactory for the C₈H₁₀ compound thereby establishing the identity of the hitherto unknown 65.

The acyclic octatetraene 66, predominating at 400° in the pyrolysate, was established as a secondary product derived from a 1,5 hydrogen shift in cyclopropane 65, the sole product derived from collapse of the tricyclic octanylidenes to product. The origin of 66 was ascertained by
independent flow (F) pyrolysis of glpc-purified 65 at 410°. The octatetraene was obtained in 72% yield as the only readily-identifiable product with no trace of 65 in the pyrolysate.

The 100 MHz nmr of 66 showed a pseudo heptuplet of two-proton magnitude at δ 2.84 (H₃). The olefinic region was more complicated giving rise to a two-proton pseudo pentuplet at 4.74 (H₁), a three-proton multiplet region at 4.84-5.32 (H₂, H₇, and H₈), and another three-proton multiplet region at 5.50-6.60 (H₄, H₅, and H₆). The proton assignments appeared justified on the basis of comparison with

the nmr spectrum of the reasonable model compound 1,2,5-hexatriene (67). The ir of 66 possessed an absorption at 1955 cm⁻¹, confirmative of the allene moiety. Other important
absorptions attributed to carbon-carbon double bond groupings were noted at 3090, 3005, 1645, 1605, 995, 910, 845 and 740 cm\(^{-1}\). The uv spectrum provided an absorption maximum at 225 nm, \(\varepsilon\) 27,100. Since no compound possessing a \textit{cis}-butadiene structural feature has been demonstrated to have an extinction coefficient greater than 10,000,\(^4\) it appears that 66, if a \textit{cis-trans} mixture, contains a sizable \textit{trans} component. Mass spectral analysis placed the parent peak at \(m/e\) 106 while elemental analysis proved satisfactory for the C\(_8\)H\(_{10}\) isomer.

A summary of the basic reactivity of the syn and \textit{anti} tricyclic heptylidenes and octanylidenes shows that four C\(_7\)H\(_8\) monomeric and dimeric species and two C\(_8\)H\(_{10}\) monomeric species were isolated. As yet unanswered are (a) the stereochemistry of the ring fusion in 52 and (b) the geometry of the butadiene moiety in 66. Probably the most

\[\text{Diagram of structures}\]
interesting products in terms of continuing interest are the isomeric cyclopropanes $54\text{-}c$ and $54\text{-}t$. Kinetic studies of both compounds will extend the body of knowledge surrounding the Cope rearrangement. Although not mentioned earlier, $54\text{-}t$, while having proved stable at $169^\circ\text{C}$ in solution, did rearrange quantitatively to give $52$ at $208^\circ\text{C}$ in solution as evidenced by uv and mass spectral fingerprints. Moreover, it would appear that $54\text{-}c$, even without further kinetic examination, will lie between $\cis\text{-}1,2\text{-}\text{divinyl-cyclopropane}$ (68) and $\cis\text{-}1,2\text{-}\text{diethyl-cyclopropane}$ (69) in proclivity towards a Cope-type rearrangement.$^{35,36}$

Concerning the observation of cycloheptatriene and toluene in the pyrolysate obtained from the tricyclic heptanylidenes, it appears reasonable to say that the cycloheptatriene derives from a protonated $5\text{-}\text{diazo tricyclic heptane}$ (70) which, upon loss of nitrogen followed by cationic rearrangement, would afford cycloheptatriene. This hypothesis would be in keeping with the discussion of diazonium or
carbonium ion intermediates (or both) obtained from $p$-tosylhydrazone salts when decomposition fails to exclude a protic environment.² The formation of toluene, which could derive from cycloheptatriene at high temperatures as outlined by Woods,⁴⁵ is also due in part to the breakdown of the $p$-toluenesulfinate anion since toluene was also observed in the pyrolysate afforded by the tricyclic octanylidenes. The end result is that cycloheptatriene and toluene are not carbene-derived and warrant no further discussion.

\[ \text{[Diagram]} \]

© '2H 70 *No
The question of paramount importance with regard to the isolation and characterization of the various products derived from the syn and anti tricyclic heptanylidenes is an intriguing one: Do the observed products stem from the novel collapse of the carbene to 1,2,5,-cycloheptatriene (20) followed by rearrangement and/or dimerization, or does cis 1-ethynyl-2-vinyl-cyclopropane (54-c) merit designation as the sole primary carbene product undergoing subsequent rearrangement to afford the other observed products?

The answer to such a mechanistic question must be based upon (a) the observations thus far obtained (Chapter III) and (b) analogy appearing in the chemical literature.
Analogy or precedent was afforded by the remarkable insight of Sasaki and coworkers who proffered a novel explanation for the considerable difference of the carbene product distributions between the aldehyde and ketone $p$-tosylhydrazones 71 and 72. It was concluded that the chrysanthemyl carbenes derived from *cis*- and *trans*-71 underwent largely fragmentation as opposed to ring expansion due to a favorable electronic effect imparted by the isobutenyl moiety. The electronic effect would result in the lowering of the transition-state energy for the fragmentation process by virtue of formation of a conjugated diene, assuming the carbene reaction proceeded via either a concerted process or via a stepwise process involving either an ion-pair or radical pair:
In the case of the chrysanthemyl carbenes derived from cis- and trans-72, the ring expansion process predominated with exclusive migration of the isobutenyl-substituted bond (C3-C1 bond), again suggesting that the electronic effect of an isobutenyl substituent plays an important role at the transition state. However, another piece of rationale was required in order to explain the drastic difference in carbene product distributions despite obvious electronic control by the isobutenyl substituent. It was Sasaki's contention that the diversity of cyclopropylcarbene reactions, such as fragmentation and ring expansion, had been explained principally by consideration of strain and electronic factors without due consideration of conformational effects. He advanced the notion that the conformational effect played a very significant role in determining the cyclopropylcarbene rearrangement reactivity. Maximum interaction of the carbene with the rearranging bond (the ring-expansion process) was possible when the substituent $R_C$ assumed an s-trans-like conformation against the cyclopropane ring while an
s-cis-like conformation afforded poor interaction, presumably facilitating fragmentation as the process of choice.

The observed ring-expansion of the chrysanthemyl carbenes of 72 was thus rationalized on the basis of the s-trans conformational effect while the chrysanthemyl carbenes of 71, minus the methyl substituent, were free to assume either conformation, the s-cis being probably no more or no less favored than the s-trans with the electronic effect exerted by the isobutenyl moiety being the decisive factor.
The development of the conformational effect as a tool in determining the cyclopropylcarbene rearrangement aptitude was further extended by Sasaki to geometrically constrained species, some of which are locked into either an s-trans or an s-cis conformation. Whereas $7_3$, an s-trans species, underwent ring expansion exclusively, $7_4$, $7_5$, and $7_6$ underwent the fragmentation reaction due to the s-cis structure presumably.

In short, precedent as provided by Sasaki would regard $\text{ois-1-ethynyl-2-vinyl}$ cyclopropane (54-c) as the primary product most likely to be obtained upon collapse of either tricyclic heptanylidene species to product. Cursory analysis of the basic results outlined in Chapter III would
tend to argue in behalf of 54-c as the sole primary product since 54-c, once formed, proved extremely labile \((t_{1/2} = 2-3 \text{ hours maximum})\) at 25° rearranging smoothly to dimer 52. Further, at present, there is no evidence to argue for reversibility in the formation of monomer 20 with the predominant formation of dimer 52 under all pyrolysis conditions arguing for an essentially irreversible reaction leading from 54-c to 52. The simple kinetic picture suggested by the observed reactivity of 54-c is supplied by the following reaction sequence treated by the steady state approximation:

\[
2C \xrightarrow{k_1} 2M \xrightarrow{k_2} D
\]

\[
\text{rate} = \frac{d[D]}{dt} = k_3 [M]^2
\]

\[
\frac{d[M]}{dt} = k_1 [C]^2 - k_2 [M]^2 - k_3 [M]^2
\]

\[
C = \text{cyclopropane 54-c}
\]

\[
M = \text{monomer 20}
\]

\[
[D] = k_1^2 [C]/(k_2 + k_3)^{1/2}
\]

\[
[D] = k_1 k_3 [C]^2/(k_2 + k_3)
\]

Assuming \(k_2 \ll k_3\), the rate expression would reduce to \(d[D]/dt = k_1 [C]^2\), the rate of formation of the intermediate.
The intermediate, once formed, goes on to product rapidly. In this situation no equilibrium is established between reactant and intermediate, the intermediate \((M = 20)\) being dubbed a van't Hoff intermediate: **Mechanism A.**

Despite the foregoing discussion of precedent and the ensuing qualitative kinetic analysis, there remain some important questions tied into the exact identity of the
primary product obtained from the tricyclic heptanylidene.
Assuming \(54-c\) to be the primary product, how does one account for the formation of \(\text{trans-1-ethynyl-2-vinyl cyclopropane (54-t)}\) and \(4\)-ethynyl-cyclopentene (55), products, which if they arise from \(54-c\), must do so by a nonconcerted process presumably involving biradical intermediates; i.e., \(54-c\) would be forced to undergo epimerization via cleavage of the C1-C2 bond to afford \(54-c\) at lower temperatures (160°C-400°C), while a 1,3 alkyl shift involving migration of the C1-C2 bond would afford \(55\) at higher temperatures (≥500°C). In reality such reactivity for \(54-c\) does not seem plausible since it would mean that a Cope-type rearrangement, a well-established concerted process as outlined under orbital symmetry considerations, \(47\) would actually be in competition with a stepwise process. Further, examination of the activation energy parameters for \(\text{cis-1,2-divinyl cyclopropane (68)}, E_a = 19.38 \pm 1.80 \text{ kcal/mole, and cis-1,2-diethynyl cyclopropane (69)}, E_a = 22.7 \text{ kcal/mole,}\)
demonstrates the facile nature of the six-electron pericyclic reactions for such substituted cyclopropane systems.\textsuperscript{35,36} However, in the case of \textsuperscript{69} surface-catalyzed reactions in the gas-phase kinetics cast doubt on the exact nature of the rearrangement of \textsuperscript{69}. In contrast to the foregoing purportedly concerted pericyclic reactions, the \textit{cis-trans} isomerizations of simple cyclopropanes typically afforded $E_a$'s in the range 59.4-65.5 kcal/mole while 1,3 alkyl shifts of simple vinyl-cyclopropanes gave rise to $E_a$'s in the range 44.5-54.6 kcal/mole.\textsuperscript{48}

![Diagram]

The point to be made is at the heart of the discussion of plausible mechanisms: if \textsuperscript{54-c} is the only true primary product, then \textsuperscript{54-t} and \textsuperscript{55} must derive from a species other than \textsuperscript{54-c}. At the same time, the low yields of \textsuperscript{54-t} (1.0-11.8%) and \textsuperscript{55} (3.8-25.9%) suggest that the importance of these two products, however deserving of mechanistic scrutiny,
should not be overly weighted so as to create havoc with the mechanistic pathway proving, in the final analysis, true for the tricyclic heptanylidenes.

The suggestion to be made at this point is to also consider an alternative mechanism which could account for the observed products. In this alternative mechanism, 1,2,5-cycloheptatriene (20) would arise via a novel six-electron reaction involving the carbene site and the C1-C6 and C2-C4 cyclopropane bonds, a postulate only briefly mentioned earlier in Chapter I. The application of the Mobius-Hückel concept as applied to organic molecules and reactions by Zimmerman\textsuperscript{49} to the cyclic arrays involved in bond-breaking and bond-forming processes in the transition states of the tricyclic heptanylidenes shows that both systems possess Hückel orbital arrays with the \textit{syn} isomer (19-s) having zero sign inversions while the \textit{anti} isomer (19-a) possesses four inversions. This is schematically outlined below. The result of this simple analysis is the tendency to accept the fact that either carbene could afford the monomeric species 20 outright without invoking an intermediate such as 54-c. It should be noted that the foregoing Hückel arrays employ the p\textsuperscript{2} configuration of the carbene, an assumption which better accommodates the developing orbital overlaps encountered in the transition state geometries of the respective carbenes as evidenced by inspection of
Hückel-Mobius:

Bond breaking

Bond forming

Bonds unchanged

dark lobes: + of basis set
light lobes: - of basis set

molecular models. Another examination of the possible "allowedness" of this carbene arrangement would be afforded by approaching the hypothetical arrangement from the viewpoint of a retro-cycloaddition involving a $\pi_4 s + \pi_2 s$ process for $19-s$ and a $\pi_4 a + \pi_2 a$ process for $19-a$ wherein the respective $\pi$ groupings have been tagged with the HOMO-LUMO designations derived from the Fukui Frontier Orbital approach to pericyclic reactions. The connecting lines between lobes of the same phase serve to demonstrate the demanded suprafacial-antarafacial interactions which afforded the allene from the respective carbenes. Again it should be noted that the $p^2$ configuration of the carbene
2 + 4 retro-cycloaddition:

has been employed in describing the electronic interactions leading to the allene as product. The exact configuration of the carbene carbon in the tricyclic heptanylidenes as well as the electronic makeup of the allene 20 will be discussed further (vide infra), but first a hypothetical picture must be drawn based upon the primary formation and subsequent reactivity of 20: Mechanism B.
Since it has been experimentally established that 54-c rearranges smoothly to 52 presumably via 20, then 20, if first formed as speculated, would be in equilibrium with isolable 54-c, the rate-determining step being that leading to formation of dimer 52. In this sense 20 would be an Arrhenius intermediate\textsuperscript{13} and the energy profile would qualitatively appear as follows. Further, an understanding of the origin of products 54-t and 55 would be more easily grasped since the initially formed species 20 could be partitioned between singlet and triplet states, the triplet state giving rise to the open-chain biradical species 77 which closes to afford either 54-t or 55 depending upon the pyrolysis temperature employed. Since both singlet and triplet state chemistry is observed for carbenes in general,\textsuperscript{1,2}
it is reasonable to assume that a triplet tricyclic heptylidene species would give rise to a triplet allene species which could then fragment to give biradical 77. A biradical such as 77 is a potential intermediate as evidenced by the assumed formation of such intermediates in the pyrolyses of (a) the salt of bicyclo [6.1.0] nona-2,4,6-triene carboxaldehyde tosylhydrazone (78)\textsuperscript{51} and (b) 7-cycloheptatrienyl diazomethane (79).\textsuperscript{52}
Contrast of the preceding discussion of Mechanism B against Mechanism A points to the fact that triplet 20, obtained in Mechanism B by collapse of a small triplet component of the tricyclic heptylidyne to triplet 20, would not be allowed under Mechanism A since, under the concerted process assumed taking place in the conversion of $54 \rightarrow 20 \rightarrow 52$, singlet cyclopropane ($54 \rightarrow c$) would give rise to singlet 20 which would dimerize as fast as it is formed.

Two alternative mechanisms have thus far been proposed. A clear choice between the mechanistic alternatives must be left to the individual reader at this point. A third mechanism, which would invoke both $54 \rightarrow c$ and 20 as primary products via competitive formation from the carbene, would only serve to beg the question of mechanism, and hence is discarded.

The structure and electronic character of 20, the key intermediate of tricyclic heptylidyne chemistry, deserves further consideration. The smallest cyclic allenes isolated to date are 1,2-cyclononadiene $^{53}$ (80) and 1,2,6-cyclononatriene $^{34}$ (81). The smallest cyclic allene yet observed is 1,2-cyclohexadiene (22) with 1,2-cycloheptadiene (21) not far behind in terms of framework distortion. As mentioned earlier in Chapter I, the observation of 21 and 22 is afforded only by isolation of their dimers and tetramers and the adducts resulting from trapping experiments. $^{14a-b,15a-b}$
In the smaller ring systems such as 21 and 22 the various authors have presented the viewpoint that these systems must be something less than a fully-bonded allenic structure; i.e., research groups such as Ball and Landor\textsuperscript{14a} and Moore and Moser\textsuperscript{14b} have proposed that the C\textsubscript{6} and C\textsubscript{7} cyclic allenes possess a planar structure in which carbon atoms 1, 2, and 3 are sp\textsuperscript{2} hybridized with unbonded electrons for the singlet species (S) residing in the hybrid orbital at C-2, while in the triplet species (T), one electron has been promoted from the nonbonding hybrid at C-2 to the nonbonding allylic orbital.

More recently Dillon and Underwood\textsuperscript{54} performed INDO-MO calculations on a large number of distorted geometries of allene as a model for medium and small cyclic allenes. Both the lowest singlet and triplet states were calculated; the effect of geometrical distortion on total energy, charge distribution, and spin distribution were also investigated. The calculations indicated that 1,2-cycloheptadiene (and larger cyclic allenes) would have a singlet ground state best considered as an allyl cation with an anion located at
basis set: dark orbitals:
in plane
light orbitals:
out-of-plane

C-2. On the other hand, 1,2-cyclohexadiene was shown by the calculations to most likely possess a triplet ground state best approximated by an allyl radical with a second unpaired electron occupying the in-plane orbital at C-2.

Returning to the question of the initial carbene configuration of the tricyclic heptanylidene, it can be seen that the singlet $p^2$ configuration assumed earlier (note Hückel-Mobius and $2 + 4$ retro-cycloaddition schemes) would give rise to a species formally containing an allyl anion with positive charge residing in the in-plane orbital at C-2. This arrangement of the singlet species disagrees with prediction. On the other hand the lower-energy $\sigma^2$ configuration of the carbene, because of its disposition away from the internal cyclopropane bonds (C1-C6 and C2-C4) would not
allow for the necessary overlaps in the transition state leading directly to monomer 20. In fact such an arrangement

\[
\begin{align*}
\sigma^2 & \quad \text{low energy singlet}
\end{align*}
\]

would most likely afford 54-c, the primary product of Mechanism A, since no other reaction appears possible. Thus determination of the singlet carbene configuration (\(\sigma^2\) or \(p^2\)) for the tricyclic heptylidene might aid in the choice of mechanistic alternatives. On the other hand, it must be remembered that the demonstration of \(p^2\) character in carbenes such as the syn and anti tricyclic heptylidenes may not guarantee subsequent unique reactivity as would be observed in the case of Mechanism B where the \(p^2\) configuration, assumed bishomoaromatic, supposedly affords the novel six-electron pericyclic reaction leading to 20. This caution arises from Bergman's assignment of bishomoaromaticity to 15, discussed in Chapter I, which undergoes the established fragmentation process as opposed to the novel pericyclic process.
The point to be made in this discussion about the electronic structure of $20$ is that $20$, if the primary carbene product of tricyclic heptanylidenes, must arise by what appears to formally be a bishomoaromatic carbene in a singlet process and would possess at least initially singlet character reverse that of prediction.

As a matter of final interest, it would be of value to attempt to place the key $C_7H_8$ species on an energy surface although it would be only a crude approximation in the case of both $20$ and the tricyclic heptanylidenes themselves. Employing Benson's additivity rules$^{55}$ for the estimation of

![Energy Diagram](image)
thermochemical properties, 54-c, 54-t, and 55 are easily calculated allowing one less kcal/mole for the heat of formation of 54-t due to the missing eis interaction as would be observed in 54-c. The straightforward calculations afford values of 90, 89, and 66 kcal/mole for 54-c, 54-t, and 55, respectively. Employing Wentrup's extrapolation of Benson rules to carbenes, a rough calculation of the energy of the tricyclic heptanylidene species itself employing the heat of formation of triplet methylene (92 ± 1 kcal/mole) for the carbene "group" affords a value of ca. 135 kcal/mole. Ring corrections used in obtaining this value are derived from bicyclo [3.1.0] hexane (32.7 kcal/mole) and cyclopropane (27.6 kcal/mole). The value does not appear altogether unreasonable since 7-cyclohepta trienyl methylene (82) has been calculated to possess a heat of formation of ca. 145 kcal/mole, a value which serves to indicate that the heat of formation for certain suitably constructed carbene species can be rather high. On the

other hand carbene species such as 83 have rather moderate heats of formation, ΔH°f = ca. 68 kcal/mole.56
The C\textsubscript{7}H\textsubscript{8} species most difficult to assess on the energy surface is the monomer 20. Perhaps the best way to view this species energetically is to assume the view of Dolbier\textsuperscript{57} who approximated a value for diradical 20 by first assuming a π-bond energy in strain-free 20 of 60 kcal/mole and subsequently subtracting out (a) 8 kcal/mole for the allene destabilization energy and (b) 15 kcal/mole for the allyl radical stabilization energy. The resulting value (37 kcal/mole) was added to the heat of formation of "strain-free" 20, 65 kcal/mole, to afford a final figure of 102 kcal/mole. This calculation, while only a rough approximation, probably represents a minimum value since Underwood's INDO-MO calculations\textsuperscript{54} of 1,2-cycloheptadiene (21) underscore the fact the 21 may indeed be a "distorted" allene as opposed to a planar species, thus by analogy raising the energy of 20 above the 102 kcal/mole figure approximated. While the energy diagram shows that the carbene will certainly convert to product(s), it is also obvious that activated 20 should convert to some or all of the species below it on the profile. In passing it should be noted that the dimer 52 afforded a calculated heat of formation of ca. 88 kcal/mole, a value which is probably high due to lack of a suitable model for ring corrections.

A discussion of the chemistry of the tricyclic octanylidenes is essentially a matter of the fragmentation
process occurring for cyclopropylcarbenes. The idea that these systems could possibly give rise to the novel cyclic allene monomer bicyclo [5.1.0] octa-3,4-diene (84) was developed early in the work with the tricyclic heptanylidenes.

Whereas the $p^2$ singlet of both tricyclic heptanylidenes would possess to a certain degree parallel geometry with regard to the adjacent cyclopropane rings, the tricyclic octanylidenes in the $p^2$ singlet state would possess the bisected geometry which plays such a vital role in the carbonium ion chemistry of these systems. It was thought that this favorable added factor might help overcome the
necessary energetics required for the trishomo interaction leading to monomer 84. Molecular models showed that the syn species was especially well set for this type of interaction.

It appears from the pyrolysis results, though, that any trishomo interaction in these systems will have to be established by trapping reactions with olefins and by Hammett studies in order to disclose the electrophilicity or nucleophilicity of these systems.

The observance of the 1,5-hydrogen shift in the product cis-1-allyl-2-ethynyl cyclopropane (65), the only primary carbene product from the syn and anti tricyclic octanylidenes, is not without precedent since Dalacker and Hopf observed a facile 1,5-hydrogen shift in a related model compound, cis-1-ethynyl-2-methyl cyclopropane (85), which smoothly converted to hexa-1,2,5-triene.

\[
\begin{align*}
\text{cis-1-allyl-2-ethynyl cyclopropane (65)} \\
\rightarrow \\
\text{hexa-1,2,5-triene (66)}
\end{align*}
\]
Analysis of conformational effects favoring a ready transfer of hydrogen in 65 shows that the situation most favored would have an orientation where the vinyl group of the allyl moiety is oriented away from the neighboring triple bonded substituent as pictured below. This situation would lead to a predominant formation of a tetraene (66) having \textit{trans} geometry for the butadiene moiety.
This is supported by the observed uv extinction coefficient of 27,100 for 66 as previously noted in Chapter III.

In retrospect, the question of operational homoaromaticity in the tricyclic heptanylidenes 19-s and 19-a and in the tricyclic octanylidenes 25-s and 25-a has been raised. To fully answer the question, further work will be required in order to demonstrate the electrophilicity or nucleophilicity of said carbenes. It can be stated, however, that such homoaromatic reactivity appears a definite possibility for 19-s and 19-a due to the nature of the observed products. The case for 25-s and 25-a is not as promising and brings to mind a mechanistic consideration which should be afforded the fragmentation process of cyclopropylcarbenes since this mechanistic pathway may prove, in the final analysis, operative for both the tricyclic heptanylidenes and octanylidenes. The consideration afforded to the fragmentation process is one whereby the process may be visualized as a concerted process employing the cheletropic designation; i.e., a reaction in which two $\sigma$-bonds which terminate at a single atom are made or broken in a concerted fashion.47 The cheletropic disengagement of acetylene from ethylene with cyclopropyl carbene as reactant has been treated by Zimmerman previously giving rise to what is now known as the Zimmerman MO following method.59 Recently Jones and Brinker60 presented an elegant simplified approach to the
MO following method in general which allows for better visualization of the overall process leading from reactant to transition state to product. The following are the "rules of thumb," developed by Zimmerman and expanded upon by Jones and Brinker, which are put to use in constructing the schematic correlation diagram for the cyclopropylcarbene fragmentation process:

(1) For the MO following, treat the carbene as the sum and difference of two "p" orbitals. "s" character is added after compatibility of reactant, transition state, and product orbitals is determined. Thus, during the "following," the orbitals of the lowest singlet state of methylene would be represented by LS-1 and LS-2. Subsequent addition of "s" character to the orbital used in the reaction ((p1 + p_n) or (p1 - p_n)) leads to the familiar filled sp^2 orbital of the carbene and depending on the orbital used in the reaction, permits prediction of the orientation of the carbene during the reaction.
(2) Number the transition state linear array beginning with one carbene orbital and ending with the other.

(3) Assign the familiar linear polyene orbital signs to the transition state orbitals.

(4) Follow each occupied reactant MO to product, using the carbene MO that is compatible with the highest occupied transition state MO.

Thus, in conclusion of this chapter, the application of the Jones-Brinker extrapolation of Zimmerman's rules to the cyclopropylcarbene cheletropic reaction affords the following correlation diagram (Scheme V). The most important observation to be obtained from the diagram is that, when "s" character is finally added to the proper carbene orbital used in the reaction (LS-1 vs. LS-2) under the auspices of rule 1, it will be added to p$_1$ + p$_6$ (LS-1), the vertical p orbital, which correlates in symmetric fashion with the bonding product orbital $\pi_{34}$. The qualitative result, an important one in light of preceding discussion concerning the reactivity of p$^2$ vs. $\sigma^2$ singlet configurations of cyclopropylcarbenes 19-s, 19-a, 25-s, and 25-a, is that the electron pair of the carbene must become oriented in an sp$^2$ hybrid in the vertical plane ($\sigma$). Once that posture is assumed only one mechanism is apt to derive, that of fragmentation. Closing the discussion on an optimistic note, suppose a structure such as 19-a through the favorable energetics imparted by homoaromaticity, were able
Scheme V

Reactants

Symmetry element: vertical plane (σ)

Transition State

Products

\[ \sigma_{23}^* - \sigma_{45} \]

\[ \sigma_{23}^* + \sigma_{45} \]

\[ p_1 - p_6 \]

\[ p_1^* + p_6 \]

\[ \pi_{12}^* - \pi_{56} \]

\[ \pi_{12}^* + \pi_{56} \]
(p₁ + p₆) + s \rightarrow sp² (vertical) = o²

to obtain the p² configuration. Could one reasonably assume a different mode of reaction for such a carbene? The conclusion could very well be yes.
CHAPTER V
EXPERIMENTAL

Melting points were taken on a Thomas-Hoover melting point apparatus and were uncorrected. Infrared spectra of synthetic intermediates were recorded on either a Perkin-Elmer Model 137 or a Model 437 spectrophotometer while the spectra of pyrolysis products were recorded on a Beckman IR 10 spectrophotometer. Nuclear magnetic resonance (nmr) spectra were obtained from a Varian Model A-60-A spectrometer and, less frequently, from a Varian Model XL-100 spectrometer. Mass spectral data were obtained from both an Hitachi Perkin-Elmer RMU-6E mass spectrometer and an AEI-MS 30 high-resolution mass spectrometer. Ultraviolet spectra were recorded on a Cary 15 double-beam spectrophotometer.

Elemental analyses were carried out by Atlantic Microlab, Inc., Atlanta, Georgia. Glpc work, analytical and preparative, was performed on a Varian Aerograph Model-A-90-P3 gas chromatograph employing the cut-and-weigh method of analysis in analytical work. Four columns were used in glpc work and are referenced as follows:

(1) column A - 3% FFAP on Chromasorb P-Regular, 5 ft x 0.25 in - aluminum.
(2) column B - 10% Carbowax 20 M + 3.5% KOH on Chromasorb P-Regular, 10 ft x 0.25 in - aluminum.

(3) column C - 6% SE-30 on Chromasorb P-Regular, 5 ft x 0.25 in - aluminum.

(4) column D - 18% DC-200 on Chromasorb P-Regular, 15 ft x 0.25 in - copper.

All compounds which were not referenced were commercially available.

Preparation of diallyl ketone (29).

Tetramethyl-1,3-cyclobutanedione (27) was prepared according to the procedure of Miller and Johnson: \[mp 113°-114° (lit^{18} mp 115°-116°).\] Reaction of allyl Grignard (1.25 moles) with 27 (0.50 mole) using the procedure of Dreyfuss\(^\text{19}\) afforded 5-allyl-5-hydroxy-2,4,4-trimethyl-7-octen-3-one (28) in 55% yield (lit\(^{19}\) 61%). Base-catalyzed cleavage of 28 (22.5 g, 0.105 mole) employing barium hydroxide\(^\text{19}\) followed by distillation of the pyrolysate (bp 45°-57°/20 mm) on a 23 mm, 36 in Nester-Faust semi-works spinning band column afforded four fractions boiling (20 mm) at 32°-38°, 40°-48°, 49°-55°, and 55°-56°. Redistillation of the third fraction and combination with the fourth fraction gave 7.5 g (0.068 mole) of diallyl ketone (bp 55°-56°/20 mm, lit.\(^{19}\) bp 51°-53°/20 mm) contaminated with 5-10% allyl propenyl ketone.
Net yield of 29 was typically 62-64% (6.8-7.1 g, 0.062-0.065 mole). Ir (film): 3025, 2960, 2920, 2870, 1730, 1640, 1420, 1385, 1360, 1325, 1285, 1215, 1135, 1105, 1070, 1050, 995, 920; nmr (CDCl3): δ 3.23 (d with splitting, J = 7 Hz, 4 H), 4.90-5.32 (AB m, terminal vinyl H, 4 H), 5.58-6.33 (m, 2 H); mass spectrum (m/e): 110 (M⁺), 69 (M⁺ - C₃H₅, major peak).

Preparation of 2,2-diallyl-1,3-dioxolane (30).

A solution of 6.95 g (0.0631 mole) of 29 in 70 ml of benzene was mixed with 5.15 g (0.0830 mole) of ethylene glycol and 0.05 g of p-toluenesulfonic acid monohydrate in a 200-ml round bottom flask. The flask was fitted with a Dean-Stark trap and a condenser (equipped with a drying tube). The mixture was refluxed until 1.1 ml of water had been collected (97% of the theoretical amount). The cooled reaction mixture was washed with 20 ml of 10% sodium hydroxide solution followed by five 10-ml washes with water. The benzene extract was dried over anhydrous K₂CO₃ and the benzene removed by rotary evaporation. The residual liquid was distilled at 20 mm affording 4.88 g (0.0316 mole) of 30 (bp 75-76°, 50%). Preparative glpc on column A (column 82°, He flow 60 ml/min) afforded an analytical sample of 30. Ir (film): 3040, 2930, 2875, 1645, 1430, 1320, 1300, 1285, 1265, 1240, 1200, 1175, 1140, 1115,
1080, 1040, 1000, 990, 920; nmr (CDCl₃): δ 2.39 (d with splitting, J = 7 Hz, 4 H), 3.90 (s, 4 H), 4.84-5.28 (AB m, terminal vinyl H, 4 H) 5.47-6.10 (m, 2 H); mass spectrum (m/e): 154 (M⁺), 113 (M⁺ - C₃H₅, major peak).

Anal. Calcd for C₉H₁₄O₂: C, 70.10; H, 9.15. Found: C, 70.35; H, 9.11.

Preparation of cis- and trans-3,4-bis (chloromethyl)-cyclopentanone (32).

A mixture of 6.75 g (0.0437 mole) of 30 and 12.1 g (0.0440 mole) of iodobenzene dichloride²⁰ in 75 ml of chloroform was heated at reflux for two hours under a slow stream of nitrogen. The chloroform solvent was removed by rotary evaporation affording a slightly colored mixture containing iodobenzene and crude cis- and trans-7,8-bis (chloromethyl)-1,4-dioxaaspiro[4.4]nonane (31). The cis-trans ratio of 31 was not established although the broad three-line multiplet centered at 3.65 δ (-CH₂Cl) indicated the presence of a cis-trans mixture. The iodobenzene was removed at 0.25 mm while heating the flask to 45°. Short-path distillation of 31 (bp 88°-95°/0.25 mm) afforded 6.80 g (0.0302 mole, 69%) of 31 possessing a brown tint (note: the use of hydroquinone stabilizer in distillations of 31 improved but did not eliminate decomposition). Crude 31 (6.75 g, 0.0300 mole) was dissolved in 70 ml of 3:1 ethanol-water containing 200 mg of
*p*-toluenesulfonic acid. The solution was heated at 35°-38° for 24 hours. The solution was poured into 500 ml of a saturated Na₂CO₃ solution and extracted with three 200-ml portions of ether. The combined ethereal extracts were washed with water until neutral followed by a final washing with 100 ml of saturated sodium chloride solution. The ethereal extract was dried over sodium sulfate and concentrated by rotary evaporation affording 5.11 g of an orange oil. The oil was fractionated through a short-path distilling head (hydroquinone stabilizer) affording the desired dichloroketone (32): 2.42 g (0.0134 mole, 45%).

I.r. (film): 2970, 2920, 1755, 1445, 1410, 1370, 1275, 1170, 1100, 770, 735; n.m.r. (CDCl₃): 6 2.17-2.58 (m, 4 H), 2.58-3.21 (m, 2 H), 3.57-3.80 (overlapping d, Jₜrans = 6 Hz, 4 H); mass spectrum (m/e): 181 (M⁺), 183 (M⁺ + 2, 66.3% of M⁺), 185 (M⁺ + 4, 11.1% of M⁺), 103 (M⁺ - C₃H₇Cl; major peak).

Preparation of *cis*– and *anti*-tricyclo [4.1.0.0²,⁴] heptan-5-ones (26-s and 26-a): method A.

A 2.42 g (0.0134 mole) mixture of crude *cis*– and *trans*-32 was added dropwise to a well-stirred 2.5 ml 50% sodium hydroxide solution in a 25 ml three-neck flask equipped with a short-path distilling head and a steam inlet (gas bubbler). After stirring for 30 min (reaction mixture had become black) a slow stream of steam was
introduced accompanied by gradual heating of the dark reaction mixture to 150° (oil bath). The reaction mixture was heated for a minimum of 2 hr periodically introducing 3-4 ml of water to maintain solvent level. The oil-water distillate was extracted with three 100-ml portions of ether and the ethereal extract dried over MgSO₄. Concentration by rotary evaporation afforded a light yellow (1.15 g) which was distilled affording 0.83 g of a colorless oil boiling 37°-42°/0.25 mm. The oil (.00769 mole, 57%) proved to be a surprisingly clean mixture of the syn (52%) and anti (48%) tricyclic ketons 26-s and 26-a by glpc on column B (column 150°, He flow 100 ml/min) with retention times of 15.7 min (anti) and 19.6 min (syn). Anti isomer (26-a): mp 41.0°-42.0° (sealed capillary, lit. 21 44°); ir (CCl₄): 2980, 1790(sh), 1720(s), 1440, 1340, 1295, 1190, 1145, 1100(w), 1075(w), 1050, 1030, 955(s), 935(s), 860; nmr (100 MHz, CDCl₃): δ 0.85 (un-symmetrical q, J = 3.5 Hz, 2 H), 1.25 (m, 2 H), 1.56 (m, 2 H), 2.08 (m, 2 H); uv (ethanol): λ_max 287 nm (ε 28); mass spectrum (m/e) 108 (M⁺), 79 (M⁺-CO-H, major peak).

Anal. Calcd for C₇H₈O: C, 77.75; H, 7.46.
Found: C, 77.61; H, 7.45.

Syn isomer (26-s): ir (film): 2980, 1795(sh), 1700(s), 1455, 1315(sh), 1285, 1185, 1150(w), 1085(w), 1040, 1015, 950, 940, 925(w), 910, 825, 800; nmr (100
MHz, CDCl₃): δ 0.76 (m, 2 H), 1.50 and 1.78 (two overlapping multiplets, 4 H), 2.18 (m, 2 H); uv (ethanol): λ_max 283 (ε 70); mass spectrum (m/e): 108 (M⁺), 79 (M⁺-CO-H, major peak).

Anal. Calcd for C₇H₈O: C, 77.75; H, 7.46. Found: C, 77.60; H, 7.53.

Preparation of cis- and trans-ethyl-2-vinyl-cyclopropane carboxylates (35).

Cis- and trans-35 were prepared from butadiene and freshly-prepared ethyl diazoacetate in 28-32% yield following the procedure of Vogel, Erb, Lenz, and Bothner-By. Analysis of the isomer mixture by glpc on column A (column 100°, He flow 25 ml/min) showed the cis-trans ratio to be 40:60. Bp 63°-64°/13 mm (lit. 61°-62°/12 mm); ir (film): 3000, 2905, 2850, 1720, 1640, 1435, 1390, 1375, 1345, 1315, 1300, 1280, 1260, 1180, 1090, 1035, 990, 905, 880, 860, 850, 820, 795, 740; nmr (CDCl₃): δ 0.80-2.28 (m, 4 H), 1.28 (t, J = 7 Hz, 3 H), 4.15 (q, J = 7 Hz, 2 H), 4.83-6.18 (m, vinyl H, 3 H); mass spectrum (m/e) 140 (M⁺), 67 (M⁺- CO₂CH₂CH₃, major peak).

Anal. Calcd for C₈H₁₂O₂: C, 68.54; H, 8.63. Found: C, 68.27; H, 8.62.

Preparation of cis- and trans-2-vinyl-cyclopropanecarbonyl chlorides (37).

Treatment of 100 g (0.713 mole) of cis- and trans-35 with 78.0 g (1.40 mole) of potassium hydroxide
in 400 ml of 50% methanol according to the procedure of Vogel and coworkers\textsuperscript{25} afforded 72.5 g (0.647 mole) of cis- and trans-2-vinyl-1-cyclopropanecarboxylic acids (36): bp 80°-82°/0.6 mm, 91%; lit.\textsuperscript{25} bp 52°-54°/0.05 mm, 90%. A mixture of cis- and trans-36 (69.0 g, 0.616 mole) was converted to the corresponding 2-vinyl-cyclopropane-carbonyl chlorides 37 (73.5 g, 0.561 mole, 90%) by treatment with 370 g (3.10 mole) of freshly-distilled thionyl chloride. The cis-trans mixture of 37 was analyzed by converting several drops with methanol to the corresponding methyl esters, which were chromatographed on column A (column 100°, He flow 30 ml/min). The cis-trans ratio was found to be 38:62. Bp 47°-48°/8-9 mm (lit.\textsuperscript{25} 49°-50°/11 mm); ir (neat, KBr liquid cell): 3035, 2930, 1770, 1640, 1430, 1350, 1295, 1230, 1190, 1150, 1110, 1080, 1060, 995(s), 915(s), 880(s), 810, 750, 725(s), 680(s); nmr (CDCl\textsubscript{3}): 6 1.05-1.90 (m, 2 H), 1.95-2.80 (m, 2 H), 4.92-5.98 (m, vinyl H, 3 H).


A solution of 25.8 g (0.460 mole) of potassium hydroxide in 43 ml water, 150 ml of diethylene glycol monoethyl ether, and 35 ml of ether were placed in a 500 ml Claisen flask equipped with a dropping funnel, a condenser, and two 500-ml Erlenmeyer receivers employing the
basic set-up described for diazomethane generation.\textsuperscript{62}  

The flask was heated at 65°-70° in a water bath while a 92.5 g (0.432 mole) solution of Diazald (N-methyl-N-nitroso-p-toluenesulfonamide, Aldrich) in 450 ml of ether was added dropwise over a period of 90 min. The ethereal diazomethane (∼ 12.9 g, 0.307 mole) was dried over KOH for 90 min at 0°. A solution of cis- and trans-37 (10.0 g, 0.0763 mole) in 20 ml of ether was added quickly dropwise to the dried ethereal diazomethane and the resulting solution was allowed to stir overnight at 25°. The yellow ether solution was concentrated by rotary evaporation giving an orange-yellow oil (∼ 10.0 g, 0.0735 mole) which was employed directly in the next step. \textit{Ir} (film): 3030, 2940, 2100(s), 1720, 1640(s), 1440, 1390(s), 1325(s), 1205, 1180, 1165(s), 1100(s), 1075(s), 1040, 995, 965, 910(s), 885, 840, 815, 785, 770, 720; \textit{nmr} (CDCl\textsubscript{3}): 0.75-2.28 (two overlapping m, 4 H), 4.77-5.84 (m, vinyl H, 3 H), 5.31 (s, diazomethyl H, 1 H).  

\textbf{Preparation of \textit{syn-} and \textit{anti-}tricyclo [4.1.0.0\textdegree,4] heptan-5-ones (26-s and 26-a): method B.}  

The crude diazoketone 38 (∼ 10.0 g, 0.0735 mole) was dissolved in 100 ml of cyclohexane and added dropwise over a period of 2 hrs to a refluxing slurry of 400 ml of cyclohexane and 25 g of anhydrous CuSO\textsubscript{4}. Upon completion of the addition and further stirring for 1 hr under reflux
the slurry was filtered and concentrated via rotary evaporation affording an orange-red oil. The oil was fractionated (short-path column) giving a fraction (slightly yellow) boiling 35°-44°/0.5 mm and weighing 2.95 g. Nmr spectral inspection indicated the distillate to be composed of the desired \( 26-s \) and \( 26-a \) contaminated with by-products possessing the vinyl-cyclopropane skeleton. Preparative glpc on column B afforded analytically pure samples of the isomeric tricyclic ketones. Column chromatography on silica gel (described next) afforded 1.01 g (0.00935 mole) of separated \( 26-s \) and \( 26-a \) (32% from the cis-acid chloride). The syn-anti ratio was 47:53.

**Anti isomer (26-a):** Anal. Calcd for \( C_7H_8O \): C, 77.75; H, 7.46. Found: C, 77.56; H, 7.42.

**Syn isomer (26-s):** Anal. Calcd for \( C_7H_8O \): C, 77.75; H, 7.46. Found: C, 77.85; H, 7.47.

**Purification and separation of syn- and anti-tricyclo[4.1.0.0\(^2,4\)]heptan-5-ones (26-s and 26-a).**

A crude 7.50 g mixture (distillate from several runs) of \( 26-s \) and \( 26-a \) obtained from reaction method B (diazoketone route) was chromatographed on 200 g (56 cm column height) of silica gel (MCB, G. 62) by eluting (dropping rate: 15 drops/min) with \( \sim 900-950 \) ml of carbon tetrachloride which both removed major impurities and effected separation of \( 26-s \) and \( 26-a \). The faster-moving
Syn isomer was stripped from the column by elution with ~ 600 ml of 1:1 carbon tetrachloride-methylene chloride followed by ~ 400 methylene chloride which served as a transition solvent between the syn and anti isomers (the use of methylene chloride required monitoring by glpc on column B of the eluent). The appearance of the anti isomer was accompanied by elution with ether which flushed the slower-moving isomer from the column. Final purification of the separated isomers was achieved by short-path distillation which removed traces of colored materials. The syn distillate proved absolutely free of the anti isomer while the anti distillate contained 2.3% of the syn isomer (by glpc). The syn-anti distribution was 1.20 g:1.36 g (47:53). The syn-anti mixtures obtained from reaction method A (bis-chloromethyl-ketone route) were separated in the same manner; a final distillation was found unnecessary since the distilled starting mixture of isomers was cleaner than the mixture obtained from method B.

The anti isomer obtained from the combination column chromatography-distillation work-up was observed to crystallize upon standing, affording a moist white solid melting 39.5°-41.0° (glpc sample: 41.0°-42.0°).
Eu(fod)$_3$ shifts in the 'H nmr spectra of syn- and anti-tricyclo [4.1.0.0$^2,4$] heptan-5-ones: structure assignment.

Treatment of 0.8 ml deuterochloroform solutions of 26-s (0.0470 g, 4.35 x 10$^{-4}$ mole) and 26-a (0.0789 g, 7.31 x 10$^{-4}$ mole) with Eu(fod)$_3$ in varying molar ratios produced interesting lanthanide-induced shifts in the 60 MHz 'H nmr spectra. Assuming the lanthanide atom to lie at a 3.0 Å distance from the oxygen atom (of each respective isomer) in the plane bisecting each system, the various lanthanide-proton distances and proton-Eu-C$_5$ angles were determined manually from a Dreiding model. Rough calculations of the agreement factor, $R_{31^a-c}$ employing shift data at maximum mole ratio, afforded $R = 0.16$ for 26-s and $R = 0.23$ for 26-a. Based upon these rough calculations of $R$ and the observed lanthanide-induced shifts in the 'H nmr spectra, the proton assignments of 26-s and 26-a were established for both the 60 and 100 MHz spectra (see Table III).

Preparation of bicyclo [3.1.0] hex-3-en-2-one (42).

Bicyclo [3.1.0] hexan-2-one (39) was prepared in 43% yield following the procedure of Nelson and Mortimer (lit. 26 64%) from 4-tosyloxy cyclohexanone. 26 Bicyclic ketone 39 was also prepared by the cyclopropanation of 2-cyclopentenone in 69% yield according to the procedure
Table I. $26-s + \text{Eu(fod)}_3$.

<table>
<thead>
<tr>
<th>Molar ratio: $\text{Eu(fod)}_3/26-s$</th>
<th>$H_1$ (Hz downfield from TMS at 60.0 MHz)</th>
<th>$H_2$</th>
<th>$H_3$</th>
<th>$H_4$</th>
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Table II. $26-a + \text{Eu(fod)}_3$.

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<tr>
<th>Molar ratio: $\text{Eu(fod)}_3/26-a$</th>
<th>$H_1$ (Hz downfield from TMS at 60.0 MHz)</th>
<th>$H_2$</th>
<th>$H_3$</th>
<th>$H_4$</th>
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Table III. Proton Assignments for 26-s and 26-a in the 100 MHz Spectra.

<table>
<thead>
<tr>
<th></th>
<th>H₁</th>
<th>H₂</th>
<th>H₃</th>
<th>H₄</th>
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</thead>
<tbody>
<tr>
<td>26-a</td>
<td>C-4, C-6</td>
<td>C-1, C-2</td>
<td><em>endo</em>: C-3 and C-7</td>
<td><em>exo</em>: C-3 and C-7</td>
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<tr>
<td>δ</td>
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<td>2.08</td>
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<td>1.25</td>
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<tr>
<td>26-s</td>
<td>C-4, C-6</td>
<td>C-1, C-2</td>
<td><em>endo</em>: C-3 and C-7</td>
<td><em>exo</em>: C-3 and C-7</td>
</tr>
<tr>
<td>δ</td>
<td>1.78</td>
<td>2.18</td>
<td>1.50</td>
<td>0.76</td>
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</table>
Russel and coworkers\(^{27}\) (lit. 65\%): bp 60°-62°/10 mm (lit.\(^{27}\) 55°/10 mm); mass spectrum (m/e) 96 (M\(^+\)), 68 (M\(^+\) - CO, major peak). The bicyclic ketone (4.0 g, .042 mole) was dissolved in 50 ml of ethylene glycol and treated dropwise with bromine (6.8 g, .043 mole) at 25°-38°. The solution became cloudy upon completion of bromine addition and was allowed to stir for 10 min longer. The solution was poured into a mixture of 14 g of Na\(_2\)CO\(_3\) in 100 ml of pentane. The pentane layer was separated and dried over Na\(_2\)SO\(_4\). Concentration by rotary evaporation afforded 6.73 g of a colored oil which was dissolved in 100 ml of DMSO (distilled from CaH\(_2\)). To the solution (under nitrogen) was added pinchwise sodium methoxide (3.78 g, 0.0701 mole) at 25°-35°. The almost black reaction mixture was stirred at 25° for 9 hrs and then gradually heated to 60° for 15 hrs. The black mixture was poured into 500 ml of H\(_2\)O and extracted with five 100-ml portions of pentane and the pentane extracts were dried over Na\(_2\)SO\(_4\). Concentration via rotary evaporation afforded an orange liquid which afforded the ethylene ketal (41) of 42 (bp 84°-90°/20 mm; lit.\(^{28}\) bp 89°-95°/28 mm): 1.65 g, 0.0119 mole, 29\% from 39. Generation of 42 from 41 was accomplished by shaking 10.0 g (0.0725 mole) of 41 with 14 ml of 3\% H\(_2\)SO\(_4\) for 10 minutes in a separatory funnel. The reaction mixture was extracted with three 50-ml portions of ether
and dried over K₂CO₃. Distillation of the concentrated liquid residue afforded 3.98 g (0.0423 mole) of 42 (bp 64°-67°/10 mm): 58% yield from 41. Glpc on column A (column 95°, He flow 60 ml/min) afforded analytically pure 42. IR (film): 3010, 2940, 1695(s), 1620, 1555, 1425, 1340, 1300, 1285, 1180, 1155, 1090, 1060, 1035, 990, 955, 915, 855, 825(s), 810(s), 765, 735; nmr (CDCl₃): δ 1.17-1.68 (m, 2 H), 2.15 and 2.50 (two overlapping m, 2 H), 5.62 (d, J = 6 Hz, 1 H), 7.68 (d of d, J = 6 and 3 Hz, 1 H); uv (ethanol): λmax 324 (ε 20), 252 (ε 2490), 213 (ε 7120); mass spectrum (m/e): 94 (M⁺), 66 (M⁺ - CO, major peak). Anal. Calcd for C₆H₆O: C, 76.57; H, 6.43. Found: C, 76.45; H, 6.44.

Preparation of anti-tricyclo [4.1.0.²,⁴] heptan-5-one (26-a).

Oil-free sodium hydride (0.80 g, 0.033 mole) was added to 50 ml of anhydrous DMSO (distilled from CaH₂) in a 100-ml 3-neck flask equipped with a solid addition funnel, a condenser, a liquid dropping funnel, and a N₂ inlet. To the mixture was added 7.60 g (0.0345 mole) of trimethylsulfoxonium iodide pinchwise. The resulting solution was allowed to stir for 30 min at 25° whereupon 2.81 g (0.0299 mole) of 42 in 10 ml of anhydrous DMSO was added slowly dropwise. The solution became orange-brown in color and was stirred at 25° for 2 hrs followed by
heating at 55°-60° for 30 min. The solution was poured into 250 ml of H₂O and extracted with three 150-ml portions of ether. The ethereal extracts were washed with 100 ml of saturated NaCl solution and dried over Na₂SO₄. Filtra-
tion and concentration via rotary evaporation of the ether solution afforded an orange oil (2.74 g) which was dist-
tilled through a short-path column at 0.25 mm (bp 36°-38°). A 2.14 g (0.0198 mole, 66%) fraction of 26-a (white solid) was obtained which partially clogged the condenser and re-
receiver elbow: mp 40.5°-41.5°; lit.²¹ mp 44°. Glpc analy-
sis on column B showed the syn-anti ratio to be 2.2:97.8.


Preparation of methyl-tricyclo [5.1.0.⁰₊₃,⁵] octyl-2-
carboxylates (45): isomeric mixture.

Methyl-1,2-dihydrobenzoate (44) was prepared in 90% yield by treatment of 1,4-dihydrobenzoic acid³⁰ (43) (30.0 g per run, 0.242 mole) with alcohol-free, KOH-dried ethereal diazomethane (∼ 22 g, 0.52 mole) generated from N-methyl-N-nitroso-p-toluenesulfonamide (Diazald): bp 44°-46°/0.75 mm; lit.³⁰ bp 33°/0.5 mm. Treatment of 36.5 g (0.264 mole) of 44 according to the procedure of Lambert and coworkers³⁰ employing methylene iodide and either the Lambert zinc-copper couple or the LeGoff couple⁶¹ afforded ∼ 17.1 g (0.103 mole) of 45
(isomeric mixture, 40%; lit. 40%). Glpc analysis on column C (column 130°, He flow 60 ml/min) indicated the presence of two principal isomers (cis, cis and cis, trans-45). Spectral and elemental analysis of the isomeric mixture (bp 45°-46°/0.5 mm; lit. 40°/0.5 mm) afforded the following: ir (film): 2990, 2950, 2870, 2830, 1730 (s), 1470, 1445, 1430, 1360, 1340, 1310, 1275 (s), 1245 (s), 1180 (s), 1130, 1105, 1085, 1020 (s), 935, 895, 870, 845, 810, 755, 715; nmr (CDCl₃): δ -0.08-1.65 (complex region, 8 H), 2.10 (narrow m, 2 H), 3.45 (broad t, 5.5 Hz, 1 H), 3.72 (s, 3 H); mass spectrum (m/e): 166 (M⁺), 79 (C₆H₇⁺, major peak).

Anal. Calcd for C₁₀H₁₄O₂: C, 72.26; H, 8.49;
Found: C, 72.27; H, 8.54.


Tricyclo[5.1.0.0³,5]octyl-2-carboxylic acid (46) was prepared by treatment of 17.1 g (0.103 mole) of 45 with 360 g of 10% NaOH solution according to the procedure of Lambert (lit. 40 yield 76%). The crude acid (12.1 g, 0.0793 mole, 77%) obtained was dissolved in a solution of 10 ml of anhydrous pyridine (distilled first from tosyl chloride, then from CaH₂, and stored over 4A sieves) and 250 ml of benzene (dried by passing through Woelm basic alumina, activity I, under nitrogen).
The acid solution was placed in a 500-ml 3-neck flask equipped with a condenser, a nitrogen inlet tube and a mechanical stirrer. The system was flushed for 20 min with nitrogen, and lead tetraacetate (53.5 g, 0.121 mole) was quickly introduced followed by gradual heating of the mixture to reflux. The mixture was refluxed for 1 hr; a heavy white precipitate of lead diacetate was observed to have formed subsequent to the vigorous evolution of \( \text{CO}_2 \) during the reaction. The reaction mixture was filtered and washed with one 75-ml portion of \( \text{H}_2\text{O} \), two 75-ml portions of 1N NaOH solution, one 75-ml portion of \( \text{H}_2\text{O} \), one 75-ml portion of 1N HCl, and two 75-ml portions of \( \text{H}_2\text{O} \). The benzene extract was dried over MgSO\(_4\), filtered, and twice distilled to give 7.31 g (0.0441 mole, 56\%) of isomeric acetates boiling 60°-63°/0.5 mm (lit. 55°/0.1 mm). Spectral and elemental analysis of the acetate mixture (glpc on column C, 135°; He flow 60 ml/min) gave the following: ir (film): 2980, 2950, 2850, 2820, 1725(s), 1475, 1440, 1350, 1240(s), 1225, 1135, 1080, 1030(s), 1005(s), 955(s), 880, 845, 780, 735; nmr (CDCl\(_3\)): \( \delta \) -0.06-1.50 (complex m region, 8 H), 1.55-2.32 (m, 2 H), 2.07 (s, 3 H), 5.20 and 5.82 (m and t, respectively, \( \text{CHOAc} \) of two isomers present, 1 H); mass spectrum (m/e): 144 (M\(^+\), \( \leq 1\% \)), 93 (\( \text{C}_7\text{H}_9\)^+, peak second in intensity), 91 (\( \text{C}_7\text{H}_7\)^+, major peak).
Anal. Calcd for $\text{C}_{10}\text{H}_{14}\text{O}_2$: C, 76.26; H, 8.49.
Found: C, 72.19; H, 8.51.

Preparation of syn- and anti-tricyclo [5.1.0.0$^{3,5}$] octan-2-ones (49-s and 49-a).

A mixture (3.55 g, 0.0214 mole) of the isomeric acetates 47 was dissolved in 35 ml of ether (anhydrous) and added slowly dropwise to a slurry of 0.900 g (0.236 mole) of lithium aluminum hydride in 75 ml of ether employing a 250-ml 3-neck flask equipped with a condenser, an addition funnel, and a stirrer. The reaction mixture was held at reflux for 30 min subsequent to completion of acetate addition. The cooled mixture was carefully hydrolyzed with 3.5 ml of 5% NaOH solution. When the solids in the flask had turned white, the mixture was filtered. The white solids were boiled twice with tetrahydrofuran whereupon the tetrahydrofuran-ether extracts were combined, dried over MgSO$_4$, filtered, and concentrated by rotary evaporation. A crude mixture of isomeric tricyclo [5.1.0.0$^{3,5}$] octan-2-ols (48) was obtained (2.55 g, 0.0206 mole, ~96%): ir (film): 3300(s); nmr (CDCl$_3$): $\delta$ 4.12 and 4.73 (pseudo d and t, respectively, CH-0 of two isomers present, 1 H).

A crude mixture of isomeric 48 (2.70 g, 0.0217 mole) was oxidized by dissolution in 50 ml of acetone followed by titration with Jones reagent$^{64}$ (2.7 N
solution) at 15°-20° until the persistence of a yellow color was noted. The excess reagent was quickly destroyed with isopropyl alcohol and 100 ml of H₂O was added to dissolve the inorganic precipitate. The resulting aqueous solution was extracted with five 80-ml portions of ether. The ethereal extracts were dried over MgSO₄, filtered, and concentrated via rotary evaporation. The crude product (2.39 g) was distilled through a short-path column affording 2.05 g (0.0168 mole, ~76%) of moderately pure 49-s and 49-a: bp 53°-54°/0.5 mm. Glpc on column B (syn-anti ratio, 77:23) afforded analytically pure samples of the tricyclic octanones (column 175°, He flow 120 ml/min) with retention times of 14.4 min (anti) and 22.8 min (syn).

**Antidi isomer (49-a):** ir (film): 3010, 2960, 2875, 2810, 1680(s), 1435, 1380, 1310, 1240, 1190, 1100, 1050, 1025, 970, 915, 835, 720; nmr (CDCl₃): δ 0.68 (narrow m, 2 H), 0.85-1.70 (m, 6 H), 2.13 (narrow m, 2 H); uv (ethanol): λ_max 283 (ε 28); mass spectrum (m/e): 122 (M⁺), 55 (M⁺ - C₅H₇, major peak).

**Anal.** Calcd for C₈H₁₀O: C, 78.65; H, 8.25; C, 78.45; H, 8.22.

**Syn isomer (49-s):** mp 43.5°-44.5°; ir (film): 3010, 2970, 2875, 2810, 1660(s), 1460, 1440, 1350, 1320, 1255, 1240, 1190, 1120, 1030, 1015, 970, 960, 925, 885, 840, 725; nmr (CDCl₃): δ 1.02 (m, 4 H), 1.73 (m, 4 H),
2.27 (narrow m, 2 H); uv (ethanol): $\lambda_{\text{max}}$ 284 (e 40); mass spectrum (m/e) 122 (M$^+$), 55 (M$^+$ - C$_5$H$_7$, major peak).

Anal. Calcd for C$_8$H$_{10}$O: C, 78.65; H, 8.25; C, 78.68; H, 8.25.

Purification and separation of syn- and anti-tricyclo[5.1.0.0$^{3,5}$]octan-2-ones (49-s and 49-a).

Attempted separation of 49-s and 49-a by column chromatography (silica gel and alumina) according to the procedure employed for the isomeric tricyclic heptanones (26-s and 26-a) proved inefficient. Separation of 49-s and 49-a was effected by subjecting the initially distilled mixture of ketones to four consecutive short-path distillations (0.5 mm) gradually raising the oil bath temperature from 25° to 68° over a time period ranging from 7.5-10 hrs. The anti isomer distilled first; fractions enriched in the syn isomer led to the crystallization of a white solid in the condenser-receiver pathway. The slightly tinted pot residue obtained at the end of a distillation proved to be pure 49-s, solidifying upon standing. An anti fraction (1.10 g, 0.00902 mole) collected in this manner proved 96.1% free of the syn isomer while a syn fraction (2.64 g, 0.0216 mole) proved 98.4% free of the anti isomer (by glpc on column A, 130°; He flow 120 ml/min).
Preparation of tosylhydrazones.

The lability of 26-s, 26-a, 49-s, and 49-a in the presence of acid precluded acid-catalyzed formation of the respective tosylhydrazones. The respective tosylhydrazones were prepared by stirring equimolar quantities of p-toluenesulfonyl hydrazide and the ketone in absolute ethanol (1 g/25 ml) for 21-24 hrs (25°). A notable exception was 26-s which within five min after mixing led to the precipitation of the desired tosylhydrazone (33-s); the resulting slurry was stirred for only 2 hrs before work-up. The crude tosylhydrazones obtained from 26-a, 49-s, and 49-a upon removal of solvent were first chromatographed on silica gel (methylene chloride eluent) and then recrystallized from ethanol at 0°. Tosylhydrazone 33-s required only recrystallization from ethanol. Syn-tricyclo [4.1.0.0^2,4] heptan-5-one tosylhydrazone (33-s): 83% yield; mp 176.0°-178° (dec); ir (KBr) 3350, 3150, 1580(sh), 1450, 1390, 1370, 1330, 1310, 1295, 1180, 1160(s), 1085, 1040, 1015, 940, 900, 825, 810, 720, 705; nmr (CDCl_3): δ 0.78 (m, cyclopropyl methylene H, 4 H), 1.96 (m, cyclopropyl methine H, 4 H), 2.40 (s, -CH_3, 3 H), 7.47 (s, -NH, 1 H), 7.53 (ABq, aromatic H, 4 H); mass spectrum (m/e) 276 (M^+), 91 (C_9H_7^+ major peak).

Anal. Calcd for C_{14}H_{16}O_2N_2S: C, 60.85; H, 5.84; N, 10.14. Found: C, 60.82; H, 5.84; N, 10.19.
Anti-tricyclo [4.1.0.0^2,4] heptan-5-one tosylhydrazone (33-a): 31% yield; mp 132°-134° (dec); ir (KBr): 3350, 3150, 2850, 1540, 1590 (sh), 1480, 1430, 1385, 1335, 1320, 1310, 1300, 1180, 1160 (s), 1085, 1025, 1010, 935, 895, 820, 805, 725, 715, 705; nmr (CDCl$_3$): δ 0.52 (m, cyclopropyl-endo H, 2 H), 1.03 (m, cyclopropyl-exo H, 2 H), 1.70 (m, cyclopropyl methine H, 4 H), 2.40 (s, -CH$_3$, 3 H), 7.27 (s, -NH, 1 H), 7.58 (ABq, aromatic H, 4 H); mass spectrum (m/e) 276 (M$^+$), 91 (C$_7$H$_7^+$, major peak).

Anal. Calcd for C$_{14}$H$_{16}$O$_2$N$_2$S: C, 60.85; H, 5.84; N, 10.14. Found: C, 60.82; H, 5.86; N, 10.14.

Syn-tricyclo [5.1.0.0^3,5] octan-2-one tosylhydrazone (50-s): 42% yield; mp 141°-146° (dec); ir (KBr): 3350, 3180, 2950 (w), 2880 (w), 1605 (doublet), 1435, 1410, 1360, 1325 (s), 1280, 1160 (s), 1120, 1075, 1035, 990, 930, 875, 850, 830, 815, 760, 735, 705; nmr (CDCl$_3$): 0.08-2.03 (complex m region, cyclopropyl methylene and methine H, 8 H), 2.15 (pseudo t, -CH$_2^-$, 2 H), 2.40 (s, -CH$_3$, 3 H), 6.68 (broad s, -NH, 1 H), 7.60 (ABq, aromatic H, 4 H); mass spectrum (m/e) 290 (M$^+$), 91 (C$_7$H$_7^+$, major peak).


Anti-tricyclo [5.1.0.0^3,5] octan-2-one tosylhydrazone (50-a): 34% yield; mp 138°-141° (dec); ir (KBr): 3350, 3150, 2850 (w), 1605 (doublet), 1430, 1390, 1355,
1320, 1275, 1160(s), 1080, 1025, 980, 955, 905, 845, 830, 820, 725; nmr (CDCl₃): -0.22 (m, 1 H), 0.60-1.98 (complex m region, 8 H), 2.17 (m, 1 H), 2.40 (s, -CH₃, 3 H), 7.35 (s, -NH, 1 H), 7.60 (ABq, aromatic H, 4 H); mass spectrum (m/e) 290 (M⁺), 91 (C₇H₇⁺, major peak).


**Preparation of sodium and potassium salts of tosylhydrazones.**

The sodium salts of 33-s, 33-a, 50-s, and 50-a were prepared under nitrogen (dry box) by dissolving the respective tosylhydrazone in dry tetrahydrofuran (refluxed over and distilled from lithium aluminum hydride) in the ratio of 1 g/35 ml and adding 1.2 equiv of oil-free sodium hydride (Alfa Inorganics) pinchwise with rapid stirring. Stirring was continued for an additional 2 hrs. An equal volume of pentane (spectrograde) was added to the tetrahydrofuran slurry (most of the desired salt had already precipitated from the tetrahydrofuran solution). The white precipitate was filtered, dried under full vacuum, and stored in an amber bottle in the dry box. Yields for the four sodium salts were in the range 97.8-100%. Similar preparation of the potassium salts of tosylhydrazones 33-s and 33-a was effected by treatment of the respective tetrahydrofuran solution with 1.2 equiv of potassium.
tert-butoxide (Alfa Inorganics). Work-up with pentane and drying afforded the potassium salts of 33-s and 33-a in quantitative yield.

Pyrolysis of tricyclo ketone tosylhydrazone sodium salts.

The two principal pyrolytic techniques employed were the (1) drop-static (D-S) technique and, to a lesser extent, the (2) flow (F) technique. The first technique involved controlled dropping of the sodium salt on a heated glass surface (160°-500°) under high vacuum (7 x 10^{-5} - 3 x 10^{-3} mm). High-boiling products (chiefly dimeric material) were immediately trapped by a cold finger disposed 3.5 cm above the heated surface while volatile products were collected in a 35 cm coil trap (cooled by liquid nitrogen) in line with two smaller back-up traps (see Figure 11). The pyrolysis vessel (Pyrex) used for this work was simply a sublimator modified with a storage neck for solids, a Rotaflo high-vacuum stopcock (Quickfit, Inc.), and a conducting tube. Adjustment of the stopcock opening allowed the sodium salt to drop from the storage neck, through the conducting tube, to the heated glass surface. Either dry ice-acetone or ice-H_{2}O was employed as the cold finger coolant. The second technique employed controlled dropping of the sodium salt down a "hot tube." Two tubes (Vycor) were used, the first having a 30 cm heat zone, the second
a 40 cm heat zone. Both tubes were designed with 120° bends at the top of the heat zone which was constructed from 24 gauge nichrome wire and asbestos tape. The tube was connected first to a solid collection trap followed by the same trap system for volatile products described for the drop-static technique. A third less-frequently used technique was the basic static (S) technique in which the entire sodium salt aliquot was simply placed in the bottom of a sublimator and pyrolyzed. Heating of the sublimators used in the pyrolytic work was accomplished by the use of a Wood's metal bath. Monitoring of temperatures was accomplished by using chromel-alumel thermocouples in conjunction with a Minneapolis-Honeywell Model 2702 potentiometer. Nitrogen evolution during pyrolysis of a sodium salt was monitored by a Televac Model 2A thermocouple vacuum gauge (Fredericks Company) which allowed for reasonably accurate readings in the range 1-500 microns.

Analytical Methods

High-boiling materials (principally dimeric products) were analyzed by gravimetric measurements in conjunction with nmr analysis employing m-dinitrobenzene (0.0149 M in CDCl₃) as a standard for proton counting. The procedure for nmr analysis was to dissolve the previously weighed material in 0.5-1.0 ml of the standard
solution recording a minimum of four integral traces for use in calculations. Volatile products were transferred on a vacuum line directly into a nmr tube containing 0.5 ml of the standard solution and analyzed via nmr initially. The volatile products (and CDCl₃) were subsequently separated from the m-dinitrobenzene internal standard by vacuum-line transferral and analyzed by glpc on column D employing 10.0 µl of either heptane (6.84 mg) or toluene (8.67 mg) as glpc internal standard.

Static pyrolysis of syn-tricyclo[4.1.0.0²,4]heptan-5-one tosylhydrazone sodium salt (34-s): initial isolation of 1,2,5-cycloheptatriene dimer (52) and trans-1-ethynyl-2-vinyl-cyclopropane (54-t).

A sublimation apparatus was loaded with 0.200 g of 34-s and immersed in the metal bath heated at 225° (P = 5 x 10⁻⁴ mm). A white waxy solid was deposited on the cold finger during the pyrolysis period of 2 hrs. The cold finger was maintained at 0°-9° throughout the period of heating. The sublimation apparatus was removed to the dry box where the white solid was removed with a spatula affording 57.3 mg of the solid with mp 46°-47°. Spectral and elemental analysis of the solid proved the compound to be the head-to-head dimer of 1,2,5-cycloheptatriene: tricyclo[7.5.0.0²,8]tetradeca-4,7,9,12-tetraene (52). This dimer was extremely sensitive to oxygen; an analytical sample of the dimer turned yellow-brown upon exposure to
air after 1 hr. The dimer also proved heat sensitive, turning yellow even in dilute solution upon prolonged heating above 50°. Analysis of the volatile fraction collected afforded a small amount of material (~2.8 mg by nmr only) which, when combined with fractions collected in subsequent pyrolyses, proved to be chiefly trans-1-ethynyl-2-vinyl cyclopropane (54-t). Analytical samples of 54-t were obtained by glpc on column D (column 68°, detector and injector 82°, He flow 12 ml/min). Nmr analysis of glpc-purified 54-t indicated that the absence of certain peaks, which appeared in the vinyl and cyclopropyl region of the nmr of crude 54, was due to the probable destruction of one isomer (54-c) under glpc conditions.

Hydrogenation of 28.4 mg (1.54 x 10^-4 mole) of 52 over 0.200 g of 5% platinum (on carbon) in 20 ml of ethyl acetate resulted in the uptake of 15.80 ml of hydrogen at 25°/764 mm (theor. 16.90 ml). Mass spectral analysis of the hydrogenated product showed the parent peak of m/e 192. Tricyclo [7.1.0.0^2,8] tetradeca-4,7,9,12-tetraene: 93% yield; mp 46°-47°; ir (CCl4, KBr liquid cells): 3020, 2960, 2910, 2850, 2810, 1650, 1440, 1415, 1360, 1325, 1235(w), 1215(w), 1190(w), 1160(w), 1090, 1070(w), 950, 930, 910, 650; nmr (CDCl3): δ 2.33 (m, 4 H), 2.35-2.90 (m overlapped by the two 4 H m, 2 H), 3.02 (m, 4 H), 5.55 (m, 6 H); uv (ethanol): λmax 254 (ε 8120), shoulders 247
(ε 7610) and 263 (ε 5500); mass spectrum (m/e, %): 184 (3.3), 169 (4.2), 156 (2.8), 155 (3.7), 154 (3.1), 153 (2.9), 143 (3.2), 142 (3.3), 141 (7.9), 130 (6.5), 129 (9.3), 128 (11.7), 127 (3.0), 118 (3.4), 117 (10.5), 116 (5.5), 115 (19.9), 106 (2.7), 105 (7.5), 104 (5.9), 103 (5.7), 102 (3.8), 93 (21.8), 92 (22.4), 91 (100.0), 90 (6.0), 89 (10.7), 83 (3.2), 82 (3.4), 80 (5.0), 79 (18.2), 78 (24.3), 77 (41.6), 76 (9.8), 75 (4.8), 74 (3.3), 67 (8.9), 66 (6.3), 65 (32.1), 64 (6.4), 63 (18.6), 62 (4.2), 55 (2.5), 53 (8.1), 52 (7.2), 51 (19.8), 50 (6.7), 44 (4.2), 41 (19.3), 40 (5.5), 39 (33.7), 38 (2.9).

Anal. Calcd for C\textsubscript{14}H\textsubscript{18}: C, 91.25; H, 8.75.
Found: C, 91.09; H, 8.76.

Trans-1-ethynyl-2-vinyl cyclopropane: 5% yield; ir (NaCl, gas): 3320, 3085, 3010, 2975, 2860(w), 2120, 1635, 1235, 1245(w), 1190, 1070, 1015, 980, 905, 850(w), 735(w), 635, 600; nmr (100 MHz, CDCl\textsubscript{3}): δ 0.80-1.40 (m, H\textsubscript{6}, H\textsubscript{7}, and H\textsubscript{8}), 1.85 (d, J\textsubscript{5,6} = 2.0 Hz, H\textsubscript{5}), 1.58-1.94 (m, H\textsubscript{4}), and an ABX pattern with multiplets centered at 4.96 (H\textsubscript{3}), 5.12 (H\textsubscript{2}), and 5.40 (H\textsubscript{1}) with J\textsubscript{1,2} = 16.8 Hz, J\textsubscript{1,3} = 0.5 Hz, J\textsubscript{1,4} = 7.5 Hz, and J\textsubscript{2,3} = 2.5 Hz; mass spectrum (m/e, %): 92 (100.0), 90 (2.9), 67 (4.2), 66 (17.3), 64 (7.4), 63 (3.0), 53 (5.6), 52 (5.9), 51 (10.1), 50 (6.5), 42 (5.5), 41 (5.1), 40 (5.4), 39 (20.1), 38 (5.4), 37 (3.2).
Anal. Calcd for C<sub>7</sub>H<sub>8</sub>: C, 91.25; H, 8.75. Found: C, 91.11; H, 8.80.

Pyrolysis of syn-tricyclo[4.1.0.0<sup>2,4</sup>]heptan-5-one tosylhydrazone sodium salt: drop-static results.

Pyrolytic conversion of 34-s was studied in the temperature range 160°-500° employing the drop-static technique (D-S). Typically 0.200 g (6.71 x 10<sup>-4</sup> mole) of the salt was added to the heated glass surface at a rate which would not allow the pressure of the system to exceed 1 mm. At temperatures below 180° decomposition appeared very slow, making it necessary to extend heating of the salt for 4-7 hrs beyond completion of the addition to insure complete conversion. The results are compiled in Table IV; the results of several static (S) runs are also included at the bottom of the table.

Flow pyrolysis of syn-tricyclo[4.1.0.0<sup>2,4</sup>]heptan-5-one tosylhydrazone sodium salt.

Flow (F) pyrolysis of 34-s (425°-500°) led to the isolation of a product not observed under shorter contact times and at lower temperatures: 4-ethynyl-cyclopentene (55). Analytically-pure 55 was obtained by glpc on column D (column 70°, He flow 12 ml/min). Rigorous determination of dimeric material was accomplished only for the case in which the salt was dropped in the "neat" state as opposed
Table IV. Reaction Product Yields from *syn*-Tricyclo
[4.1.0.0\(^2_4\)] heptan-5-one Tosylhydrazone
Sodium Salt (0.200 g per run).

<table>
<thead>
<tr>
<th>Technique(^{a})</th>
<th>T °C</th>
<th>%52(^{b})</th>
<th>%54-(t)(^{c})</th>
<th>%55(^{c,e})</th>
<th>%56(^{c})</th>
<th>%57(^{c})</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-S</td>
<td>160</td>
<td>93</td>
<td>4.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>D-S</td>
<td>190</td>
<td>81</td>
<td>11.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>D-S</td>
<td>250</td>
<td>84</td>
<td>11.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>D-S</td>
<td>300</td>
<td>88</td>
<td>2.6</td>
<td>-</td>
<td>1.3</td>
<td>-</td>
</tr>
<tr>
<td>D-S</td>
<td>400</td>
<td>93</td>
<td>1.1</td>
<td>-</td>
<td>-</td>
<td>1.4</td>
</tr>
<tr>
<td>D-S</td>
<td>500</td>
<td>92</td>
<td>-</td>
<td>3.8</td>
<td>-</td>
<td>2.6</td>
</tr>
<tr>
<td>S</td>
<td>225</td>
<td>93</td>
<td>5(^d)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>S</td>
<td>235</td>
<td>78</td>
<td>9(^d)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>S(^f)</td>
<td>240</td>
<td>87</td>
<td>10(^d)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^{a}\)Cold finger maintained at 0°-10°. \(^{b}\)Gravimetric and
nmr analysis. \(^{c}\)Nmr and glpc analysis. \(^{d}\)Nmr analysis only.
\(^{e}\)Consistently observed in flow-pyrolysis work. \(^{f}\)0.275 g
of the salt.
to the "diluted" state in which the salt was diluted with either Chromasorb P-Reg or Woelm basic alumina (activity I). The flow-pyrolysis results appear in Table V. 4-ethynyl-cyclopentene: ir (NaCl, gas): 3325, 3070, 2940, 2865, 2125, 1620, 1450, 1325, 1250, 1180(w), 1050, 1030, 1010, 935, 910, 765, 745, 690, 625; nmr (CDCl₃): δ 2.04 (d, J = 2.0 Hz, acetylenic H), 2.20-3.20 (complex m region, allyl and propargyl H, 5 H), 5.68 (s, olefinic H, 2 H); mass spectrum (m/e, %): 92 (100.0), 90 (3.0), 67 (5.4), 66 (12.8), 64 (7.2), 63 (3.2), 53 (3.1), 52 (7.8), 51 (4.5), 42 (4.5), 41 (4.1), 40 (16.9), 39 (4.6).

**Anal. Calcd for C₇H₈:** C, 91.25; H, 8.75. Found: C, 91.11; H, 8.80.

**Pyrolysis of anti-tricyclo[4.1.0.0²⁴]heptan-5-one tosyl-hydrazine sodium salt (34-a).**

Pyrolysis of 34-a under static conditions at 240° (cold finger: 0°-10°) using 0.200 g (6.71 x 10⁻⁴ mole) of the salt afforded 56.3 mg (93% yield) of a white waxy material, mp 46°-47°, whose nmr, ir, uv, and mass spectra were virtual fingerprints of the dimer (52) obtained from pyrolysis of 34-s. Nmr analysis of the volatile fraction showed a trace of 54-t (≈ 1.2 mg, 2%). The results of three drop-static (D-S) runs are summarized in Table VI. Elemental analysis of 52 was satisfactory.

**Anal. Calcd for C₁₄H₁₈:** C, 91.25; H, 8.75. Found: C, 91.17; H, 8.78.
Table V. Reaction Product Yields from Flow Pyrolysis of syn-Tricyclo [4.1.0.0^2,4] heptan-5-one Tosyl-hydrazone Sodium Salt.

<table>
<thead>
<tr>
<th>T °C</th>
<th>Heat, Zone Path Length</th>
<th>%52^b</th>
<th>%54-^t^c</th>
<th>%55^c</th>
<th>%56^c</th>
<th>%57^c</th>
</tr>
</thead>
<tbody>
<tr>
<td>500^d,g</td>
<td>40 cm</td>
<td>a</td>
<td>-</td>
<td>6.9</td>
<td>5.9</td>
<td>15.2</td>
</tr>
<tr>
<td>500^d,g</td>
<td>40 cm</td>
<td>a</td>
<td>-</td>
<td>11.4</td>
<td>6.5</td>
<td>3.4</td>
</tr>
<tr>
<td>500^e,g</td>
<td>40 cm</td>
<td>39</td>
<td>-</td>
<td>15.1</td>
<td>0.7</td>
<td>5.7</td>
</tr>
<tr>
<td>425^f,h</td>
<td>30 cm</td>
<td>a</td>
<td>-</td>
<td>9.5</td>
<td>13.4</td>
<td>45.3</td>
</tr>
<tr>
<td>500^f,i</td>
<td>30 cm</td>
<td>a</td>
<td>-</td>
<td>25.9</td>
<td>10.0</td>
<td>9.5</td>
</tr>
</tbody>
</table>

^a Collected as a crude yellow-brown oil from the lower (exit) region of the pyrolysis tube and examined by nmr only to establish product identity. ^b Gravimetric and nmr analysis. ^c Nmr and glpc analysis. ^d Al2O3-salt mixture. ^e "Neat" salt. ^f Chromasorb P (Reg)-salt mixture. 90.200 g of the salt. ^g 90.290 g of the salt. ^i 0.325 g of the salt.
Table VI. Reaction Product Yields from *anti*-Tricyclo [4.1.0.0²,⁴] heptan-5-one Tosylhydrazone Sodium Salt (0.200 g per run).

<table>
<thead>
<tr>
<th>Technique&lt;sup&gt;a&lt;/sup&gt;</th>
<th>T °C</th>
<th>%&lt;sub&gt;52&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;</th>
<th>%&lt;sub&gt;54-t&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt;</th>
<th>%&lt;sub&gt;55&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt;</th>
<th>%&lt;sub&gt;56&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt;</th>
<th>%&lt;sub&gt;57&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-S</td>
<td>250</td>
<td>90</td>
<td>6.5</td>
<td>-</td>
<td>2.0</td>
<td>-</td>
</tr>
<tr>
<td>D-S</td>
<td>300</td>
<td>94</td>
<td>2.6</td>
<td>-</td>
<td>3.0</td>
<td>-</td>
</tr>
<tr>
<td>D-S</td>
<td>400</td>
<td>88</td>
<td>1.0</td>
<td>-</td>
<td>1.2</td>
<td>3.9</td>
</tr>
<tr>
<td>S</td>
<td>240</td>
<td>93</td>
<td>2&lt;sup&gt;d&lt;/sup&gt;</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

<sup>a</sup>Cold finger maintained at 0-10°.  
<sup>b</sup>Gravimetric and nmr analysis.  
<sup>c</sup>Nmr and glpc analysis.  
<sup>d</sup>Nmr analysis only.
Pyrolysis of syn- and anti-tricyclo [5.1.0.0^{3,5}] octan-2-one tosylhydrazone sodium salts (51-s and 51-a).

Investigation of the pyrolytic behavior of the sodium salts 51-s and 51-a in the temperature range 260°-400° resulted in the isolation of two products which were obtained from the pyrolysis of either salt. The drop-static technique (D-S) was used typically employing 0.100 g (3.21 x 10^{-4} mole) of the respective sodium salt. In the temperature range 260°-385°, cis-1-allyl-2-ethynyl-cyclopropane (65) was isolated as the major product with the minor product octa-1,2,5,7-tetraene (66) increasing in proportion with rise in temperature. At 400° product inversion occurred with 66 becoming the major product and 65 the minor product. Separation and purification of 65 and 66 was achieved on column D (column 82°, He flow 12 ml/min) with respective retention times of 24.8 min and 32.8 min. The results of the pyrolytic conversions of sodium salts 51-s and 51-a are listed in Table VII. cis-1-allyl-2-ethynyl-cyclopropane: ir (NaCl, gas): 3320, 3080, 3010, 2920, 2850(w), 1825, 1645, 1435, 1340, 1280, 1195, 1035, 990, 910, 740, 635, 600; nmr (CDCl₃): δ 0.47 (m, H₅), 1.02 (complex m, H₇ and H₈), 1.38 (complex m, H₆), 1.81 (d, J₅,₆ = 2.0 Hz, H₅), 2.23 (m, H₄, 2 H), and an ABX pattern with multiplets centered at 5.02 (H₃), 5.10 (H₂), and 5.95 (H₁) with J₁,₂ = 17.6 Hz, J₁,₃ = 9.7 Hz, and J₁,₄ = 6.4 Hz;
Table VII. Reaction Product Yields from syn- and anti-Tricyclo[5.1.0.0³,5] octan-2-one Tosylhydrazone Sodium Salts (0.100 g per run).

<table>
<thead>
<tr>
<th>Sodium Salt</th>
<th>T(^a) °C</th>
<th>(%65)(^b)</th>
<th>(%66)(^b)</th>
<th>65:66</th>
</tr>
</thead>
<tbody>
<tr>
<td>syn</td>
<td>260</td>
<td>70.3</td>
<td>-</td>
<td>100:--</td>
</tr>
<tr>
<td>syn</td>
<td>330</td>
<td>67.2</td>
<td>2.2</td>
<td>97:3</td>
</tr>
<tr>
<td>syn</td>
<td>370</td>
<td>66.9</td>
<td>13.0</td>
<td>84:16</td>
</tr>
<tr>
<td>syn</td>
<td>385</td>
<td>32.0</td>
<td>20.0</td>
<td>62:38</td>
</tr>
<tr>
<td>syn</td>
<td>400</td>
<td>1.8</td>
<td>25.7</td>
<td>7:93</td>
</tr>
<tr>
<td>anti</td>
<td>260</td>
<td>62.4</td>
<td>-</td>
<td>100:--</td>
</tr>
<tr>
<td>anti</td>
<td>400</td>
<td>18.2</td>
<td>37.0</td>
<td>33:67</td>
</tr>
</tbody>
</table>

\(^a\)Cold finger temperature 0\(^\circ\)-10\(^\circ\). \(^b\)Nmr and glpc analysis.
mass spectrum (m/e, %): 106 (2.5), 105 (13.3), 103 (2.7),
93 (3.1), 92 (25.7), 91 (100.0), 89 (2.9), 79 (10.8), 78
(18.0), 77 (9.5), 67 (6.8), 66 (7.7), 65 (29.5), 64 (2.7),
63 (9.5), 62 (4.4), 55 (3.3), 54 (38.2), 53 (8.5), 52 (9.5),
51 (14.3), 50 (8.3), 41 (15.3), 40 (35.5), 39 (44.8), 38
(6.2), 37 (2.7).

Anal. Calcd for C₆H₁₀: C, 90.50; H, 9.50. Found:
C, 90.30; H, 9.62.

Octa-1,2,5,7-tetraene: ir (NaCl, gas): 3090, 3005,
2910, 1955, 1805, 1645(b), 1605, 1435, 1300, 1255, 995,
910, 845, 740; nmr (100 MHz, CDCl₃): δ 2.84 (pseudo h,
H₃, 2 H), 4.74 (pseudo p, H₁, 2 H), 4.94-5.32 (m, H₂, H₇,
and H₈), 5.50-6.60 (m, H₄, H₅, and H₆); uv (ethanol):
λ_max 225 (e 27,100); mass spectrum (m/e, %): 106 (11.8),
105 (24.0), 103 (8.0), 92 (7.9), 91 (100.0), 80 (2.9), 79
(27.0), 78 (42.5), 77 (27.9), 67 (37.6), 66 (8.9), 65
(31.3), 63 (7.2), 54 (5.0), 53 (9.1), 52 (10.7), 51 (21.1),
50 (10.7), 41 (51.0), 40 (6.6), 39 (47.5), 38 (6.5).

Anal. Calcd for C₆H₁₀: C, 90.50; H, 9.50. Found:
C, 90.31; H, 9.56.

Flow pyrolysis of eis-1-allyl-2-ethynyl-cyclopropane (65).

Flow pyrolysis of 65 was carried out at 410° under
a controlled vacuum of 0.02-0.40 mm. The cyclopropane
(0.0262 g, 2.47 x 10⁻⁴ mole) was placed in an open-ended
capillary which was then set inside the solid addition apparatus previously described for the controlled addition of solids. The loading procedure was carried out under nitrogen in the dry box. The cyclopropane was subsequently allowed to slowly bleed through the pyrolysis region (40 cm heat zone) by careful control of the Rotaflo stopcock, vaporization and pyrolysis of 65 being completed within five min. Nmr inspection and glpc analysis (column D) of the pyrolysate showed no trace of starting material. The only identifiable product was octa-1,2,5,7-tetraene (66) which was formed in 72% yield: 0.0190 g, 1.79 x 10^-4 mole. Uv inspection showed only the characteristic absorption at 225 nm (ε 27,100) obtained also for the octatetraene product isolated previously from the tosylhydrazone sodium salt pyrolyses.

**Pyrolysis of trans-1-ethynyl-2-vinyl-cyclopropane (54-t).**

The trans cyclopropane (54-t) (0.0141 g, 1.53 x 10^-4 mole) was placed in 0.5 ml of deuterochloroform in an ordinary nmr tube. The solution was degassed (five times) and the tube sealed. The tube was subsequently heated at 100 ± 2° in a well-stirred kinetic oil bath for 198 min (3.30 hrs) without any change in the nmr spectrum of the starting material. Heating at 169 ± 3° for 137 min (2.28 hrs) produced no change also. The cyclopropane was
separated from the deuterochloroform via glpc (column D) and placed in 0.5 ml of benzene-d$_6$ in order to avoid possible acid-catalyzed reactions at higher temperatures (> 169°). The benzene-d$_6$ solution (10 µl benzene: nmr internal standard) was placed in a thick-wall nmr tube and was degassed and sealed as before. The nmr tube was placed inside a thickwall glass sleeve containing benzene in a volumetric amount proportional to the benzene-d$_6$ volume within the sealed nmr tube. This was done so as to maintain equal pressures inside and outside the sealed nmr tube. The glass sleeve was sealed under vacuum and the cyclopropane subjected to heating at 208 ± 2° for 128 min (2.13 hrs). Nmr inspection showed that the cyclopropane had quantitatively converted to the 1,2,5-cycloheptatriene dimer (52). Verification of this fact was supplied by uv and mass spectral analysis which supplied spectra which were fingerprints of dimer 52 obtained directly from the pyrolysis of either syn- or anti-tricyclo [4.1.0.0$^2$,4] heptan-5-one tosylhydrazone sodium salts.


The sodium salt (0.200 g, 6.71 x 10$^{-4}$ mole) of syn-33 was placed in a 3-oz Fisher-Porter Aerosol Compatibility tube employing 20 ml of diglyme (distilled from
CaH$_2$ and stored over CaH$_2$ under nitrogen) as reaction solvent. Styrene (3.60 g, 0.0346 mole) was introduced after having first removed the stabilizer by chromatography on Woelm basic alumina (activity I). The charged tube (magnetic stirrer included) was immersed in a G.E.-S.F.-97 oil bath heated at 135 ± 3° for 153 min (2.55 hrs). The volume of evolved nitrogen was determined upon cooling of the reaction mixture to 25°: 12.60 ml (16.25 ml theor.), 78%. The reaction mixture was filtered and the mixture diluted with 20 ml of H$_2$O. Extraction of the aqueous diglyme solution with 80 ml of pentane afforded a pentane extract from which a white solid (polystyrene) precipitated. The pentane layer was filtered several times to remove precipitating polystyrene and finally washed with two 20-ml aliquots of H$_2$O. The pentane layer was dried over Na$_2$SO$_4$ and concentrated by rotary evaporation affording a slightly colored liquid residue. Excess styrene was removed at 3-10 mm leaving a residue (oil-solid mixture) which was diluted with 100 ml pentane, filtered again several times to remove polystyrene, and worked up with H$_2$O as before. Drying and concentration in vacuo afforded a residue which was suitable for preparative layer chromatography (silica gel). One elution with pentane afforded a broad fast-moving band ($R_f = 0.71$) which was subsequently exposed to the atmosphere for a period of ~5 days. The band (now colored)
was rechromatographed using three elutions with pentane. The fastest-moving band \((R_f = 0.75)\) afforded 0.0344 g \((1.76 \times 10^{-4} \text{ mole, 26\%})\) of 2-phenyl-spiro \([\text{cyclopropane-1,5'-syn-tricyclo [4.1.0.0^2,4]}\text{ heptane}] (61)\) which, by nmr spectral inspection, appeared to be a mixture of the two possible isomers. The trapping reaction was repeated at \(210 \pm 3^\circ\) employing 0.200 g \((6.71 \times 10^{-4} \text{ mole})\) of the sodium salt, 20 ml of tetraglyme (refluxed over and distilled from CaH₂), and 6.99 g \((0.0672 \text{ mole})\) of styrene (salt-styrene ratio 1:100 as opposed to 1:50 in the first run). The reaction mixture was heated for a period of 83 min \((1.38 \text{ hr})\). The volume of nitrogen evolved measured 13.90 ml \((16.25 \text{ ml theor.})\), 86\%. Work-up as before and preparative layer chromatography afforded 0.0453 g \((2.31 \times 10^{-4} \text{ mole})\) of 61 (isomeric mixture): 34\% yield. 2-phenyl-spiro \([\text{cyclopropane-1,5'-syn-tricyclo [4.1.0.0^2,4]}\text{ heptane}]\): ir \((\text{CCl}_4, \text{KBr liquid cells})\): 3070, 3040, 3010, 1605, 1500, 1465, 1265, 1095, 1070, 1040, 1025, 905, 865, 700(s); nmr \((\text{CDCl}_3)\): \(\delta -0.05-0.73 \) (complex m, 4 H) 0.75-1.93 (complex m, 4 H), 1.25 (d, 7.5 Hz, 2 H), 2.15 and 2.30 (overlapping t, 7.5 and 7.0 Hz, respectively, 1 H), 7.18 (d, 5 H); uv \((\text{ethanol})):\ \lambda_{\text{max}} 276 (c 378), 267 (c 527), 262 (c 527), 226 (c 7490); mass spectrum \((m/e, \%)\): 196 (8.2), 181 (12.1), 168 (10.9), 167 (17.1), 166 (9.7), 165 (13.2), 155 (18.1), 153 (10.0), 149 (16.3), 142 (27.5), 141
(26.3), 130 (9.1), 129 (25.6), 128 (20.9), 118 (20.0), 117 (28.4), 116 (10.6), 115 (25.0), 106 (15.0), 105 (88.5), 104 (32.5), 103 (23.8), 93 (9.4), 92 (65.0), 91 (100.0), 89 (12.5), 83 (8.5), 79 (31.3), 78 (20.6), 77 (40.0), 65 (23.8), 63 (14.4), 58 (35.0), 57 (9.7), 55 (8.8), 53 (8.4), 52 (8.8), 51 (26.3), 50 (9.4), 43 (82.5), 41 (22.2), 39 (34.4).

Found: C, 91.65; H, 8.27.


The sodium salt (0.200 g, 6.71 x 10⁻⁴ mole) of syn-33 was placed in a 3-oz Fisher-Porter Aerosol Compatibility tube employing 20 ml of anhydrous tetruglyme as reaction solvent. Dimethyl maleate (> 99% pure by glpc analysis after chromatography on silica gel 60-Merck) was introduced as a 100-fold excess of trapping agent: 9.69 g (0.0672 mole). The charged tube (magnetic stirrer included) was immersed in the G.E.-S.F.-97 oil bath heated at 210 ± 3° for 83 minutes (1.38 hr). Upon cooling the dark reaction mixture to 25°, the volume of evolved nitrogen was determined: 8.75 ml (16.25 ml theor.), 54%. The tetraglyme solution was diluted with 80 ml of H₂O and extracted with 200 ml of pentane. The pentane layer was filtered
free of a white solid (dimethyl fumarate) and washed with five 50-ml aliquots of H_2O. The pentane layer was dried over Na_2SO_4 and concentrated by rotary evaporation. The moist white solid obtained was largely dimethyl fumarate (via isomerization of dimethyl maleate under the reaction conditions employed). The solid material was carefully tritirated with 30 ml of pet ether (low boiling) followed by trituration with 30 ml of pentane. The residue obtained by concentration of the pet ether-pentane triturate was largely the fumarate but suitable for preparative layer chromatography (silica gel). Three elutions with hexane afforded a broad slow-moving band (R_f = 0.34) which was re-chromatographed using four elutions with benzene. Two closely spaced bands (R_f = 0.60 and 0.53, respectively) were obtained, the large slower-moving band being chiefly dimethyl fumarate. The faster-moving band (0.0614 g, 2.60 x 10^-4 mole, 39% yield) proved to be the carbene adduct, trans-2,3-dicarbomethoxy-spiro [cyclopropane-1,5'-syn-tricyclo [4.1.0.0^2,4] heptane] (62): mp 72°-74°; ir (CCl_4, KBr liquid cells): 3080, 3040, 3010, 2950, 2920, 2850, 1740(s), 1455, 1440(s), 1360, 1340(s), 1290(s), 1260, 1230(s), 1195, 1165(s), 1095, 1070, 1035, 1015, 900, 870, 830, 695, 670, 660; nmr (CDCl_3): δ 0.52 (m, 4 H), 1.70 (m, 4 H), 2.42 (d, 5.8 Hz, part of ABq, 1 H), 2.65 (d, 5.8 Hz, part of ABq, 1 H), 3.72 (s, 3 H), 3.76 (s, 3 H); mass spectrum (m/e, %): 236 (< 1.0), 204 (4.0), 178 (5.0),
177 (31.3), 176 (12.7), 174 (5.4), 161 (7.4), 149 (6.9),
146 (9.6), 145 (66.0), 144 (11.8), 135 (6.1), 134 (6.6),
131 (7.4), 127 (9.1), 121 (4.2), 119 (6.3), 118 (16.5),
117 (100.0), 116 (32.4), 115 (46.6), 113 (16.9), 105 (10.9),
104 (7.5), 103 (11.0), 102 (4.1), 99 (18.8), 92 (22.3),
91 (84.5), 90 (4.6), 89 (7.5), 85 (8.0), 79 (23.6), 78
(10.8), 77 (19.4), 71 (8.4), 69 (6.6), 67 (4.6), 66 (6.9),
65 (23.9), 64 (4.0), 63 (11.0), 59 (31.2), 58 (4.9), 57
(9.5), 56 (5.2), 55 (13.6), 54 (4.0), 53 (12.7), 52 (8.9),
51 (18.3), 50 (7.4), 45 (10.1), 44 (30.2), 43 (10.8), 42
(5.3), 41 (27.4), 40 (9.5), 39 (36.8), 38 (6.6), 36 (4.9).

**Anal.** Calcd for C_{13}H_{16}O_{4}: C, 66.09; H, 6.83.
Found: C, 66.01; H, 6.85.

Attempted low-temperature isolation of key intermediates in the pyrolysis of *syn*-tricyclo [4.1.0.0^{2,4}] heptan-5-one tosylhydrazone sodium salt.

The low-temperature isolation unit (see footnote on page 50) employed for the attempted trapping of key intermediates in the pyrolysis of *syn*-33 sodium salt was designed and built with the capacity for easily inter-changeable optics to facilitate inspection of both the *uv-visible* and the *ir* regions of interest. For infrared work, cesium iodide (CsI) optics were generally employed; spectra were recorded by a Perkin-Elmer Model 621 Infrared Spectrometer. Ultraviolet-visible work was
performed with the use of calcium fluoride (CaF₂) optics; spectra were recorded by a Jarrel-Ash ultraviolet sensor-
photomultiplier-recorder system (ultraviolet source: deuterium lamp; visible source: tungsten lamp). Typically
5 mm of argon was first deposited on the matrix window (at 6°K) while maintaining a dewar pressure in the range
1.5 x 10⁻⁶ - 4.2 x 10⁻⁵ mm. Employing the drop-static
technique (D-S), the sodium salt was then pyrolyzed at
250° in a glass vessel (without a cold finger). The volatile pyrolysate was fed by a 19 cm glass connector to the
matrix window. The amount of sodium salt pyrolyzed was
in the range 0.075-0.100 g (2.52 x 10⁻⁴ - 3.36 x 10⁻⁴
mole). Controlled dropping of the salt was effected by
the use of an ion gauge which effectively monitored nitro-
gen evolution; the maximum pressure of the system at any
time was observed to be 9.0 x 10⁻⁵ mm. At completion of
the pyrolysis, 22-25 mm of argon was observed to have been
delivered to the matrix window during the period of py-
rolysis. Matrices generated in this manner were generally
well-set except for minor "bubbling" at the center of the
matrix window. Uv-visible inspection of the matrix in
the range 200-500 nm showed only very strong absorption
in the 254 nm region characteristic of the 1,2,5-cyclo-
heptatriene dimer (52). Ir inspection was more informative
although it appeared most absorptions were due to the
presence of 1-ethynyl-2-vinyl cyclopropane (54-t and/or 54-c) and the dimer (52). The following absorptions were recorded in the ir region 200-4000 cm\(^{-1}\) (50-2.5 \(\mu\)): 3305 (s), 3080, 3005, 2905, 2845, 2795, 2125, 2043, 2035 (shoulder), 1633, 1600(b), 1437, 1405, 1355(w), 1345, 1285(w), 1270(w), 1208(w), 1183, 1100, 1090, 1078, 1065, 1035, 1015, 1003, 980, 953, 943(w), 923, 915, 893(s), 868, 845, 780, 770, 750, 725, 703, 685, 645(s), 637(s), 620, 588, 500, 485, 368, 343, 323, 310, 295. The nature of the absorption at 2043 cm\(^{-1}\) with a shoulder at 2035 cm\(^{-1}\) was of principal interest (1,2,5-cycloheptatriene?) although the absorption might easily be accounted for by the syn-5-diazo-tricyclo [4.1.0.0\(^{2,4}\)] heptane species (59). However, no uv \(\lambda_{\text{max}}\) was readily observed for 59 although the concentration and expected small extinction coefficient (\(c\ 10\)) of 59 may have combined to give an absorption of negligible intensity which was lost in baseline noise. The two strongest ir absorptions at 3305 and 893 cm\(^{-1}\) were apparently due to cyclopropanes 54.

Generation of syn- and anti-5-diazo-tricyclo [4.1.0.0\(^{2,4}\)] heptanes (59): isolation of cis-1-ethynyl-2-vinyl-cyclopropane (54-c).

Static pyrolysis (S) of 0.400 g (0.0134 mole) of either 34-s or 34-a, maintaining a cold finger temperature of -72\(^\circ\) to -65\(^\circ\)C while raising the metal bath temperature
from 140°-225° over a period of 30 min, afforded observation of a red liquid condensed on the cold finger. Even at these low temperatures, it appeared that the red liquid, syn- or anti-5-diazo-tricyclo [4.1.0.0²,⁴] heptane (59), slowly lost nitrogen (perhaps photochemistry induced) as evidenced by the gradual "bubbling-up" of the material deposited on the cold finger accompanied by dissipation of the red color of the condensate. The pyrolysis period was arbitrarily for 60-90 min at which point the metal bath was removed. The cold finger was maintained at low temperatures for 30-45 min longer at which time the cold finger was allowed to warm to 25°. The nonvolatile material left behind on the cold finger after disappearance of the red color attributed to the respective diazo compounds was a deep yellow in color. Nmr inspection showed the yellow material to be a complex mixture of dimer (52) and largely unidentifiable products showing broad absorptions in the region δ 0.2-2.65. Ir inspection showed a sharp absorption of moderate intensity at 1645 cm⁻¹ which might have been indicative of the presence of tricyclic heptan-5-one azine material. The results of two pyrolysis runs showed the various nonvolatiles to have formed in ca. 58-65% yield via gravimetric analysis. Examination of the volatile material from both runs afforded the isolation of cis-1-ethynyl-2-vinyl cyclopropane (54-c) as well as cycloheptatriene (56) and trans-1-ethynyl-2-vinyl-cyclopropane (54-t) in the amounts
specified in Table VIII. The cis compound 54-c demonstrated unusual reactivity, rearranging quantitatively to afford dimer 52 upon nmr spectral inspection after 36 hrs at 25°. A rough attempt via nmr at determination of the half-life of 54-c at 25° (concentration: ∼ 0.35 M in deuterochloroform) placed $t_{1/2}$ (for a rate-determining unimolecular process) at 2.8 hrs although within experimental error it would be more appropriate to place the figure between two and three hrs. Mass spectral analysis showed the parent peak at m/e 92 (40.9% vs. 100% for 54-t) although the spectrum obtained was largely a fingerprint of dimer 52 (base peak m/e 91, 100.0%) due to probable pyrolysis for 54-c in the tip of the syringe used for mass spectral injection.

Cis-1-ethynyl-2-vinyl-cyclopropane (54-c): ir (principal peaks only, CDCl₃, KBr liquid cell): 3310, 3085, 2120, 1635, 985, 600; nmr (100 MHz, CDCl₃): δ 0.78 (m, H₈), 1.20 (m, H₇), 1.48-1.84 (m, H₄ and H₆), 1.88 (d, J₅,₆ = 2.0 Hz), and an ABX pattern with multiplets centered at 5.10 (H₃), 5.24 (H₂), and 5.64 (H₃) with J₁,₂ = 15.8 Hz, J₁,₃ = 8.5 Hz, J₁,₄ = 7.5 Hz, and J₂,₃ = 2.5 Hz. It should be noted that spectroscopic work (ir and nmr) was complicated by the presence of cycloheptatriene and the growth of dimer 52 via the facile rearrangement of 54-c at 25°.
Table VIII. Volatile Product Yields from Static Pyrolysis of *syn*- and *anti*-Tricyclo [4.1.0.02,4] heptan-5-one Tosylhydrazone Sodium Salts: 140°–225°

<table>
<thead>
<tr>
<th>Sodium&lt;sup&gt;a,b&lt;/sup&gt; Salt</th>
<th>54-&lt;sup&gt;c&lt;/sup&gt;c</th>
<th>54-t&lt;sup&gt;c&lt;/sup&gt;</th>
<th>56&lt;sup&gt;c&lt;/sup&gt;</th>
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<tr>
<td>34-s</td>
<td>17</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td>34-s</td>
<td>16</td>
<td>5</td>
<td>8</td>
</tr>
<tr>
<td>34-a</td>
<td>23</td>
<td>-</td>
<td>3</td>
</tr>
</tbody>
</table>

<sup>a</sup>Cold finger maintained at -73° to -65°. <sup>b</sup>0.400 g of the salts. <sup>c</sup>Nmr analysis only; benzene (8.7 mg): internal standard.
APPENDIX

NMR AND IR SPECTRA OF RELEVANT COMPOUNDS
Figure A-1. $^1$H 100 MHz nmr of syn-tricyclo [4.1.0.0$^2$,4] heptan-5-one (26-s). 1000 and 250 sweep width.
Figure A-2. 100 MHz nmr of anti-tricyclo [4.1.0.0²,4] heptan-5-one (26-a). 1000 and 250 cps sweep width.
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He married the former Mary Jane Champion and, after five years of marriage, they were blessed with a fine son, Austin Edward. Together they will head north to Wilmington, Delaware to become part of the Dupont working family.
I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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