

boxylate, and 2.0 ml. of *o*-xylene was heated at 120° for 4 hr. The solvent was removed (reduced pressure), and the resulting white solid residue was recrystallized from methanol. Adduct **9** was recovered, 0.147 g. (97%), m.p. 121–123°. This sample shows an identical infrared spectrum with that of the analytical sample of **9**.

C. *With 2*. A mixture of 0.213 g. (1.78 mmoles) of **2**, 0.251 g. (1.78 mmole) of dimethyl acetylenedicarboxylate, and 2.0 ml. of toluene was heated at the refluxing temperature (nitrogen atmosphere) for 3 hr. The solvent was removed (reduced pressure), and the resulting yellowish oil, 0.485 g., was chromatographed on 20 g. of silicic acid. Elution with 50-ml. portions of chloroform gave 0.455 g. (97.5%, fractions 1–4) of a

colorless oil. The infrared spectrum of this oil is consistent with structure **14**, *i.e.*, absorptions at 5.80, 6.10, 7.90, 10.10, and 10.95 μ .

After standing overnight, the total amount of oily product was rechromatographed on 50 g. of silicic acid. Elution with 50-ml. portions of chloroform gave 0.307 g. (66.3% based on **2**, fractions 14–24) of **15**. The absorption spectra are described above.

Acknowledgment. The authors are grateful to Mrs. M. S. Bentley for infrared measurements, G. L. Carlson for obtaining the Raman spectra, F. J. Michalek, C. J. Lindemann, and W. R. Freeman for the g.l.p.c. analyses and collections, and R. E. Rhodes for the mass spectrometric determinations.

Thermally Induced Reactions of Some Novel Allenes

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Contribution from the Union Carbide Research Institute, Union Carbide Corporation, Tarrytown, New York. Received May 14, 1965

The present work describes the thermally induced reactions of both cyclic and open-chain allenes which contain an additional double bond or allenic grouping in the molecule. When heated, neat or in a hydrocarbon solvent, the allenes underwent both dimerization and isomerizations. In the vapor phase only isomerization took place. In a number of cases the isomerizations led to novel olefins in excellent yields. Particularly interesting is the formation of 3,4-diisopropylidenecyclobutene (XVIII) from 2,7-dimethyl-2,3,5,6-octatetraene (XVII). The results have been rationalized on the basis of the stability of assumed biradical intermediates.

Introduction

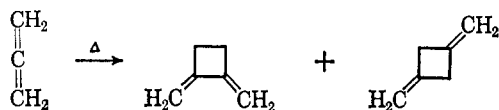
The thermally induced reactions of allenic derivatives were first investigated by Lebedev^{1,2} more than one-half century ago. He claimed that besides other products cyclobutanes were formed by 1,2-additions, and this was later verified by other workers.³ It has been shown that allene itself gives 1,2- and to a minor extent 1,3-dimethylenecyclobutane, in addition to other products, when heated at 150° in a sealed tube for 3 days² or passed through a 500–510° hot tube.⁴ Just in recent years this reaction has been investigated more thoroughly with a wide variety of allenic derivatives,

including cycloaddition of allenes to activated olefins, such as acrylonitrile, yielding methylenecyclobutane derivatives.⁵ Addition of allenes to normal olefins or acetylenes does not generally take place. A few examples of intramolecular cycloadditions of dienes are known,⁶ but similar reactions of allenic derivatives have not been reported. The reason is simply that such allenes, containing two allenic groupings or an additional double bond, have until recently been virtually unknown.

With the development of the new synthesis of allenes from *gem*-dibromocyclopropanes,^{5–7} cyclic allenes became readily available for the first time,⁸ and a number of allenic compounds of the type described above have been prepared^{9,10} by the same method. A study of the thermally induced reactions of these compounds appeared promising, and the present paper describes such an investigation.

Results

Heating 1,2-cyclononadiene (I) in a sealed tube at 130° for 18 hr. afforded a crystalline mixture. This was separated by careful chromatography on alumina into two compounds, both dimers. The closely similar spectra include ultraviolet bands in the 260-m μ region, characteristic of a rigid diene chromophore,¹¹ and weak



(1) S. V. Lebedev, *J. Russ. Phys. Chem. Soc.*, **43**, 820 (1911); *Chem. Abstr.*, **6**, 478, 1373 (1912).

(2) S. V. Lebedev, *J. Russ. Phys. Chem. Soc.*, **45**, 1357 (1913); *Chem. Abstr.*, **9**, 799 (1915).

(3) For principal references see J. D. Roberts and C. M. Sharts, *Org. Reactions*, **12**, 1 (1962); E. Vogel, *Angew. Chem.*, **72**, 4 (1960).

(4) A. T. Blomquist and J. A. Verdol, *J. Am. Chem. Soc.*, **78**, 109 (1956); see also B. Weinstein and A. H. Fenselau, *Tetrahedron Letters*, 1463 (1963).

(5) W. von E. Doering and P. M. LaFlamme, *Tetrahedron*, **2**, 75 (1958).

(6) W. R. Moore and H. R. Ward, *J. Org. Chem.*, **25**, 2073 (1960).

(7) L. Skattebøl, *Tetrahedron Letters*, 167 (1961); *Acta Chem. Scand.*, **17**, 1683 (1963).

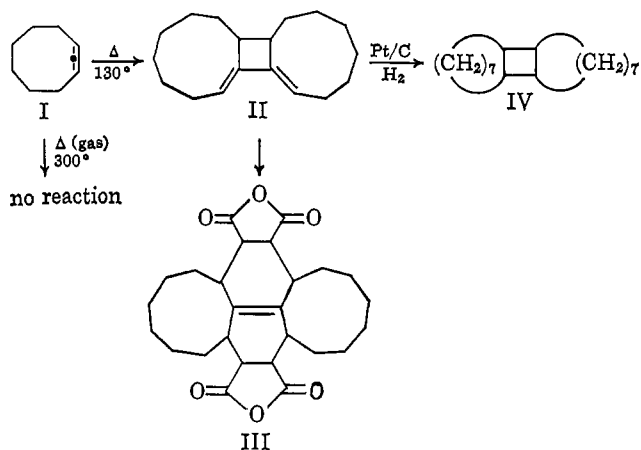
(8) Cyclic allenes had previously only been obtained admixed with the corresponding acetylenes: A. T. Blomquist, R. E. Burge, and A. C. Sucsy, *J. Am. Chem. Soc.*, **74**, 3636 (1952); A. T. Blomquist, L. H. Liu, and J. C. Bohrer, *ibid.*, **74**, 3643 (1952); see also ref. 13.

(9) L. Skattebøl, *Chem. Ind. (London)*, 2146 (1962).

(10) L. Skattebøl, unpublished results.

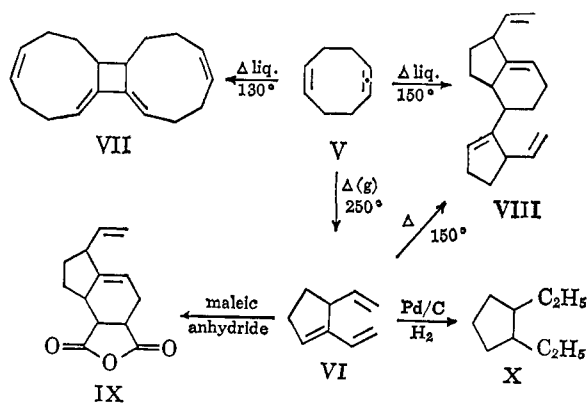
(11) For references see A. Titov, *Russ. Chem. Rev.*, **30**, 327 (1961). 1,2-Dimethylenecyclobutane absorbs at 237 and 246 m μ with a shoulder at 255 m μ : A. T. Blomquist and J. A. Verdol, *J. Am. Chem. Soc.*, **77**, 1806 (1955).

C=C infrared absorption at 1660–1690 cm^{-1} . With maleic anhydride the diadduct III was formed, and catalytic hydrogenation gave a compound with properties in agreement with structure IV. Hence, the dimers are most probably stereoisomers of tricyclo[9.7.0.0^{2,10}]octadeca-2,18-diene (II). Formation of III is readily understood on the assumption that condensation of II with maleic anhydride produces a cyclobutene derivative which does not survive the reaction conditions,¹² but undergoes valence isomerization to a conjugated diene; this reacts with a second mole of maleic anhydride to give III. It has not yet been possible to establish the configuration of either isomer of II.



In a recent paper Ball and Landor¹³ have shown that 1-chlorocycloheptene and 1-chlorocyclooctene with sodamide in liquid ammonia give dimers homologous to II. The present results substantiate their assumption that each was formed from the respective intermediate cyclic allene. These authors also isolated only diadducts of the type III from the dimers and maleic anhydride. In our experiments the vapor of 1,2-cyclononadiene (I) passed unchanged through a tube kept at 300°.

The behavior of 1,2,6-cyclononatriene (V) proved to be considerably more complex. Heating this allene neat or dissolved in *n*-hexane at temperatures from 90 to 150°, for 6 to 65 hr., yielded varying amounts of the isomer 2,3-divinylcyclopentene (VI), dimers VII and



VIII, and some polymeric material. At lower temperatures dimer VII was the main product while at

(12) Blomquist and Verdol¹¹ obtained both mono- and diadducts from reaction of 1,2-dimethylenecyclobutane with maleic anhydride.

(13) W. J. Ball and S. R. Landor, *J. Chem. Soc.*, 2298 (1962).

higher temperatures VIII was predominant. In a dilute ($\sim 0.1 M$) *n*-hexane solution VI became the main product, and it was the sole product when the vapor of V was passed through a hot tube kept at 250°.¹⁴

The structure of VI was established by analysis and spectroscopic evidence. It readily gave an adduct (IX) with maleic anhydride, and catalytic hydrogenation yielded the stereoisomeric 1,2-diethylcyclopentanes (X). The structural examination of the dimers was hampered by the fact that we were not able to separate them completely. Dimer VII analyzed for $\text{C}_{18}\text{H}_{24}$, and shows an ultraviolet absorption maximum at 252 $\text{m}\mu$. Infrared bands at 3020, 3000, 1700, and 1645 cm^{-1} strongly indicate two essentially different double bonds, and a broad band at 725 cm^{-1} is characteristic of a *cis* double bond. This information and the formation of adduct XI with maleic anhydride prove the presence of two conjugated double bonds. The infrared spectra of the hydrogenation product and tricyclo[9.7.0.0^{2,10}]octadecane (IV) were almost identical, which suggested the structure tricyclo[9.7.0.0^{2,10}]octadecatetraene for this dimer. Attempts to determine the positions of the double bonds by ozonolysis have, however, failed. There is n.m.r. absorption at τ 7–8.8 by saturated protons, and the olefinic protons absorb at 3.9–4.9; the peak area ratio is 7:17. This and the other data agree well with structure VII, the most likely on the basis of analogy. Remaining discrepancies for this structure, however, was the failure to obtain a maleic anhydride diadduct even under quite rigorous conditions and the lack of fine structure in the ultraviolet absorption.¹⁵

The second dimer was found to be identical with the product obtained by heating 2,3-divinylcyclopentene (VI) at 150°. Only end absorption was observed in the ultraviolet, and strong maxima in the infrared spectrum at 1630, 992, and 910 cm^{-1} establish the presence of vinyl groups. The latter conclusion is confirmed by the n.m.r. spectrum which also shows a 1:2 ratio of olefinic to saturated protons. No reaction occurred with maleic anhydride, and the infrared spectra of the hydrogenation product and compound IV were entirely different. All this agrees with structure VIII.

Heating 1,2,6,7-cyclodecatetraene (XII) as a dilute heptane solution in a sealed tube at 150° for a few hours produced mainly polymeric material besides a small amount of a highly unstable isomeric compound. The latter was formed almost quantitatively when the vapor was passed through a glass tube maintained at 300°, and it was subsequently proven to be 2,3-divinyl-1,3-cyclohexadiene (XIII). The analysis and spectra agree with this structure,¹⁶ and the infrared spectrum of the hydrogenation product was identified as that of 1,2-diethylcyclohexane (XIV).¹⁷ With maleic anhydride a mixture of di- and triadducts were formed (XV, XVI).

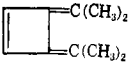



(14) E. Vogel, W. Grimme, and E. Dinne, *Angew. Chem.*, 75, 1103 (1963), have reported the same result.

(15) K. Untch and D. J. Martin, *J. Am. Chem. Soc.*, 87, 4501 (1965), have independently studied the thermal reaction of V. They present convincing evidence for the structure VII. We are indebted to Dr. Untch for this information prior to publication.

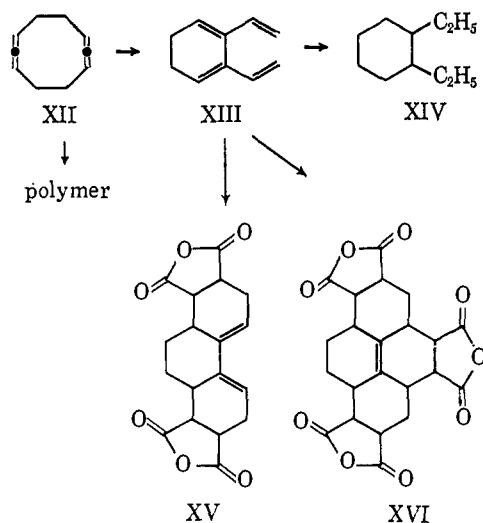
(16) Vogel and Harris have obtained virtually the same result and furthermore, 1,2,6-cyclodecatetraene has been rearranged to 2,3-divinylcyclohexene: E. Vogel, private communication.

(17) C. A. Grob, H. Link, and P. W. Schiess, *Helv. Chim. Acta*, 46, 483 (1963). We are indebted to Professor Grob for a copy of the infrared spectrum of XIV.

Table I. Thermally Induced Reactions of Allenes

| Allene | Temp., °C. ^a | Products | Total yield, % |
|------------------------------------------|-------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------|
| 2,7-Dimethyl-2,3,5,6-octatetraene (XVII) | 250 |  XVIII | ~100 |
| 1,2,5-Hexatriene (XXI) | 300 | No reaction ^b | ... |
| 1,2,6-Heptatriene (XXII) | 300 | 3-Methylene-1,5-hexadiene (XXIII) | 98 |
| 1,2,6,7-Octatetraene (XXIV) | 310 | 3,4-Dimethylene-1,5-hexadiene (XXV) ^c | ~100 |
| 1,2,7-Octatriene (XXVI) | 410 |  XXVII  XXVIII ^d | 93 |
| 1,2,7,8-Nonatetraene (XXIX) | 390 |  (XXX) ^e | 32 ^g |
| 1,2,8,9-Decatetraene (XXXI) | 300 | No reaction ^f | |

^a This is not necessarily the minimum temperature at which reaction will take place. ^b At 400° both terminal and disubstituted acetylenic compounds were detected by g.l.p.c. and infrared spectroscopy. ^c Another very unstable compound of unknown structure was also formed. ^d A small amount of a third compound, presumably 1-hepten-7-yne, was also formed. ^e Some unreacted allene was invariably present. ^f At 440° XXXI was converted in low yield into a complex mixture of compounds. ^g Conversion.



The results described so far have all involved reactions of cyclic Allenes. A number of open-chain Allenes were also investigated as to their thermal reactions, and the results from these experiments are given in Table I. All the reactions were carried out by passing the vapor of the respective allene under reduced pressure through a hot tube packed with glass wool. The products were trapped at -78° .

The only "conjugated" diallene available to us was 2,7-dimethyl-2,3,5,6-octatetraene (XVII). This is obtained in more than 90% yield¹⁰ from the reaction of methyl lithium with 2,2,2',2'-tetrabromo-3,3,3',3'-tetramethylbicyclopropyl,¹⁸ and is thus undoubtedly the most readily available diallene, at present. At 250° it produced a very unstable liquid, subsequently proved to be 3,4-diisopropylidenecyclobutene (XVIII), in high yield. The instability precluded any analysis, but structural evidence was obtained from the various spectra. The ultraviolet absorption maxima at 221 $m\mu$ (ϵ 37,900) and 265 $m\mu$ (ϵ 5700) compare very well with those reported for similar compounds: 1-methyl-3,4-dimethylenecyclobutene¹⁹ absorbs at 210 and

245 $m\mu$, and 1,2-dimethyl-3,4-dimethylenecyclobutene shows maxima at 213 and 249 $m\mu$.²⁰ The stretching vibration of the endocyclic double bond gives rise to an infrared band at 1610 cm^{-1} while the same vibration for the exocyclic bonds appears as a weak band at 1660 cm^{-1} . The n.m.r. spectrum is very simple: three singlets with peak area ratio 1:3:3. The weakest singlet at τ 3.31 is due to the olefinic protons, and the methyl protons give rise to the other two singlets, at τ 8.13 and 8.27. Hydrogenation over a palladium-on-carbon catalyst afforded a stereoisomeric mixture of 1,2-diisopropylcyclobutanes (XIX) as the sole product. In one experiment the hydrogenation was terminated after approximately 1 mole of hydrogen had been absorbed, and the product was shown to contain a considerable amount of 1,2-diisopropylidenecyclobutane (XX).²¹ This suggested the possibility that the endocyclic double bond could be selectively hydrogenated under the proper conditions. Success was achieved with the use of Lindlar's lead-poisoned catalyst²²; the hydrogenation practically stopped after the consumption of about 1 mole of hydrogen, and the product consisted essentially of the diene XX.

The other reactions described in the table required generally more vigorous conditions; thus, in the case of 1,2,5-hexatriene (XXI) and 1,2,8,9-decatetraene (XXXI) no reactions were observed at 300°, and at 400° only low yields of complex mixtures were obtained. These were not further investigated. On the other hand, 1,2,6-heptatriene (XXII) reacted readily at 300° to give exclusively 3-methylene-1,5-hexadiene (XXIII), which was characterized by analysis, spectroscopic evidence, and formation of a maleic anhydride adduct. The diallene 1,2,6,7-octatetraene (XXIV) was completely converted at 300° into a mixture of two compounds, of which 3,4-dimethylene-1,5-hexadiene

(19) J. K. Williams and W. H. Sharkey, *J. Am. Chem. Soc.*, **81**, 4269 (1959).

(20) R. Criegee, J. Dekker, W. Engel, P. Ludwig, and K. Noll, *Ber.*, **96**, 2362 (1963); G. W. Griffin and L. I. Peterson, *J. Am. Chem. Soc.*, **85**, 2268 (1963).

(21) I. N. Nazarov and N. V. Kuznetsov, *Izv. Akad. Nauk, SSSR, Otd. Khim. Nauk*, 259 (1960).

(22) H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952).

(18) L. Skattebøl, *J. Org. Chem.*, **29**, 2951 (1964).

(XXV) constitutes about 50%. The substance was very unstable, and the structural proof had to rest on spectroscopic arguments, which are quite convincing, however, since both the infrared and n.m.r. spectra clearly show the presence of vinylic protons only, and the ultraviolet spectrum exhibits a maximum of high intensity at 216 $m\mu$. The second component was also very unstable and could not be isolated sufficiently pure for a structural determination.

The reaction of 1,2,7-octatriene was particularly interesting because bicyclic compounds were formed besides a small amount of an acetylenic substance. One of the compounds proved to be bicyclo[4.2.0]oct-1-ene. Hydrogenation afforded the saturated compound.²³ The structure of the second substance is not quite certain, but the evidence available agrees with the structure 6-methylenebicyclo[3.2.0]heptane (XXVIII). The compound gives rise to bands at 1640 and 880 cm^{-1} in the infrared spectrum, indicative of a methylene double bond. The n.m.r. spectrum of the hydrogenation product, besides exhibiting complex absorption due to saturated methylene and methine protons, shows a doublet, centered at τ 9.21, due to a methyl group coupled to a single proton. In both the n.m.r. and infrared spectra this compound is similar to the hydrogenation product from XXX (see below). The acetylenic component shows both vinyl and ethynyl absorption in the infrared spectrum, and *n*-octane was obtained by hydrogenation. We believe this compound is 1-hepten-7-yne.

Finally, heating the vapor of 1,2,7,8-nonatetraene (XXIX) at 390° yielded a mixture of essentially two compounds. These have been identified as starting material and 6,7-dimethylenebicyclo[3.2.0]heptane (XXX). The latter exhibits ultraviolet maxima at 246.5 $m\mu$ (ϵ 11,500) and 256.5 $m\mu$ (ϵ 8600) with a shoulder at 238 $m\mu$ which suggests a rigid diene chromophore.¹¹ The presence of methylene double bonds is shown by infrared bands at 3080, 1650, and 880 cm^{-1} . The n.m.r. spectrum is consistent with the structure XXX, and catalytic hydrogenation proceeded smoothly to the corresponding saturated compound.

Discussion

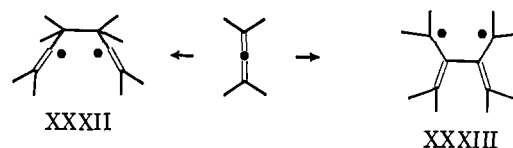
It is assumed that the first step in a thermally induced 1,2-cycloaddition, whether inter- or intramolecular, produces a transient biradical or at least proceeds through a transition state of considerable biradical character. Some evidence for such biradicals is available,³ but very little is known about their nature; in some reactions they appear to have a considerable lifetime.²⁴ Any stabilizing effect on the biradicals is expected to be an important factor in determining the direction of addition.

Thermal 1,2-cyclodimerization of allene gives mainly 1,2-dimethylenecyclobutane.⁴ The attack might be on either the terminal or the central carbon of the allene system, depending on the stabilities of the two resulting biradicals. Vinyl radicals, as in XXXII, are little known, but they are expected to be of high energy.²⁵

(23) W. Reppe, O. Schlichting, K. Klager, and T. Toepel, *Ann.*, **560**, 1 (1948). We prepared the compound by hydrogenating bicyclo[4.2.0]oct-7-ene.

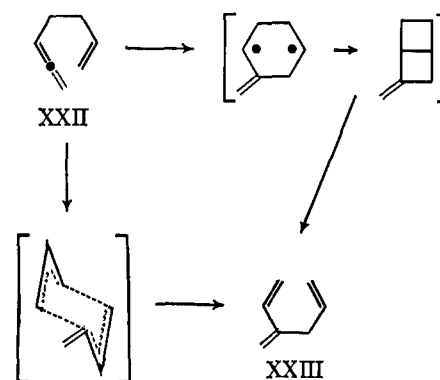
(24) L. K. Montgomery, K. Schueller, and P. D. Bartlett, *J. Am. Chem. Soc.*, **86**, 622 (1964).

(25) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 50.



The biradical XXXIII, on the other hand, can be stabilized by allylic resonance only to the extent that the $CH_2\cdot$ groups are in fact twisted away from the 90°, allenic orientation pictured, toward proper coplanarity with their respective vinyl groups. Presumably some such twisting will have occurred at the transition state, and it is possible, also, that the twist around the new, central bond will not be so great as to preclude some 1,3-diene stabilization. Some recent work by Jacobs and Illingworth²⁶ and by Griesbaum and co-workers^{27,28} has shown that thiyl radicals add preferentially at the terminal carbon of allene, but that with methyl substitution central attack becomes increasingly important; ethane- and benzenethiyl radicals attacked 3-methyl-1,2-butadiene exclusively at the center carbon of the allenic grouping.²⁶ It has also been found that the amount of terminal attack decreased with increasing reaction temperature.²⁷ The free-radical, gas phase addition of hydrogen bromide to allene²⁸ at room temperature occurred almost exclusively by central attack; terminal attack became significant at lower temperatures in the liquid phase. Altogether, this suggests that the 1,2-cycloadditions of substituted allenes studied here probably go preferentially by the way of central attack through biradicals like XXXIII. In similar reactions between allenic and olefinic double bonds, bond formation will occur between the central carbon of the allenic system and the carbon of the double bond which would result in the most stable radical; in the case of a vinyl group the terminal carbon will be preferentially attacked.

Our results, with one exception, is in agreement with this concept. The products from the cyclic allenes could also have been explained by terminal attack, but reactions of the allenes XXII and XXIV provided clear evidence for the general concept of central attack.



Terminal attack would not have produced the compounds XXIII and XXV, but rather bicyclo[3.2.0]hept-1-ene and bicyclo[4.2.0]octa-1,5-diene, respectively.

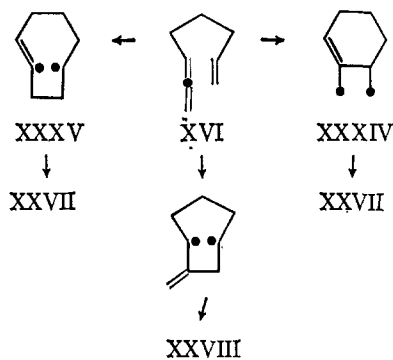
(26) T. L. Jacobs and G. E. Illingworth, *J. Org. Chem.*, **28**, 2692 (1963).

(27) K. Griesbaum, A. A. Oswald, E. R. Quiram, and W. Naegle, *ibid.*, **28**, 1952 (1963).

(28) K. Griesbaum, A. A. Oswald, and D. N. Hall, *ibid.*, **29**, 2404 (1964); see also P. I. Abell and R. S. Anderson, *Tetrahedron Letters*, 3727 (1964).

The bicyclo[2.2.0]octane derivatives, the supposed intermediates, will not survive the reaction conditions since the parent compound isomerizes rapidly to 1,5-hexadiene even at 230°. No evidence for the presence of discrete intermediates in these reactions has been obtained. Indeed, bond formation at the central carbon atom of the allenic grouping could be part of a concerted process, e.g., Cope rearrangement.³⁰ A few words should be mentioned about the feasibility of the Cope rearrangement in these allenic systems. Evidence provided by Doering and Roth³¹ shows that the six-membered transition state, pictured for the Cope rearrangement, prefers to adopt a chair-like conformation rather than a boat- or roof-like one. This implies that steric factors would be important, and consequently, if such an ideal conformation could not be attained a different reaction path might result. This has been demonstrated experimentally.³² In the case of the open-chain allenes XXII and XXIV the ideal conformation can easily be adopted and hence, a concerted mechanism is quite possible. With both the cyclic allenes, however, such a chair-like conformation is virtually impossible, at least by molecular models, and it seems that a concerted process would be unlikely. On the basis of the present experimental evidence no definite choice of mechanism, whether concerted or stepwise, can be made; both would lead to the observed products.³³

The apparent exception was found in the reaction of 1,2,7-octatriene (XVI). In order to explain the formation of bicyclo[4.2.0]oct-1-ene (XXVII) central attack must lead to a primary biradical XXXIV. Terminal attack, however, would also give XXVII through the biradical XXXV, and we have no way of distinguishing between these two paths. The expected methylene-



bicyclooctene XXVIII was also formed, but molecular models seem to indicate more strain in the reaction leading to this compound than to XXVII. No quite satisfactory explanation for the preferred formation of XXVII is apparent. The formation of 6,7-dimethylenebicyclo[3.2.0]heptane (XXX) as the sole product from

(29) S. Cremer and R. Srinivasan, *Tetrahedron Letters*, 24 (1960); C. Steel, R. Zand, P. Hurwitz, and S. G. Cohen, *J. Am. Chem. Soc.*, 86, 679 (1964).

(30) For a review on the Cope rearrangement see S. J. Rhoads in "Molecular Rearrangements," P. de Mayo, Ed., John Wiley and Sons, Inc., New York, N. Y., 1963 p. 655.

(31) W. von E. Doering and W. R. Roth, *Tetrahedron*, 18, 67 (1962).

(32) E. Vogel, *Angew. Chem.*, 74, 829 (1962); G. S. Hammond and C. D. DeBoer, *J. Am. Chem. Soc.*, 86, 899 (1964); D. J. Trecker and J. P. Henry, *ibid.*, 86, 902 (1964).

(33) Recent results in this laboratory have shown that the spiro-pentane derivative tricyclo[4.1.0.0^{4,6}]heptane⁹ rearranged thermally and quantitatively to the triene XXIII. This is hardly a concerted process, and a reasonable intermediate is indeed the biradical (or bicyclic compound) depicted above leading to XXIII.

XXIX at 400° fits in well with the general concept. Only about 30% conversion to XXX was achieved, which appears to be approximately the equilibrium concentration at that temperature. The isomerization of the conjugated diallene XVII is probably close to a concerted process. Terminal attack would in this case be energetically most unfavorable.

The results are generally in accordance with previous experience that allenes undergo thermally induced cycloadditions more readily than corresponding olefins.³ It has been reported³⁴ that the vapor of 1,5-hexadiyne isomerized at 350° to 3,4-dimethylenecyclobutene, an interesting compound first synthesized by Blomquist and Maitlis.³⁵ Perhaps 1,5-hexadiyne isomerizes to the corresponding diallene 1,2,4,5-hexatetraene (XXXV) before cyclizing. So far, attempts to obtain pure XXXV have failed,¹⁰ and neither 1,6-heptadiyne nor 1,7-octadiyne has isomerized under our conditions at temperatures up to 450°.

Experimental Section³⁶

Gas Phase Reactions. General Method. The vapor phase experiments were carried out utilizing a 540 × 20 mm. Pyrex tube surrounded by an oven. Regulation of the temperature was achieved by means of a variable transformer, and the temperature was measured by introducing a thermocouple into a small indentation in the wall of the tube.

In a typical experiment, the tube was packed with Pyrex glass wool and allowed to heat to the desired temperature. The compound to be reacted (0.5 to 4 g.) was placed in a flask which was fitted to the entrance of the reaction tube through a splash barrier tube. At the exit end of the tube there was fitted a vacuum adapter connected to a flask. When the desired temperature was reached, the tube was evacuated for 1 min. to remove water vapor after which time the receiving flask was immersed in a Dry Ice-acetone bath. The system was kept under vacuum until all of the compound had passed into the receiver. The time necessary varied from 1 to 18 hr. dependent on the vacuum applied and the volatility of the compound. Nitrogen was then introduced into the system, and the product was analyzed by gas-liquid partition chromatography (g.l.p.c.).

Tricyclo[9.7.0.0^{2,10}]octadeca-9,11-diene (II). A sealed tube containing 11.1 g. (92 mmoles) of 1,2-cyclononadiene (I) was heated at 130° for 18 hr. The contents of the tube solidified after cooling to room temperature. Extraction with hot ethanol, filtration, and subsequent evaporation of solvent gave 10.7 g. (96%) of tricyclo[9.7.0.0^{2,10}]octadeca-9,11-diene (II), m.p. 64–76°.

Anal. Calcd. for C₁₈H₂₈: C, 88.45; H, 11.55; mol. wt., 244. Found: C, 88.42; H, 11.93; mol. wt., 266.

Complete conversion of I to II was also achieved by heating the allene at 150° for 6 hr.

Thin layer chromatography of a hexane solution of II on silica gel revealed the presence of two isomers with almost the same R_f value. Attempts to analyze the mixture by gas chromatography were unsuccessful.

(34) W. D. Huntsman and H. J. Wristers, *J. Am. Chem. Soc.*, 85, 3308 (1963).

(35) A. T. Blomquist and P. M. Maitlis, *Proc. Chem. Soc.*, 332 (1961).

(36) All melting points and boiling points are uncorrected.

Careful column chromatography on alumina gave quite pure samples of the two isomers. The major component was recrystallized from *n*-propyl alcohol: m.p. 80–83°; λ_{\max} 250 μ (ϵ 12,200), 258.5 (15,800), and 269 (11,800); ν_{\max} (KBr) 1690 cm^{-1} (C=C). The minor component was also recrystallized from propanol: m.p. 108–110°; λ_{\max} 253.5 μ (ϵ 11,100), 263 (14,900), and 273.5 (11,000); ν_{\max} (KBr) 1660 cm^{-1} (C=C). The n.m.r.³⁸ spectra of both isomers exhibit complex absorption in the region τ 7.0–9.0 due to the saturated protons, and the olefinic protons give rise to a triplet at 4.43, $J = 8.5$ c.p.s., of which each band is a weakly split multiplet. The ratio of olefinic to saturated protons, based on integrated peak areas, is approximately 1:14.

Maleic Anhydride Adduct III. A solution of 1.2 g. (5.0 mmoles) of II and 2.0 g. (20 mmoles) of sublimed maleic anhydride in 10 ml. of dry toluene was heated under reflux for 16 hr. The adduct partly crystallized during the reaction. Filtration and recrystallization from benzene gave 1.1 g. (34%) of III, m.p. 312–313°, ν_{\max} (KBr) 1830 and 1780 cm^{-1} ((CO)₂O).

Anal. Calcd. for C₂₆H₃₂O₆: C, 70.89; H, 7.32. Found: C, 70.82; H, 7.27.

One experiment with equimolar amounts of II and maleic anhydride and xylene as solvent gave after 2 hr. of heating under reflux 50% of III, m.p. 308–311°. In addition a small amount of another substance, m.p. 162–188°, probably crude monoadduct, was isolated.

Tricyclo[9.7.0.0^{2,10}]octadecane (IV). The isomeric mixture of 5.3 g. (21.5 mmoles) of II in 100 ml. of *n*-hexane was hydrogenated for 16 hr. at 50° and 40 p.s.i. of hydrogen with 1.5 g. of 5% Pt-C catalyst. Filtration and evaporation of the solvent afforded 5.2 g. of a liquid residue, which crystallized by cooling. Recrystallization from absolute ethanol gave pure IV, m.p. 58–59°. The infrared and n.m.r. spectra showed the absence of double bonds, and only end absorption was observed in the ultraviolet spectrum.

Anal. Calcd. for C₁₈H₃₂: C, 87.02; H, 12.98. Found: C, 87.34; H, 12.78.

Dimerization of 1,2,6-Cyclononatriene (V). At 130°. Heating a sealed tube with 4.0 g. (33.3 mmoles) of V at 125–130° for 16 hr. afforded a viscous liquid. Thin layer chromatography revealed the presence of four components. Analysis by g.l.p.c. was not successful. Distillation gave 1.7 g. of tricyclo[9.7.0.0^{2,10}]octadecatetraene (VII), b.p. 120° (0.04 mm.), n^{24D} 1.5662, λ_{\max} 252 μ (ϵ 9200).

Anal. Calcd. for C₁₈H₂₄: C, 89.94; H, 10.06; mol. wt., 240. Found: C, 89.61; H, 10.38; mol. wt., 268.

The main infrared and n.m.r. absorption are discussed in the theoretical part. The presence of weak bands at 992 and 910 cm^{-1} in the former indicates strongly that some of the dimer VIII is present in the sample. Heating V at 95° for 64 hr. gave essentially the results described above, but the ultraviolet spectrum exhibited an additional maximum at 243 μ . Dimerization of V takes place slowly even at 40°, as

(37) *n*-Heptane was used as solvent for the ultraviolet measurements if not stated otherwise.

(38) N.m.r. spectra were obtained with a Varian A-60, using carbon tetrachloride as solvent and tetramethylsilane as internal standard.

evidenced by the gradual development of the 250- μ maximum in a sample kept at this temperature for 14 days.

Maleic Anhydride Adduct. A solution of 1.2 g. (5.0 mmoles) of the dimer VII and 0.98 g. (10 mmoles) of sublimed maleic anhydride in 10 ml. of benzene was heated under reflux for 16 hr. Solvent and excess maleic anhydride were evaporated, and the residue was recrystallized from benzene to give 0.4 g. of the monoadduct, m.p. 215–217°, ν_{\max} (KBr) 1850 and 1765 cm^{-1} ((CO)₂O).

Anal. Calcd. for C₂₂H₂₆O₃: C, 78.07; H, 7.74. Found: C, 77.67; H, 7.76.

The viscous residue (1.5 g.) showed an infrared spectrum similar to that of the crystalline adduct. **Hydrogenation** of 1.6 g. (6.7 mmoles) of VII in 25 ml. of *n*-hexane at 50° and 40 p.s.i. of hydrogen with 250 mg. of 5% Pd-C catalyst gave 1.1 g. of a liquid, b.p. 116–117° (0.03 mm.), n^{24D} 1.5075. The product failed to crystallize. The infrared and n.m.r. spectra are very similar to those of tricyclo[9.7.0.0^{2,10}]octadecane (IV).

At 150°. A sealed tube containing 4.0 g. (33.3 mmoles) of V was heated at 150° for 19 hr. The infrared spectrum of the crude product revealed the absence of starting material. Distillation gave 1.85 g. (46%) of a viscous liquid, b.p. 100° (0.04 mm.), n^{24D} 1.5326. The infrared spectrum was practically identical with that of VIII described below, but for a weak band at 725 cm^{-1} . The latter indicates that a small amount of dimer VII was present.

2,3-Divinylcyclopentene (VI). *A.* A solution of 10.0 g. (83 mmoles) of 1,2,6-cyclononatriene (V) in 40 ml. of *n*-hexane was heated in a sealed tube at 120–130° for 17 hr. Evaporation of the solvent and subsequent fractionation of the residue gave 4.2 g. (42%) of VI: b.p. 54° (20 mm.); n^{24D} 1.4947; λ_{\max} 233 μ (ϵ 20,900) with shoulders at 228 and 240 μ ; ν_{\max} (liq.) 3110, 3080, 1645, 1596 cm^{-1} (C=C), and 991, 901 cm^{-1} (CH=CH₂). The n.m.r. spectrum exhibits complex absorption in the region τ 3.35–5.25 due to the olefinic protons. The tertiary proton gives rise to a broad triplet centered at τ 6.60, and the other saturated protons show complex absorption at 7.5–8.5. The peak area ratio is 7:1:4, respectively. The infrared and ultraviolet spectra of the distillation residue (5 g.) showed that the dimers VII and VIII were present.

Anal. Calcd. for C₉H₁₂: C, 89.94; H, 10.06. Found: C, 89.82; H, 10.33.

B. 1,2,6-Cyclononatriene (5.0 g., 40 mmoles) was passed through the hot tube, at 235° (0.5 mm.). Distillation of the product gave 4.6 g. (92%) of VI, b.p. 53° (20 mm.), n^{23D} 1.4953. The spectroscopic data were identical with those described under A.

Maleic Anhydride Adduct X. To a solution of 0.98 g. (10 mmoles) of sublimed maleic anhydride in 10 ml. of benzene was added 1.2 g. (10 mmoles) of VI. After standing overnight the solvent was evaporated leaving 2.1 g. (99%) of crude adduct, m.p. 86–89°. Recrystallization from cyclohexane gave pure 9-vinylbicyclo[4.3.0]non-1-ene-3,4-dicarboxylic acid anhydride (X): m.p. 91–92°; ν_{\max} (KBr) 1830, 1720 cm^{-1} ((CO)₂O) and 1640, 982, 909 cm^{-1} (CH=CH₂).

Anal. Calcd. for C₁₃H₁₄O₃: C, 71.54; H, 6.47. Found: C, 71.84; H, 6.60.

1,2-Diethylcyclopentane (XI). A solution of 1.0 g. (8.3 mmoles) of VI in 40 ml. of acetic acid was hydrogenated at room temperature and 40 p.s.i. of hydrogen using 1.5 g. of 5% Pd-C as catalyst. The product consisted of a mixture of 54% *cis*-XI, $n^{24}\text{D}$ 1.4278, and 46% of *trans*-XI, $n^{24}\text{D}$ 1.4339, as shown by g.l.p.c. The pure isomers were obtained by preparative g.l.p.c. and their infrared spectra were identical with those of authentic samples prepared according to the literature.³⁹

Dimerization of 2,3-Divinylcyclopentene (VI). A sealed tube with 2.5 g. (21 mmoles) of VI and a few crystals of hydroquinone was heated at 150° for 65 hr. The ultraviolet spectrum of the crude product shows only end absorption. Distillation afforded 1.3 g. (52%) of 5-(5-vinyl-1-cyclopentenyl)-9-vinylbicyclo[4.3.0]non-1-ene (VIII), b.p. 110° (0.8 mm.), $n^{24}\text{D}$ 1.5264.

Anal. Calcd. for $\text{C}_{18}\text{H}_{24}$: C, 89.94; H, 10.07; mol. wt., 240. Found: C, 89.62; H, 10.10; mol. wt., 249.

When compound VI was heated at 125° for 2 days, the reaction mixture still contained some unreacted starting material as evidenced by an absorption maximum at 233 μ in the ultraviolet spectrum.

2,3-Divinyl-1,3-cyclohexadiene (XIII). The vapor of 370 mg. (2.8 mmoles) of 1,2,6,7-cyclodecatetraene (XII) was passed through the tube at 300° (0.5 mm.) affording as the sole product 370 mg. (100%) of XIII: $n^{25}\text{D}$ 1.5401; λ_{max} 208 μ (ϵ 12,600) and 231 μ (ϵ 16,800); ν_{max} (liq.) 1645, 1625, 1610 (C=C), 991, 902 (CH=CH₂), and 832 cm^{-1} (C=CH). In the n.m.r. spectrum the vinyl groups give rise to a characteristic ABC pattern, and the cyclic olefinic protons appear as a weakly split multiplet at τ 3.03. The cyclic methylene protons give rise to a triplet at τ 7.91. The ratio of olefinic to saturated protons on the basis of peak areas is 2:1.

Anal. Calcd. for $\text{C}_{10}\text{H}_{12}$: C, 90.85; H, 9.14. Found: C, 90.68; H, 9.50.

Heating a dilute solution of the diallene in *n*-heptane in a sealed tube produced some XIII, but the main product was a hydrocarbon polymer.

Maleic Anhydride Adducts XV and XVI. To a solution of 2.0 g. (15 mmoles) of XIII in 25 ml. of dry benzene was added 5.9 g. (60 mmoles) of freshly sublimed maleic anhydride. When the exothermic reaction had subsided the solution was heated with reflux under nitrogen for 30 min. A solid separated and was filtered (5.3 g.), m.p. 290–300°. This was separated by sublimation into two compounds. The minor component was shown to be XV: m.p. 200–201°; λ_{max} (acetonitrile) 257 μ (ϵ 3100); ν_{max} 1850 and 1770 cm^{-1} ((CO)₂O).

Anal. Calcd. for $\text{C}_{18}\text{H}_{16}\text{O}_6$: C, 65.85; H, 4.91. Found: C, 64.81; H, 4.91.

The major component was identified as XVI, m.p. 280–285° dec., ν_{max} 1850 and 1775 cm^{-1} ((CO)₂O).

Anal. Calcd. for $\text{C}_{22}\text{H}_{18}\text{O}_6$: C, 61.97; H, 4.26; mol. wt., 419. Found: C, 62.95; H, 4.33; mol. wt., 426.

1,2-Diethylcyclohexane (XIV). A solution of 500 mg. (3.8 mmoles) of XIII in 25 ml. of pentane was hydrogenated at 40 p.s.i. of hydrogen and 250 mg. of 5%

Pd-C catalyst. The product consisted of four components, and a mixture of the major two was separated by preparative g.l.p.c. They were identified as a mixture of *cis*- and *trans*-XIV, $n^{25}\text{D}$ 1.4458 (lit.¹⁷ $n^{25}\text{D}$ 1.4453). The infrared spectrum was identical with that of an authentic sample.¹⁷ The other two components, also separated by g.l.p.c. as a mixture, were most probably 1,2-diethylcyclohexene and 2,3-diethyl-1,3-cyclohexadiene as indicated by infrared and ultraviolet spectra; the latter shows maxima at 211 and 263 μ .

3,4-Diisopropylidenecyclobutene (XVIII). The vapor of 500 mg. (3.7 mmoles) of 2,7-dimethyl-2,3,5,6-octatetraene (XVII) was passed through the tube at 300° (0.1 mm.). The theoretical amount (500 mg.) of XVIII was obtained, m.p. 13–14°. The compound is very unstable and rapidly forms insoluble polymeric material at room temperature. No satisfactory analysis could be obtained. A 13% yield of XVIII was obtained by heating a *n*-heptane solution of XVII in a sealed tube at 150° for 24 hr. The residue was polymeric material.

1,2-Diisopropylcyclobutane (XIX). A solution of 1.6 g. (12 mmoles) of XVIII in 20 ml. of *n*-hexane was hydrogenated at 25° with hydrogen of atmospheric pressure and 100 mg. of 5% Pd-C catalyst. The product (1.5 g.) consisted of two compounds based on g.l.p.c. These were separated by preparative g.l.p.c. The major (90%) component, XIX, had $n^{25}\text{D}$ 1.4245 (lit.¹ $n^{20}\text{D}$ 1.4279). The infrared spectrum is in agreement with this structure. The minor component (10%), $n^{25}\text{D}$ 1.4315, was found to be a stereoisomer of the former by the identity of their infrared spectra. The n.m.r. spectrum of the former exhibits a broad multiplet centered at τ 8.37, and the methyl groups give rise to a unsymmetric doublet at 9.19, $J = 5.5$ c.p.s. The peak area ratio is approximately 2:3. It was not possible to establish the configuration on the basis of the spectrum; although, by analogy,⁴⁰ it is suggested that the major component is the *cis* isomer.

1,2-Diisopropylidenecyclobutane (XX). A solution of 0.7 g. (5.2 mmoles) of XVIII in 25 ml. of *n*-hexane was hydrogenated at 25° and normal pressure over 250 mg. of Lindlar's catalyst.²² After about 6 hr. the absorption of hydrogen had almost ended (only 3 ml. was consumed during an additional 12 hr.). G.l.p.c. revealed the presence of essentially two components. The minor (10%) was shown to be XIX by its g.l.p.c. retention time. The major component (90%) was obtained pure by preparative g.l.p.c. and subsequently proven to be XX: $n^{23}\text{D}$ 1.5026; λ_{max} 253 μ (ϵ 17,000) (lit.²¹ $n^{20}\text{D}$ 1.5032; λ_{max} 253.5 μ); ν_{max} (liq.) 1660 (C=C) and 1370 cm^{-1} (CH₃). The n.m.r. spectrum exhibits a singlet at τ 7.70 for the methylene protons and the methyl protons give rise to singlets at 8.28 and 8.43. The peak area ratio is 2:3:3. The compound is quite unstable.

3-Methylene-1,5-hexadiene (XXIII). The vapor of 940 mg. (10 mmoles) of 1,2,6-heptatriene (XXII) was passed through the tube at 300° (10 mm.) yielding 920 mg. (98%) of XXIII: $n^{23}\text{D}$ 1.4540; λ_{max} 223 (ϵ 20,400), 210 sh. (15,300), and 230 sh. (17,900); ν_{max} (liq.) 992,

(39) G. Chiurdoglu, *Bull. soc. chim. Belges*, **42**, 347 (1933).

(40) R. L. Burwell, *Chem. Rev.*, **57**, 895 (1957).

916 cm^{-1} ($\text{CH}=\text{CH}_2$), and 892 cm^{-1} ($\text{C}=\text{CH}_2$). The n.m.r. spectrum shows a complex absorption in the region τ 3.35–5.2 due to olefinic protons. The characteristic ABC pattern for the vinyl group is recognizable. The saturated protons give rise to a multiplet centered at τ 7.09. The peak area ratio is 4:1.

Anal. Calcd. for C_7H_{10} : C, 89.29; H, 10.71. Found: C, 89.11; H, 10.85.

Hydrogenation of 0.9 g. (9.6 mmoles) of XXIII in 25 ml. of pentane and 250 mg. of 5% Pt-C catalyst gave 3-methylhexane as the sole product, b.p. 89° , n^{24}_{D} 1.3820. The infrared spectrum is identical with that of an authentic sample.

Maleic Anhydride Adduct. A solution of 0.92 g. (9.8 mmoles) of XXIII and 0.98 g. (10 mmoles) of maleic anhydride in 25 ml. of benzene was heated with reflux under nitrogen for 2 hr. After standing overnight volatile material was distilled leaving a solid residue. The liquid contained some unreacted XXIII as shown by g.l.p.c. Recrystallization of the solid from carbon tetrachloride gave 1.3 g. (69%) of 4-(2-propenyl)-4-cyclohexane-1,2-dicarboxylic acid anhydride: m.p. $50\text{--}51^\circ$; ν_{max} (KBr) 1840, 1790 ($(\text{CO})_2\text{O}$), 1640, 993, 915 cm^{-1} ($\text{CH}=\text{CH}_2$).

Anal. Calcd. for $\text{C}_{11}\text{H}_{12}\text{O}_3$: C, 68.72; H, 6.30. Found: C, 68.54; H, 6.29.

3,4-Dimethylene-1,5-hexadiene (XXV). The vapor of 800 mg. (8.3 mmoles) of 1,2,6,7-octatetraene (XXIV) was passed through the tube at 310° (0.2 mm.). The product was shown by g.l.p.c. to consist of equal amounts of two components. Only one was separated by preparative g.l.p.c.; the other appeared to undergo decomposition on the column. The compound was identified as XXV: n^{23}_{D} 1.4937; λ_{max} 216 $\text{m}\mu$ (ϵ 34,000); ν_{max} 990, 917 ($\text{CH}=\text{CH}_2$), and 898 cm^{-1} ($\text{C}=\text{CH}_2$). The n.m.r. spectrum exhibited absorption due to olefinic protons only. A quadruplet centered at τ 3.60 is characteristic of the two β -vinyl hydrogens, and the eight methylene protons give rise to three multiplets at 4.67–5.06. Peak area ratio is 1:4. The compound polymerizes very readily.

Bicyclo[4.2.0]oct-1-ene (XXVII) and 6-Methylenebicyclo[3.2.0]heptane (XXVIII). The vapor of 3.0 g. (25.5 mmoles) of 1,2,7-octatriene (XXVI) was passed through the tube at 410° (0.03 mm.). The product was passed through a second time affording 2.8 g. (93%) of a liquid, which was subsequently shown by g.l.p.c. to consist of three compounds in 29, 36, and 35%, respectively. Only the last compound could be separated in a reasonably pure state (92%) by preparative g.l.p.c. and was shown to be XXVII. Only end absorption was observed in the ultraviolet spectrum. The infrared spectrum shows double bond absorption at 1690 cm^{-1} and the absence of methyl groups. The

presence of an olefinic proton is revealed by a multiplet at τ 4.85, and the saturated protons give rise to complex absorption in the 7–9 region. The peak area ratio is approximately 1:11. The other two compounds could only be isolated as a mixture. The infrared spectrum, however, indicated strongly by the presence of bands at 3300 and 2120 ($\text{C}=\text{CH}$), 1665, 992, and 910 cm^{-1} ($\text{CH}=\text{CH}_2$) that one of the products was 1-octen-7-yne. Furthermore, bands at 1640 and 880 cm^{-1} suggested a methylene double bond, and a sharp band at 1380 cm^{-1} shows the presence of a methyl group. *Hydrogenation* of the original reaction mixture in *n*-hexane over 5% Pt-C catalyst gave a product consisting essentially of four components, these were separated by preparative g.l.p.c. The compound with the lowest retention time was identified as *n*-octane by comparison with an authentic sample. The second component, 93% pure, n^{23}_{D} 1.4291, contained a methyl group as shown by a band at 1380 cm^{-1} in the infrared spectrum. The n.m.r. spectrum shows complex absorption between τ 7.8 and 9.2. A doublet centered at τ 9.21, $J = 6.5$ c.p.s., is readily recognized and is assigned to a methyl group coupled to an adjacent single proton. On the basis of this and evidence described above, the structure 6-methylbicyclo[3.2.0]heptane has been assigned to the hydrogenation product; hence, the original compound has the structure XXVIII. The third component could not be isolated pure enough for further study, but the fourth compound was separated pure (>99%), n^{22}_{D} 1.4616, and shown to be bicyclo[4.2.0]heptane by comparison with a synthetic sample,²³ and thus supporting the structure XXVII for the unsaturated compound.

6,7-Dimethylenebicyclo[3.2.0]heptane (XXX). The vapor of 1.4 g. (15 mmoles) of 1,2,7,8-nonatetraene (XXIX) was passed through the tube at 390° (0.025 mm.) affording 1.2 g. of a liquid consisting of starting material and 32% of XXX. The latter was obtained 93% pure by preparative g.l.p.c., n^{23}_{D} 1.4997. Several passes through the tube at $390\text{--}400^\circ$ did not appreciably reduce the amount of starting material in the product. In the n.m.r. spectrum the olefinic protons give rise to a triplet at τ 4.93, $J = 1$ c.p.s., and a doublet at 5.35, $J < 1$ c.p.s. The tertiary protons appear as a broad multiplet centered at τ 6.80, and the cyclopentyl protons give rise to a multiplet centered at 8.32. The peak area ratio is approximately 2:1:3, respectively. *Hydrogenation* of XXX in *n*-hexane over 5% Pt-C catalyst gave 6,7-dimethylbicyclo[3.2.0]heptane, n^{23}_{D} 1.4504. The infrared spectrum shows the presence of methyl groups by a strong band at 1380 cm^{-1} . In the n.m.r. spectrum the methyl groups give rise to a doublet centered at τ 9.15, $J = 6.5$ c.p.s., and the other protons appear as broad absorption at 8.40.