Analysis of Monochloro Acids. The methyl esters were analyzed by gc as described.[24] Methyl 7-chlorooctanoate was further identified by gc isolation and nmr spectrum: 1.50 (d, J = 6 cps, CH_3), 2.25 (t, J = 7 cps, α-CH_2), 3.62 (s, $-OCH_3$), and 3.90 (sextet, J = 6 cps, -CHCl-). The doublet at 1.50 and the sextet at 3.90 in the ratio 3:1 are unique features of methyl 7-chlorooctanoate and would not be found in any of the other six isomeric methyl monochlorooctanoates.

Analysis of Monochloro Alcohols. The mixtures of monochloro alcohols were oxidized to the monochlorocarboxylic acids by heating with 70% HNO_3 for 1 hr at 100°. Traces of $NaNO_2$ were added to initiate oxidation. Yields from the oxidation were near quantitative. The monochlorocarboxylic acids were converted to methyl esters and analyzed by gc as described above.

(24) N. Deno, R. Fishbein, and C. Pierson, *J. Amer. Chem. Soc.*, **92**, 1451 (1970).

The same analysis could be obtained by direct gc of the alcohols using the same column as with methyl esters. Like the methyl esters, retention times increased with increasing separation of the chloro substituent and the functional group. The precision was not as good because of broader bands and some tailing.

Analysis of Monochloro Ethers. The same gc column was used as with the methyl esters. It was assumed that retention times increased with separation of chloro substituent and ether function. The identification of the major (92%) product, 5-chlorohexyl methyl ether, was supported by the nmr spectrum of a gc isolated sample: δ 0.8–1.8 (m, CH_2), 1.45 (d, J = 6 cps, CH_3), 3.20 (s, $-OCH_3$), 3.2–3.5 (m, $-CH_2O-$), and 3.95 (sextet, J = 6 cps, -CHCl-). The 1.45 doublet and 3.95 sextet were unique features of 5-chlorohexyl methyl ether and would not be found in the other five isomeric monochlorohexyl methyl ethers.

Analysis of Monochlorooctanoamides. These were converted to the methyl monochlorooctanoates for analysis.

Electrophilic Additions to 2-Methyl-1-(tetramethylcyclopropylidene)propene. Generation of Cyclopropylidenecarbinyl Cations

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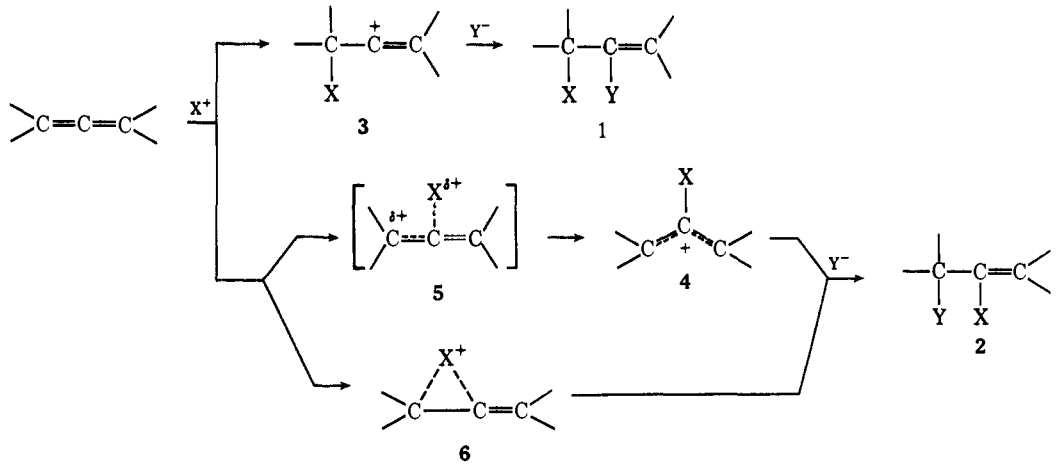
Received June 18, 1970

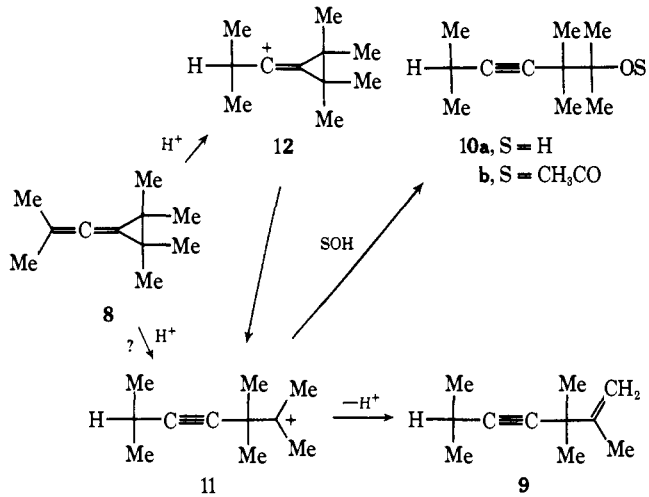
Abstract: Allene **8** undergoes protonic attack largely at a *terminal* carbon atom, in contrast to other tetraalkylallenes, because of special stabilization of vinyl cation **12** by the cyclopropane ring. The major products (isomer **9** and adducts **10a–d**) contain the structure of ring-opened cation **11** but products related to cation **12** (**22c** and **23**) have been detected. A minor protonation route is normal *central* attack which gives cation **17** followed by (or synchronous with) electrocyclic ring opening to cation **18** and ultimate formation of triene **15**; the latter is the major acid-catalyzed rearrangement product of diene **13**, formed from **8** under basic conditions. Chlorination (product **24**), bromination (products **25–32**), and addition of chlorosulfonyl isocyanate (product **33**) also occur by predominant terminal electrophilic attack. However, epoxidation gives adduct **36** and acetoxymercuration in methanol gives adduct **39**, each with attachment of the electrophilic species at the central carbon atom of **8**. In these cases, nucleophilic opening of a bridged cation is postulated as the product-determining step.

Electrophilic additions to allenes[1] can give two possible product orientations (**1** or **2**) dependent on allene and electrophile structure. Addition of protonic acids to allene itself gives adducts of structure **1** by terminal attack, presumably *via* a vinyl cation (**3**),[2,3] rather than by central attack *via* an allyl cation (**4**). Even though cation **4** is surely more stable than cation **3**, it was pointed out[2a] that the transition state for central attack (**5**) must largely maintain the twisted allene geometry and hence a better model for it would be an α-vinyl primary cation. However, addition of potentially bridging electrophiles such as the halogens[4a,b] or sulfenyl halides[2a,4c] gives type **2** products even for the parent allene. As alkyl groups are substituted on the allenic bond, the path leading to **2** becomes more and more favored for nonbridging electrophiles owing to stabilization of transition state **5**. Thus tetramethylallene (**7**) gives type **2** products with hydrogen halides,[5] halogens,[6] sulfenyl halides,[4c] mercuric salts,[7] peracids,[8] and chlorosulfonyl isocyanate.[9] We report herein the unusual behavior of 2-methyl-1-(tetramethylcyclopropylidene)-propene (**8**)[10] toward electrophilic reagents, compared to **7** as a model for tetraalkylallenes. While our work was in progress, Crandall and coworkers[11] reported that allene **8** reacted with acetic acid–sulfuric acid to produce a mixture of 2,3,3,6-tetramethyl-1-hepten-4-yne (**9**), 2,3,3,6-tetramethyl-4-heptyn-2-ol (**10a**), and the corresponding acetate (**10b**), all products containing the

(1) D. R. Taylor, *Chem. Rev.*, 67, 317 (1967); K. Griesbaum, *Angew. Chem., Int. Ed. Engl.*, 5, 933 (1966).
(2) (a) T. L. Jacobs and R. N. Johnson, *J. Amer. Chem. Soc.*, **82**, 6397 (1960); (b) K. Griesbaum, W. Naegele, and G. G. Wanless, *ibid.*, **87**, 3151 (1965); (c) K. Griesbaum, *Angew. Chem., Int. Ed. Engl.*, **8**, 933 (1969).
(3) P. J. Stang and R. Summerville, *J. Amer. Chem. Soc.*, **91**, 4600 (1969).
(4) (a) H. G. Peer, *Recl. Trav. Chim. Pays-Bas*, **81**, 113 (1962); (b) W. H. Mueller, P. E. Butler, and K. Griesbaum, *J. Org. Chem.*, **32**, 2651 (1967); (c) W. H. Mueller and P. E. Butler, *ibid.*, **33**, 1533 (1968).
(5) J.-P. Bianchini and A. Guillemonat, *Bull. Soc. Chim. Fr.*, 2120 (1968).
(6) M. L. Poutsma, *J. Org. Chem.*, **33**, 4080 (1968).
(7) W. L. Waters and E. F. Kiefer, *J. Amer. Chem. Soc.*, **89**, 6261 (1967).
(8) J. K. Crandall and W. H. Machleder, *ibid.*, **90**, 7292 (1968).
(9) E. J. Moriconi and J. F. Kelly, *J. Org. Chem.*, **33**, 3036 (1968).
(10) H. D. Hartzler, *J. Amer. Chem. Soc.*, **83**, 4990 (1961).
(11) J. K. Crandall, D. R. Paulson, and C. A. Bunnell, *Tetrahedron Lett.*, 5063 (1968).



added proton at a *terminal* carbon atom. This reversal in normal orientation of addition was ascribed to the unique overlap of the cyclopropyl σ bonds with the remote π bond of **8**. Terminal protonic attack could thus lead to cation **11** (the assumed precursor of **9** and **10**) either directly or *via* an intermediate, stabilized vinyl cation **12**. We have studied this system in more detail with several electrophilic reagents and have obtained information both with respect to the existence of cation **12** and the dependence of the balance of terminal and central electrophilic attack on allene **8** on the nature of the attacking electrophile.



Vinyl cations of general structure **12** (cyclopropylidenecarbinyl cations) have been postulated previously during solvolysis of homopropargyl derivatives.[12-14] They bear an obvious resemblance to the α-cyclopropylvinyl cations recently studied both directly by solvolysis of 1-cyclopropyl-1-haloethylenes[15] and indirectly during solvolysis of homoallenyl derivatives.[16] Stabilization of vinyl cations by α-phenyl[17] and α-vinyl[18] groups compared to simple vinyl cations[3,19] has also been reported.

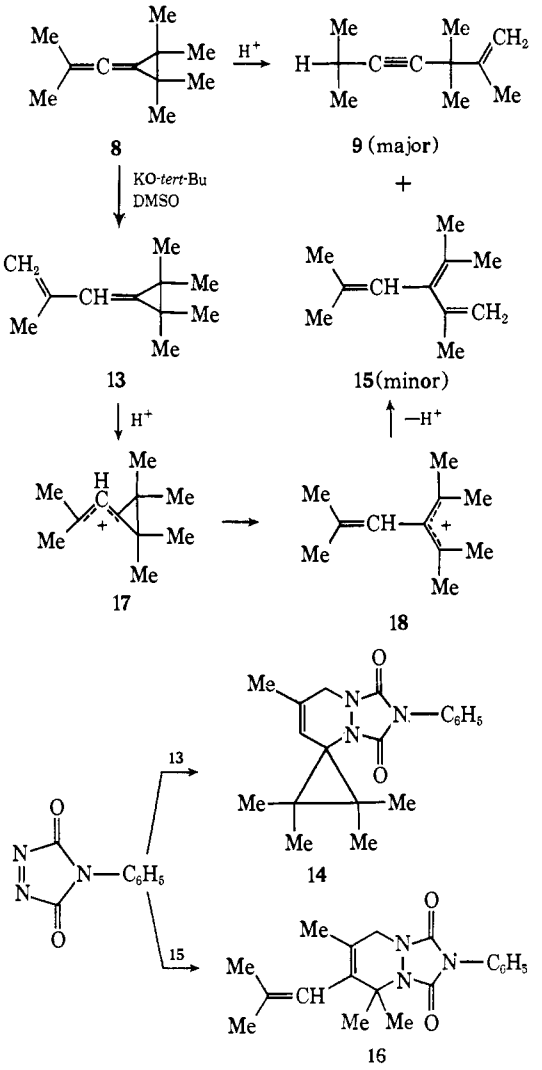
Results

Since treatment of allene **8** with acid catalysts gave minor products in addition to enyne **9**, it was desirable to have available other isomers for comparison. Isomerization of allene **8** with potassium *tert*-butoxide in DMSO[20] gave 2-methyl-3-(tetramethylcyclopropylidene)propene (**13**) in 64% isolated yield[21] characterized as its Diels–Alder adduct **14** with 4-phenyl-1,2,4-triazoline-3,5-dione.[22]

Treatment of diene **13** with a catalytic amount of *p*-toluenesulfonic acid monohydrate (TSA) in benzene solution at 25° led to rearrangement to still another $C_{10}H_{18}$ isomer **15** assigned as 2,5-dimethyl-3-isopropenyl-2,4-hexadiene based on spectral data (see Experimental Section); these indicated severe twisting of the isobutenyl group. Condensation with the same dienophile gave adduct **16** which showed enhanced absorption at 215–230 nm (dienic system) compared to adduct **14**. A reasonable pathway for conversion of diene **13** to triene **15** would be terminal protonation to form allylic cation **17** followed by electrocyclic ring opening to allylic cation **18** and deprotonation. However, in view of the known concerted character of the formation of allylic cations from solvolysis of most cyclopropyl derivatives,[23,24] it is not clear from this observation whether cation **17**, one resonance form of which contains a formal cyclopropyl cation structure, is a true intermediate in the conversion of diene **13** to cation **18**.

Whereas the isolated yield of triene **15** from diene **13** was only 54%, glpc studies on a benzene solution 0.49

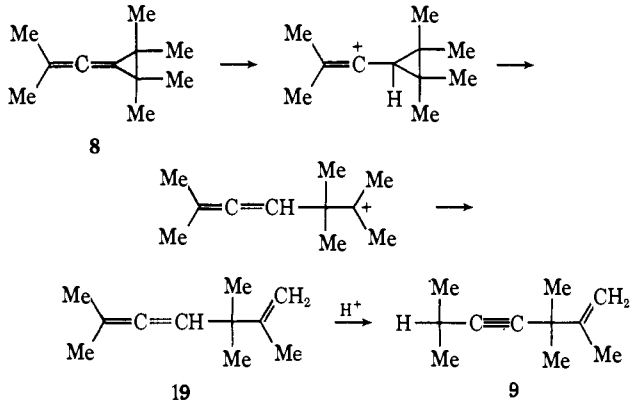
(12) M. Hanack, V. Vött, and H. Ehrhardt, *Tetrahedron Lett.*, 4617 (1968), and previous papers.
(13) J. W. Wilson, *J. Amer. Chem. Soc.*, **91**, 3238 (1969).
(14) H. R. Ward and P. D. Sherman, Jr., *ibid.*, **89**, 1962 (1967).
(15) S. A. Sherrod and R. G. Bergman, *ibid.*, **91**, 2115 (1969) [this paper contains a particularly extensive list of references to vinyl cations]; M. Hanack and T. Bässler, *ibid.*, **91**, 2117 (1969); D. R. Kelsey and R. G. Bergman, *ibid.*, **92**, 228 (1970).
(16) R. S. Bly and S. U. Koock, *ibid.*, **91**, 3292, 3299 (1969); T. L. Jacobs and R. S. Macomber, *ibid.*, **91**, 4824 (1969); M. Hanack and J. Häffner, *Chem. Ber.*, **99**, 1077 (1966); R. Garry and R. Vessière, *Bull. Soc. Chim. Fr.*, 1542 (1968); M. Bertrand and M. Santelli, *Chem. Commun.*, 718 (1968).
(17) C. A. Grob and G. Cseh, *Helv. Chim. Acta*, **47**, 194 (1964); W. M. Schubert and G. W. Barfknecht, *J. Amer. Chem. Soc.*, **92**, 207 (1970); L. L. Miller and D. A. Kaufman, *ibid.*, **90**, 7282 (1968); D. S. Noyce and M. D. Schiavelli, *ibid.*, **90**, 1020, 1023 (1968); R. C. Fahey and D. J. Lee, *ibid.*, **88**, 5555 (1966); **90**, 2124 (1968); Z. Rappoport and J. Kaspi, *ibid.*, **92**, 3220 (1970).
(18) C. A. Grob and R. Spaar, *Tetrahedron Lett.*, 1439 (1969).
(19) P. E. Peterson and J. M. Indelicato, *J. Amer. Chem. Soc.*, **91**, 6194 (1969); P. E. Peterson and J. E. Duddy, *ibid.*, **88**, 4990 (1966); Z. Rappoport, *Advan. Phys. Org. Chem.*, 7, 98 (1969).
(20) See, *e.g.*, W. Smadja, *Ann. Chim. (Paris)*, 10, 105 (1965).
(21) See T. C. Shields, W. E. Billups, and A. R. Lepley, *J. Amer. Chem. Soc.*, **90**, 4749 (1968), and T. C. Shields and P. D. Gardner, *ibid.*, **89**, 5425 (1967), for other examples of allylidenecyclopropanes.
(22) R. C. Cookson, S. S. H. Gilani, and I. D. R. Stevens, *J. Chem. Soc. C*, 1905 (1967).
(23) See P. R. von Schleyer, T. M. Su, M. Saunders, and J. C. Rosenfeld (*J. Amer. Chem. Soc.*, **91**, 5174 (1969)) for recent results and references.
(24) See J. A. Landgrebe and L. W. Becker (*ibid.*, **89**, 2505 (1967)) for a stabilized cyclopropyl cation.



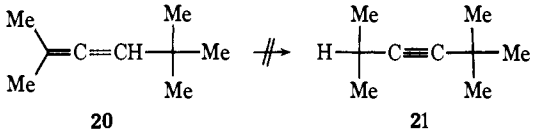
M in diene **13** and 0.035 *M* in TSA at 25° showed 85% efficiency to **15** at 85% conversion of **13**. The reaction was much more rapid when catalyzed by boron trifluoride etherate but the yield of **15** was only 15–20%, the remainder being higher molecular weight products. Triene **15** is itself very slowly consumed by catalytic amounts of TSA in refluxing benzene.

When a benzene solution of allene **8** (0.58 *M*) and TSA (0.022 *M*) was held at reflux, three products appeared in a ratio of *ca.* 10:2:1. The first two are enyne **9** and triene **15**, respectively, while the least prevalent component has not been identified. The total concentration of $C_{11}H_{18}$ isomers (**8** + **9** + **15**) did not change significantly over the course of reaction (24 hr). Note that, on the basis of results at 25° outlined above, diene **13**, if formed from allene **8**, would have been converted to triene **15** very rapidly at reflux. Rearrangement of allene **8** could also be effected by catalytic amounts of boron trifluoride etherate in benzene at 25° with an ultimate yield of **9** of 68%; the ratio of **9**:**15** was *ca.* 20:1 and the total concentration (**8** + **9** + **15**) slowly fell. In a control experiment a synthetic mixture of $C_{11}H_{18}$ isomers (allene **8**–enyne **9**–diene **13**–triene **15**, 60:4:16:20) was treated with boron trifluoride etherate at 25° in benzene. As expected, very rapid disappearance of **13** and appearance of **15** was followed by slower conversion of **8** largely to **9**.

Although the route from allene **8** to enyne **9** postulated by Crandall[11] is most reasonable and is supported by our work, the following less likely route was considered. This and similar routes would require acid-catalyzed conversion of a highly alkylated allene (**19**)

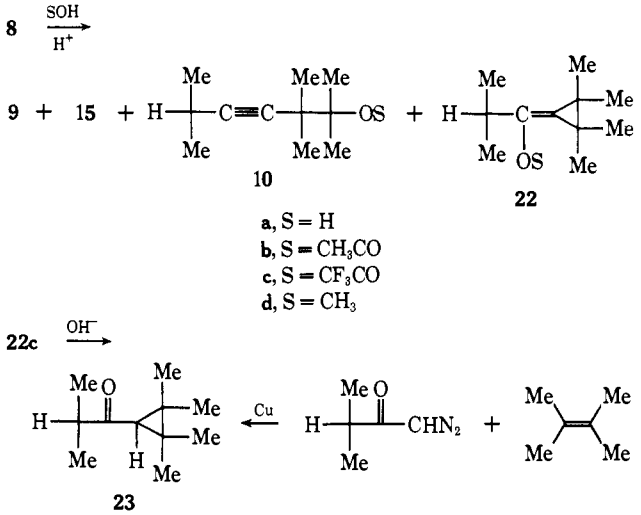


to an acetylene rather than a conjugated diene as usually observed.[2a,b,6] As a model for **19**, 2,5,5-trimethyl-2,3-hexadiene (**20**)[25] was treated with boron trifluoride etherate; **20** indeed disappeared but none of the known[25] acetylenic isomer **21** appeared.



A semiquantitative evaluation of the relative reactivity of allene **8** toward TSA in benzene compared to model **7** was carried out by following the decrease of the two allenes in competitive experiments at ~25° and at reflux. While such an experiment may be complicated if cationic intermediates derived from one allene attack the other, there is enough difference in rates of disappearance to be sure that allene **8** is considerably *less* reactive than tetramethylallene. A reactivity difference of ~10 can be calculated if parallel first-order disappearance is assumed.

Addition of 1 equiv of trifluoroacetic acid in benzene to a solution of allene **8** in benzene at 0–25° led partly



(25) R. M. Fantazier and M. L. Poutsma, *J. Amer. Chem Soc.*, 90, 5490 (1968).

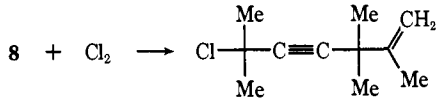
to rearrangement to form isomers **9** and **15** (**9**:**15** = 3.7) and partly to formation of three adducts in the ratio of *ca.* 7:1:1. The major adduct is 2,3,3,6-tetramethyl-4-heptyn-2-yl trifluoroacetate (**10c**) which could be saponified to form alcohol **10a**. Saponification of a sample enriched in one of the minor adducts gave isopropyl 2,2,3,3-tetramethylcyclopropyl ketone (**23**) and hence is assigned as the enol ester, 2-methyl-1-(tetramethylcyclopropylidene)-1-propyl trifluoroacetate (**22c**); spectra were consistent with this structure (see Experimental Section). Ketone **23** was prepared by copper-catalyzed addition[26] of isopropyl diazomethyl ketone[27] to tetramethylethylene. The second minor adduct has not been isolated pure nor identified.

Treatment of an acetic acid solution of allene **8** with sulfuric acid at 80° gave enyne **9**, major adduct **10b**, and alcohol **10a** as reported by Crandall.[11] Under our analytical conditions for this experiment, small amounts of triene **15** would have been missed.

Similarly, acid-catalyzed addition of methanol gave as the major adduct 2,3,3,6-tetramethyl-4-heptyn-2-yl methyl ether (**10d**). No ketone **23** could be detected after reaction or after treating the reaction mixture with aqueous acid; hence production of enol ether **22d** is unlikely.

Treatment of **8** with water–tetrahydrofuran–sulfuric acid at reflux led to very slow reaction to form isomers **9** and **15** (relatively more **15** was formed in this experiment than in any other), alcohol **10a**, and several minor products. One of these (3% yield) had the same retention time as ketone **23** but no more rigorous identification was achieved. In a control run, ketone **23** was shown to disappear slowly under the reaction conditions.

Chlorination of allene **8** in carbon tetrachloride solution under oxygen in the presence of solid sodium carbonate[6] gave cleanly 6-chloro-2,3,3,6-tetramethyl-1-hepten-4-yne (**24**); no rearrangement to enyne **9** was catalyzed by the by-product hydrogen chloride. In



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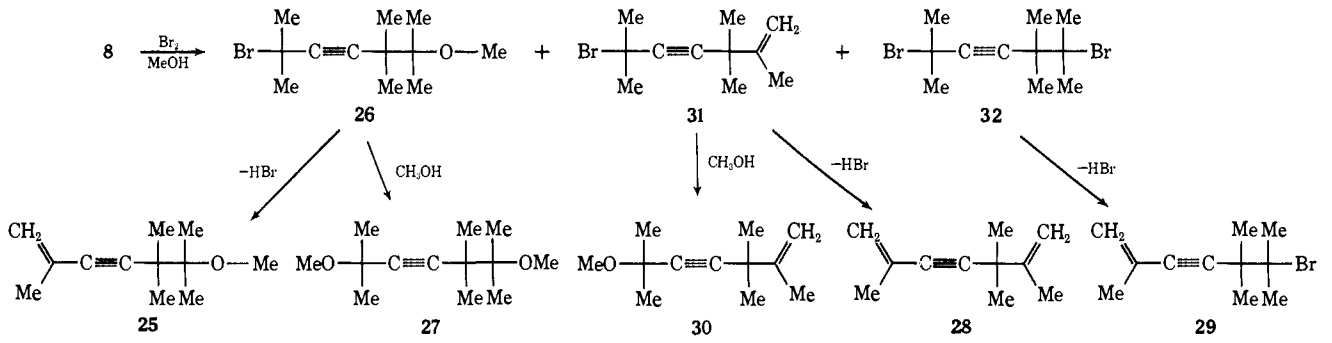
contrast, bromination in methylene chloride led to more than stoichiometric consumption of **8** and no product isolation was attempted.

Bromination of allene **8** in methanol at 25° gave a complex residue after solvent removal which showed a major component by glpc analysis. Preparative glpc collection of this "peak" gave a material with quite different spectral properties from the original residue. This "pyrolysis" product, free from bromine and showing ir and uv[28] spectra expected for a $CH_2{=}CR{-}C{\equiv}C{-}$ group, is assigned as 2,3,3,6-tetramethyl-6-hepten-4-yn-2-yl methyl ether (**25**), and its immediate precursor is therefore reasonably assigned as 6-bromo-2,3,3,6-tetramethyl-4-heptyn-2-yl methyl ether (**26**); spectral properties of the residue were fully in accord with this assignment for the major initial product although we have failed in all attempts to purify it. When this residue was refluxed in methanol, adduct **26** was converted to the corresponding diether, 2,5,5,6-tetramethyl-6-methoxy-3-heptyn-2-yl methyl ether (**27**). From chromatography (Florisil) of the residue from a similar bromination carried out at −15° was obtained a minor amount of a mixture of two "nonpolar" compounds tentatively assigned as 2,3,3,6-tetramethyl-1,6-heptadien-4-yne (**28**) and 6-bromo-2,5,5,6-tetramethyl-1-hepten-3-yne (**29**). Treatment of another crude bromination mixture with sodium methoxide in methanol gave a mixture of diether **27**, ether **25**, and a still different bromine-free ether **30**. Finally, bromination in methanol–water (10:1) at 0° gave diether **27** and substance **30** directly. Isolation of **30** from this source allowed its assignment as 2,5,5,6-tetramethyl-6-hepten-3-yn-2-yl methyl ether. From this combination of results we propose that the initial bromination products of **8** in methanol are bromo ether **26** (major), 6-bromo-2,3,3,6-tetramethyl-1-hepten-4-yne (**31**) (minor), and 2,6-dibromo-2,5,5,6-tetramethyl-3-heptyne (**32**) (trace); subsequently isolated products are formed by methanolysis and dehydrobromination of these products (Scheme I).

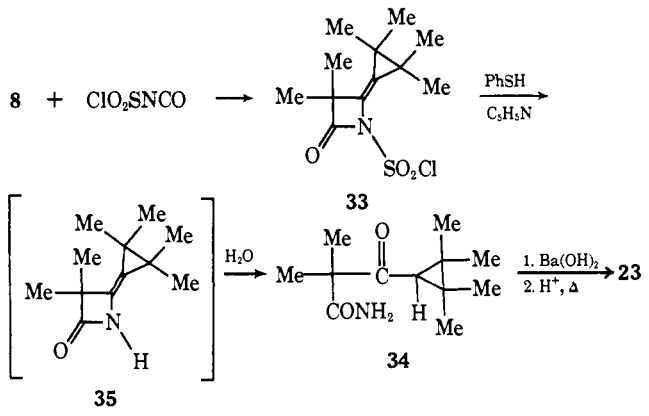
Scheme I



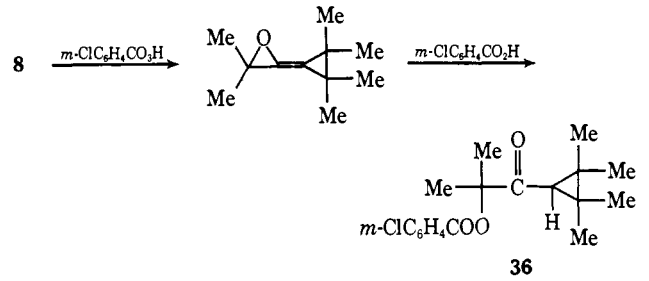
Chlorosulfonyl isocyanate, known to react with allenes,[9] reacted with **8** to give a crystalline cycloadduct (**33**) across the dimethyl-substituted double bond in *ca.* 50% yield. However, cleavage of the chlorosulfonyl group by pyridine thiophenol gave, instead of the usual β-lactam,[9] a ketoamide (**34**) which could be hydrolyzed and decarboxylated to give ketone **23**. Hence adduct **33** must have the positively polarized carbonyl group attached to the terminal allenic carbon; loss of the chlorosulfonyl group would then lead to enamide **35** which would be expected to hydrolyze to form **34**.

Treatment of allene **8** with *m*-chloroperbenzoic acid in methylene chloride gave a keto ester adduct **36** (70%

(26) F. Serratosa and J. Quintana, *Tetrahedron Lett.*, 2245 (1967).
(27) H. E. Smith and R. H. Eastman, *J. Amer. Chem. Soc.*, 79, 5500 (1957).
(28) C. N. R. Rao, "Ultraviolet and Visible Spectroscopy," Butterworths, London, 1961, p 27.

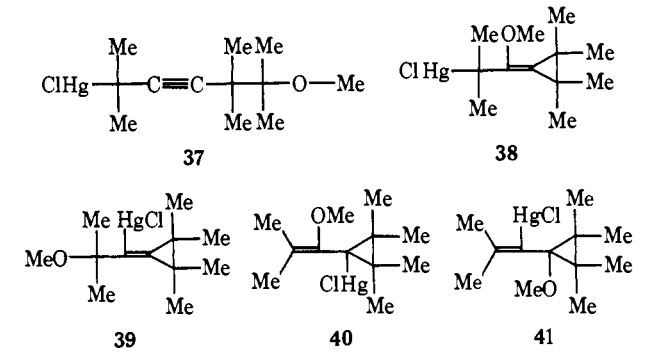


crude yield) analogous to the major product reported for peracetic acid by Crandall,[11] the apparent result of addition of 1 mol of *m*-chlorobenzoic acid to an intermediate allene epoxide.[8] No hydroxyl-containing material of opposite direction of ring opening, analogous

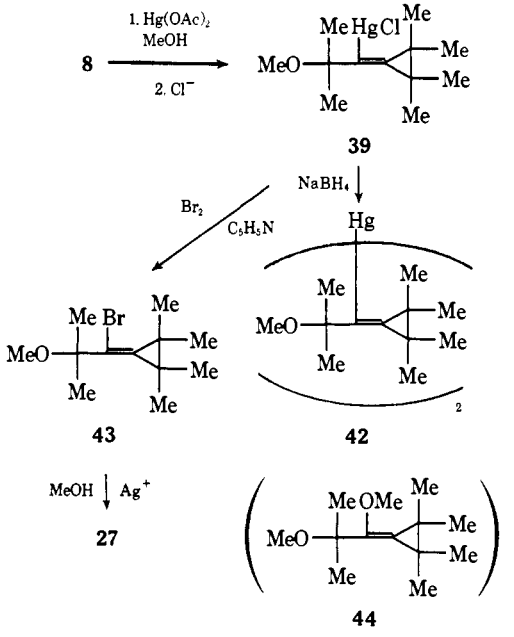


to Crandall's minor product,[11] was found in our system but small amounts could have been lost in the residue.

Reaction of allene **8** with mercuric acetate in methanol gave an adduct isolated as a crystalline mercurichloride. Based on the result of electrophilic additions already given above, structures **37**–**39** deserved serious consideration along with **40** and **41** as less likely choices. Neither ir nor Raman spectroscopy showed a triple bond or



ordinary double bond (1700–1600 cm^{-1}), and therefore **37**, **40**, and **41** seem unlikely; however, the weak band observed at 1740 cm^{-1} is not unreasonable for the methylenecyclopropane double bond in **39**[29] or possibly **38**. The base peak in the mass spectrum occurred at *m/e* 73, rationally associated with the stable ion Me_2C^+OMe easily derived from **37** or **39**. The nmr spectrum showed a methoxy singlet and three high-field singlets (six protons each) with satellites corresponding to $J_{^{199}Hg-^1H}$ = 19.5, 11.4, and <2 Hz for these three singlets. Since such coupling constants are typical for for four-bond $^{199}Hg-^1H$ coupling but are much too small for three-bond coupling,[7,30,31] only structures **39** and **41** with the mercury atom attached to the central allenic cation would fit the nmr spectrum. The only structure then which is consistent with all the spectral evidence is **39**, 2-methoxy-2-methyl-1-(tetramethylcyclopropylidene)-1-propylmercuric chloride. Reduction of **39** with sodium borohydride in alkaline aqueous medium[32] gave the corresponding bisorganomercury derivative **42** rather than reductive demercuration.[32,33] Reduction with lithium aluminum hydride led to deoxymercuration to form allene **8** as the only identifiable product;[32] at least this reduction tends to confirm the retention of the original carbon skeleton in **39**. Bromination in pyridine[33] did achieve demercuration to give a bromo ether **43**, different from **26**, whose ir absorption at 1750 cm^{-1} is again in accord with the methylenecyclopropane structure. Treatment of this product with silver ion in methanol at 25° gave silver bromide and the previously encountered ring-opened diether **27**. That this diether indeed has structure **27** and not enol ether structure **44** was demonstrated by its stability toward acidic methanol–water. This sequence of reactions is also then in accord with structure **39** for the initial mercuration product.



Discussion

Acid-catalyzed rearrangement of allene **8** as well as acid-catalyzed addition of hydroxylic solvents, chlorination, bromination, and cycloaddition with chlorosulfonyl isocyanate give products from terminal electrophilic attack, an orientation different from that ob-

(29) This is somewhat lower frequency than normally observed for methylenecyclopropanes [see L. J. Bellamy, "Advances in Infrared Group Frequencies," Methuen, London, 1968, pp 24, 32; *cf.* M. S. Newman and T. B. Patrick, *J. Amer. Chem. Soc.*, **91**, 6461 (1969)] but there is some evidence that the presence of mercury on a double bond lowers the frequency somewhat [H. D. Kaesz and F. G. A. Stone, *Spectrochim. Acta*, **15**, 360 (1959); D. J. Foster and E. Tobler, *J. Org. Chem.*, **27**, 834 (1962)].

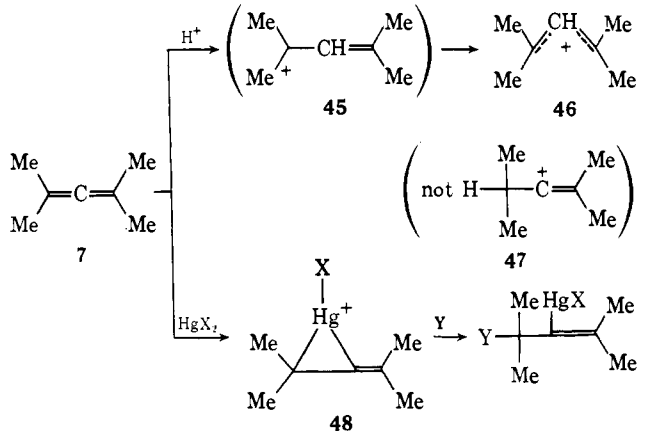
(30) E. F. Kiefer and W. L. Waters, *J. Amer. Chem. Soc.*, **87**, 4401 (1965).

(31) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon, Oxford, 1966, pp 688, 690.

(32) F. G. Bordwell and M. L. Douglass, *J. Amer. Chem. Soc.*, **88**, 993 (1966).

(33) W. L. Waters, W. S. Linn, and M. C. Caserio, *ibid.*, **90**, 6741 (1968).

tained with tetramethylallene (7).[5,6,9] However, epoxidation and mercuration give products with the electrophilic atom ultimately attached to the central carbon, analogous to the products from 7. As already outlined above for highly alkylated allenes, and for 7 in particular, product orientation has been rationalized[7] in terms of two extreme mechanisms of electrophilic attack: initial product-determining addition to form the more stable open carbonium ion[34] followed by rapid capture by nucleophile or proton loss[35] (as exemplified by addition of hydrogen halides[2,5]) or initial formation of a bridged ion intermediate followed by subsequent product-determining, nucleophilic opening of the three-membered ring (as exemplified by mercuration[7,33,36]).



For 7, both routes predict the same product orientation (*i.e.*, cation **45**, and surely **46**, is more stable than cation **47**) as long as it is assumed that nucleophilic attack on a bridged ion such as **48** should occur at the sp^3- rather that sp^2-hybridized carbon. Hence, in this context, the reactions of **8** with the proton, the halogens, and chlorosulfonyl isocyanate are "abnormal" while reactions with peracids and mercuric salts are "normal."

An intriguing difference between allene **8** and model 7 is that the analog of vinyl cation **47** for **8** (namely, cation **12**) may receive unique stabilization by the neighboring cyclopropane ring which is held in the "bisected geometry" by the remaining π bond.[37] Thus the preferred protonation of **1** at the terminal carbon atom is likely due to a reversal of the usual order of stability of ions of the form **47** and **45** for the special case of **12** and the 90°-rotated form of **17**. Yet overall, allene **8** is less reactive toward protonation than 7 whereas arguments based only on relative cation stabilities would have predicted the reverse. Such a comparison is obviously oversimplified because of ground-state differences; for example, the characteristic allene band in **8** occurs at 40–50 cm^{-1} higher frequency[10] than typical allenes. Also the cyclopropane methyl groups in **8** may exert some steric hindrance to central protonation not present in a normal allene.

(34) See C. U. Pittman, Jr. [*Chem. Commun.*, 122 (1969)] for direct observation of 46.

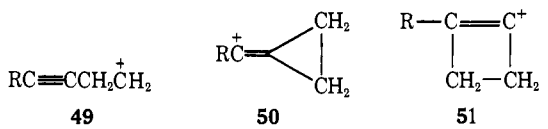
(35) Arguments based on relative cation stability would be invalid if vinyl cation formation were rapid but reversible before capture. This seems unlikely especially in view of the incorporation of only *one* deuterium atom in 1,3-dimethylallyl cation derived from 1,3-dimethylallene in FSO_3D–SbF_5 (ref 34).

(36) R. D. Bach, *J. Amer. Chem. Soc.*, 91, 1771 (1969).

(37) For current views on the geometry of cyclopropylcarbinyl cations, see, *inter alia*, M. Hanack and H.-J. Schneider, *Angew. Chem., Int. Ed. Engl.*, 6, 666 (1967); G. A. Olah, D. P. Kelly, C. L. Jeuell, and R. D. Porter, *J. Amer. Chem. Soc.*, 92, 2544 (1970).

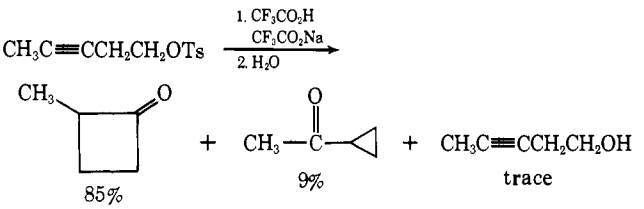
Cations of general structure **11** and **12** have been postulated to occur during solvolysis of homopropargyl derivatives in solvents of high ionizing power and low nucleophilicity which proceed *via* triple bond participation to form products related to cations having homopropargyl (**49**), cyclopropylidenecarbinyl (**50**), and cyclobutenyl (**51**) structures.[12,13]

Thus trifluoroacetolysis of the tosylate of 3-pentyn-1-ol gave mainly cyclobutyl product with some cyclo-

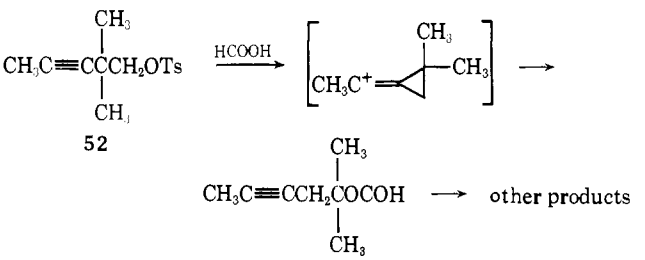


49 **50** **51**

propyl and traces of open-chain product,[38] while the *m*-nitrobenzenesulfonate gave almost entirely cyclo-



butyl product.[38] However, scrambling of deuterium label between the methylene positions indicated an intermediate of symmetry such as **50** at some point along the reaction coordinate.[12] Similar formation of cyclobutyl products occurred for secondary homopropargyl derivatives.[39] In contrast, solvolysis of a neopentyl-type homopropargyl derivative (**52**) gave only products derived from the open-chain tertiary ion resulting from "triple bond migration" but again an intermediate or transition state of cyclopropylidenecarbinyl symmetry is implied.[13] In none of these cases however is it fully clear whether structures **49–51** represent distinct energy minima or contributors to one or more delocalized



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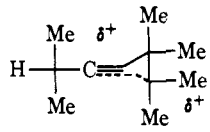
ions.[37,40] Terminal protonation of allene **8**, aided by developing interaction between the cyclopropane ring and the remote double bond, represents an alternative to solvolysis as an entry into a similar set of cations. In this case the predominant formation of open-chain rearrangement and solvent-incorporated products and the absence of identified cyclobutyl products demonstrate a strong driving force to proceed to a cation with charge distribution approximated by tertiary cation **11**, as in Wilson's[13] case. However, the observation of small amounts of product **22c** and the cycloadduct **33** demonstrate at least the intermediacy of a cationic species

(38) M. Hanack, I. Herterich, and V. Vött, *Tetrahedron Lett.*, 3871 (1967).

(39) M. Hanack, S. Bocher, K. Hummel, and V. Vött, *ibid.*, 4613 (1968).

(40) For a recent review of the related homoallyl–cyclopropylcarbinyl–cyclobutyl cation problem, see D. Bethell and V. Gold, "Carbonium Ions," Academic Press, London, 1967, p 266.

resembling cyclopropylidenecarbinyl structure **12**. In the absence of further evidence it is impossible to say whether **11** and **12** are distinct energy minima or whether structure **53** (with a majority of positive charge at the tertiary center) represents the cationic intermediate.



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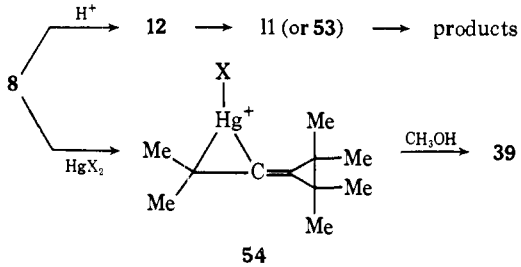
Observation of product **15** shows that terminal protonation, although favored, is not exclusive; some central protonation must also occur. Preliminary results on addition of electrophiles to diene **13** suggest that cation **17** can be trapped as a vinylcyclopropane derivative before ring opening to form cation **18**.

In the other extreme, mercuration, of all the reactions studied, seems the most likely to give bridged ion intermediates.[7,33,36] The formation of "normal" product **39**, rather than **37** or **38**, as the major mercuration product indeed supports the intermediacy of mercurinium ion **54** rather than mercurated analogs of **11** and/or **12**. Hence we suggest that the reversal in orientation of electrophilic additions to allene **8** occurs at the point where the product-controlling step changes from being initial attack governed by relative carbonium ion stabilities to being nucleophilic opening of a bridged ion.



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Chlorination, bromination, and addition of chlorosulfonyl isocyanate fit the carbonium ion pathway. Epoxidation gave as the major product, both for us and for Crandall,[11] a "normal" product indicative of SN2 rather than SN1 opening[41] of a protonated epoxide intermediate. However, since Crandall[11] also observed a minor product with "abnormal" orientation, the competitive pathways are probably closely balanced in this case.

Experimental Section

Infrared spectra were recorded on a Beckman IR10 spectrometer in carbon tetrachloride solution. Nmr spectra were recorded on a Varian A-60 spectrometer in carbon tetrachloride solution and results are expressed in parts per million downfield from internal TMS. Glpc analyses were carried out on a Micro-Tek GC 2500R instrument using silicone grease or bis(2-ethylhexyl)sebacate columns and a thermal conductivity detector; experimentally determined area calibration factors were used when comparing $C_{11}H_{18}$ isomers, but equal molar response was assumed when comparing $C_{11}H_{18}$'s with adducts. Boron trifluoride etherate trifluoroacetic acid, and chlorosulfonyl isocyanate were distilled before use. Allene **8** was prepared from 3-chloro-3-methyl-1-butyne[42] and tetramethylethylene by the method of Hartzler.[10] Tetramethylallene (**7**) was obtained from Columbia Organic Chemicals.

3-(Tetramethylcyclopropylidene)-2-methylpropene (13). A mixture of 10.00 g of allene **8**, 17.50 g of potassium *tert*-butoxide, and 350 ml of DMSO was heated at 100° for 2 hr. Flooding with water, extraction with methylene chloride, and evaporation gave a residue, still containing some DMSO, which was partitioned between hexane and water. Drying (Na_2SO_4) of the hexane layer and evaporation gave 8.45 g of residue which showed no residual **8** and a single major new product of similar retention time by glpc analysis. Short-path distillation gave 6.4 g (64%) of **13**: bp 77–80° (28 mm); $n^{20}D$ 1.4817; ir 1770 (vw), 1615 (m) (conj C=C), and 885 cm^{-1} (vs) ($R_2C{=}CH_2$); nmr δ 6.22 (m, 1), 4.80 (m, 2), 1.80 (m, 3), 1.18 (s, 6), and 1.12 (s, 6); uv (hexane) λ_{max} 232 nm (ϵ 20,300) [lit.[21] 3-(2′,2′-dimethylcyclopropylidene)propene: λ_{max} 230 nm (ϵ 21,875)]; mass spectrum (70 eV) *m/e* (rel intensity) 150 (95) and 135 (100).

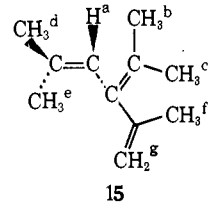
Anal. Calcd for $C_{11}H_{18}$: C, 87.92; H, 12.08. Found: C, 87.57; H, 11.92.

Potassium *tert*-butoxide in refluxing *tert*-butyl alcohol did not effect the isomerization of **8** to **13**.

Condensation of Diene 13 with 4-Phenyl-1,2,4-triazoline-3,5-dione. A solution of 205 mg (1.17 mmol) of the red dione[43] in 10 ml of benzene was added dropwise to a solution of 176 mg (1.17 mmol) of diene **13** in 1 ml of benzene. Decoloration was practically instantaneous but a pale pink color persisted when 1 equiv had been added. Evaporation gave a residue which solidified on cooling; trituration with hexane left 306 mg of crude Diels–Alder adduct **14**, mp 164.5–173.5°. Crystallization from 95% ethanol gave 175 mg, mp 174–175°, not increased by further crystallization, and 27 mg, mp 166–170°. Nmr bands ($CDCl_3$) occurred at δ 7.2–7.6 (m, 5) (C_6H_5), 5.82 (m, 1) (=CH–), 4.07 (s, 2) (=C—CH_2N), 1.90 (m, 3) (=C—CH_3), 1.38 (s, 6) (saturated CH_3), and 1.07 (s, 6) (saturated CH_3). The uv spectrum is shown in Figure 1 along with that of the butadiene–triazolinedione adduct, mp 158–159.5° (lit.[22] mp 157–159°). The enhanced absorption on either side of 215–220 nm may well represent conjugative interaction between the cyclopropane ring and the heterocyclic ring as well as the double bond.

Anal. Calcd for $C_{19}H_{23}N_3O_2$: C, 70.15; H, 7.08; N, 12.92. Found: C, 70.53; H, 7.11; N, 12.97.

2,5-Dimethyl-3-isopropenyl-2,4-hexadiene (15). A solution of 5.5 g of diene **13** and 0.8 g of *p*-toluenesulfonic acid monohydrate (TSA) in 100 ml of benzene was allowed to stand at room temperature for 20 hr. Glpc analysis revealed no residual **13** and the presence of a major new product of similar retention time. After passage through a short bed of Florisil, the benzene eluent was evaporated to give a residue (4.45 g) which was distilled bulb-to-bulb at 20 mm to give 2.96 g (54%) of triene **15**, >95% pure by glpc analysis: $n^{21}D$ 1.4713; ir 1635 (w) and 895 cm^{-1} (s) ($R_2C{=}CH_2$); broad uv plateau at 225–210 nm (ϵ 9600) followed by increasing end absorption; mass spectrum (70 eV) *m/e* (rel intensity) 150 (45) and 135 (100). The nmr spectrum (C_6H_6) showed δ 5.72 (at least ten lines, 1), 5.00 (d, J = 2.7 Hz of q, J = 1.5 Hz, 1), 4.80 (d, J = 2.7 Hz of q, J = 1.0 Hz, 1), 1.78 (d, J = 1.5 Hz overlapped with additional lines, 6), 1.70 (d, J = 1.45 Hz, 3), 1.64 (d, J = 1.1 Hz, 3), and 1.575 (d, J = 1.3 Hz, 3). Irradiation of the δ 5.72 region collapsed each of the doublets at δ 1.78, 1.70, 1.64, and 1.575 and allowed recognition of the "additional lines" near δ 1.78 as a d, J = 1.5 Hz of d, J = 1.0 Hz centered at δ 1.75. The large homoallylic coupling of H^a to $CH_3{}^b$ and $CH_3{}^c$ in **15** compared to the allylic coupling to $CH_3{}^d$ and $CH_3{}^e$ supports a conformation with the isobutenyl group twisted out of plane (to avoid the serious CH_3–CH_3 interactions) and allowing maximum overlap of the C–H^a bond with the C=C($CH_3{}^b$)($CH_3{}^c$) π bond.[44] The uv spectrum seems reasonable for a par-



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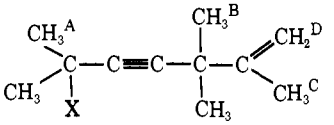
(41) R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 737 (1959).

(42) G. F. Hennion, J. J. Sheehan, and D. E. Maloney, *J. Amer. Chem. Soc.*, 72, 3542 (1950).

(43) Kindly supplied by Dr. D. R. Arnold.

(44) N. S. Bhacca and D. H. Williams, "Applications of Nmr Spectroscopy in Organic Chemistry," Holden-Day, San Francisco, Calif., 1964, pp 108–114.

Table I. Nmr Spectra of Methylated 1-Hepten-4-ynes



Compd	X	δ (multiplicity, J, Hz) H_A	H_B	H_C	H_D	X
9[a]	H	1.12 (d, 6.5)	1.26 (s)	1.82 (br s)	4.67 (m) 4.93 (m)	2.51 (7, 6.5)
24	Cl	1.78 (s)	1.32 (s)	~1.8 (br s)	4.72 (m) 4.97 (m)	
30	OCH_3	1.38 (s)[b]	1.35 (s)[b]	1.88 (br s)	4.80 (m) 5.08 (m)	3.30 (s)

[a] Reference 11 gives 1.15, 1.28, 1.82, 4.68, 4.95, and 2.50 for the corresponding δ values. [b] These assignments might well be reversed.

tially twisted remaining diene[18] (note the CH_3^e–CH_3^f interaction) but not for any linear triene.[45]

Condensation of Triene 15 with 4-Phenyl-1,2,4-triazoline-3,5-dione. A solution of 376 mg (2.14 mmol) of the dione in 20 ml of benzene was added dropwise to a solution of 319 mg (2.12 mmol) of triene **15** in 2 ml of benzene. Decoloration was rapid up to the equivalence point but was qualitatively slower than for the parallel reaction of diene **13**. Evaporation gave a residue which solidified on cooling, mp 139–145°. Crystallization from 95% ethanol gave 458 mg of adduct **16**, mp 152.5–154°, not increased by further crystallization, and 26 mg, mp 150–154°. Nmr bands ($CDCl_3$) occurred at δ 7.2–7.6 (m, 5) (C_6H_5), 5.63 (m, 1) (=CH–), 4.05 (broad s, 2) (=C—CH_2—N), 1.85 (m, 3) (=C—CH_3), 1.67 (m, 3) (=C—CH_3), and 1.58 (s with shoulder on highfield side, 9) (=C—CH_3 and $(CH_3)_2$C—N). The uv maximum (218 nm) was more intense than that of adduct **14** (Figure 1) as expected for the added diene chromophore (again having steric restrictions to full planarity).

Anal. Calcd for $C_{19}H_{23}N_3O_2$: C, 70.15; H, 7.08; N, 12.92. Found: C, 70.20; H, 7.02; N, 12.97.

2,3,3,6-Tetramethyl-1-hepten-4-yne (9). A solution of 3.8 g of allene **8** in 60 ml of benzene was treated with 3–4 small drops of boron trifluoride etherate and held at 40° for 2 hr before washing with water and drying ($CaCl_2$). After removal of benzene at reduced pressure, distillation through a short Vigreux column gave 2.24 g of product **9**, bp 71–72° (40 mm), contaminated by 10% triene **15** by glpc analysis. In other smaller scale runs, more careful distillation gave 98% pure **9**: $n^{23}D$ 1.4433; ir 1655 (m) and 895 cm^{-1} (s) (R_2C=CH_2); Raman 2245 cm^{-1} (RC≡CR′); uv end absorption, $\epsilon_{210\ nm}$ 270; nmr (see Table I); mass spectrum (70 eV) *m/e* (rel intensity) 150 (100), 135 (92), 107 (75) (P − C_3H_7), and 78 (86).

Acid-Catalyzed Rearrangements Involving Isomers 8, 9, 13, and 15. A. Diene 13 to Triene 15. A solution of 44 mg of diene **13** (0.49 *M*) and 4 mg of TSA (0.035 *M*) in 0.6 ml of benzene, containing 15 μl of toluene as internal standard for glpc analysis, was allowed to stand at room temperature. After 3 and 6 hr, the conversions of diene **13** were 60 and 85% and the efficiencies for formation of triene **15** were 85 and 86%, respectively, based on glpc comparison to the toluene standard. A solution of 140 mg of diene **13** (0.42 *M*) and 8 μl of boron trifluoride etherate (*ca.* 0.02 *M*) in 2.2 ml of benzene, containing 20 μl of toluene, was allowed to stand at room temperature. After 7 min, a sample was quenched with water. Glpc analysis showed 99% conversion of **13** and formation of **15** in 17.5% yield.

B. Allene 8 to Enyne 9 and Triene 15. A solution of 173 mg of allene **8** (0.58 *M*) and 7.6 mg of TSA (0.022 *M*) in 2 ml of benzene, containing 25 mg of toluene, was held at reflux. Glpc aliquots showed the gradual loss of allene **8** and formation of enyne **9**, triene **15**, and a third unidentified product in *ca.* one-half the amount of **15**; no diene **13** was detected. The solution composition by glpc analysis based on toluene standard and *normalized* to the initial concentration of **8** as "100%" was 69% **8**, 27% **9**, and 5% **15** after 1.25 hr; 49% **8**, 41% **9**, and 7% **15** after 3.5 hr; and 36% **8**, 55% **9**, and 8% **15** after 21 hr; *i.e.*, the total concentration of $C_{11}H_{18}$ isomers did not decrease significantly with time. A solution of 410 mg of allene **8** (0.55 *M*) and 20 μl of boron trifluoride etherate (*ca.* 0.02 *M*) in 5 ml of benzene, containing 40 mg of toluene, was allowed to stand at room temperature. Glpc aliquots, after quenching with water, showed behavior similar to the TSA-catalyzed run. The solution composition by glpc analysis again *normalized* to the initial concentration of **8** was 81% **8**, 7% **9**, and a trace of **15** after 5 min; 77% **8**, 19% **9**, and a trace of **15** after 30 min; 25% **8**, 49% **9**, and 3% **15** after 3 hr; 3% **8**, 63% **9**, and 3% **15** after 5 hr; and <1% **8**, 67% **9**, and 3% **15** after 21 hr; *i.e.*, the final yield of $C_{11}H_{18}$ isomers was 70%.

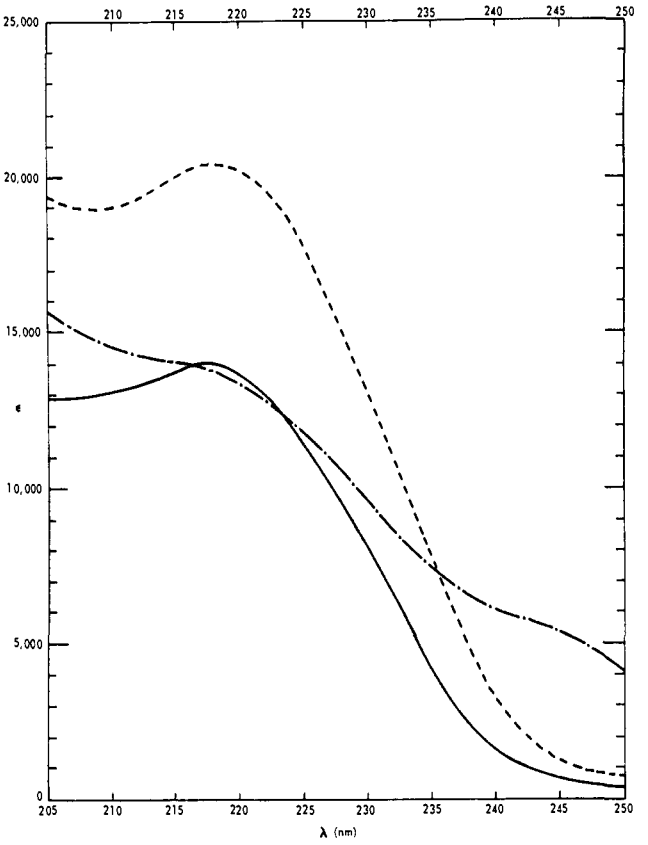
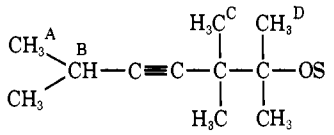


Figure 1. Uv spectra of adducts of 4-phenyl-1,2,4-triazoline-3,5-dione with butadiene (——), diene **13** (**14**, — · — ·), and triene **15** (**16**, ------).

C. Behavior of Mixed $C_{11}H_{18}$ Isomers. A solution of 312 mg of mixed $C_{11}H_{18}$ isomers (60% allene **8**, 16% diene **13**, 20% triene **15**, and 4% enyne **9**) (0.42 *M*) and 7 μl of boron trifluoride etherate (*ca.* 0.01 *M*) in 5 ml of benzene, containing 32 mg of toluene standard, was allowed to stand at room temperature. Aliquots were quenched with water before glpc analysis. The normalized composition was 48% **8**, 0% **13**, 24% **15**, and 13% **9** ($\Sigma_{C_{11}H_{18}}$ = 85%) after 10 min; 25% **8**, 0% **13**, 28% **15**, and 29% **9** (Σ = 82%) after

(45) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1962, p 228.

Table II. Nmr Spectra of Adducts **10**



Compd	S	δ (multiplicity, J, Hz) H_A	H_B	H_C[a]	H_D[a]	Other
10a[b]	H	1.14 (d, 7)	2.52 (7, 7)	1.15 (s)	1.18 (s)	OH 1.70 (s)
10b[c]	$COCH_3$	1.12 (d, 7)	2.48 (7, 7)	1.17 (s)	1.55 (s)	$OCOCH_3$ 1.90 (s)
10c	$COCF_3$	1.13 (d, 6.5)	2.50 (7, 6.5)	1.22 (s)	1.68 (s)	
10d	CH_3	1.10 (d, 7)	2.47 (7, 7)	1.11 (s)	1.19 (s)	OCH_3 3.17 (s)

[a] The assignments for H_C and H_D might be reversed for **3a** and **3d**. [b] Reference 11 gives 1.15, 2.52, 1.16, 1.20, and 1.87 for the corresponding δ values. [c] Reference 11 gives 1.16, 2.51, 1.22, 1.59, and 1.94 for the corresponding δ values.

1 hr; 2% **8**, 0% **13**, 29% **15**, and 48% **9** (Σ = 79%) after 4 hr; and 0% **8**, 0% **13**, 27% **15**, and 47% **9** (Σ = 74%) after 24 hr.

Acid-Catalyzed Rearrangement of 2,5,5-Trimethyl-2,3-hexadiene (20). A solution of 100 μl of **20**[25] in 300 μl of benzene in an nmr tube was treated with 1 small drop of boron trifluoride etherate. After 1 hr at 25°, the nmr spectrum was very complex but neither allene **20** nor 2,3,5-trimethyl-3-hexyne (**21**)[25] could be detected; the isopropyl hydrogen of **21** occurs[25] in a region which was not obscured by whatever products were formed in the reaction mixture.

Competitive Reactivities of Allene 8 and Tetramethylallene (7) toward Acid. To a refluxing solution of 300 mg of **7** (0.52 *M*) and 200 mg of **8** (0.22 *M*) in 6 ml of benzene containing toluene as an internal standard was added 25 mg of TSA (0.02 *M*). After 15 min at reflux, glpc comparison to the internal standard showed 99.5% conversion of **7** and 37% conversion of **8**.

A similar solution, 0.51 *M* in **7**, 0.56 *M* in **8**, and 0.016 *M* in TSA was held at room temperature. The conversions of **7** and **8**, read from a smoothed curve through data points taken every 30 min, were 35 and 4.5, 70 and 8.5, and 89 and 17%, respectively, after 1, 2, and 4 hr.

Reaction of Allene 8 with Trifluoroacetic Acid. Addition of solid allene **8** to neat trifluoroacetic acid at 25° led to very exothermic reaction and charring. A solution of 2.31 g (20.3 mmol) of trifluoroacetic acid in 5 ml of benzene was added dropwise with stirring at 0° to a solution of 4.96 g (33.0 mmol) of allene **8** in 8 ml of benzene. After 20 min at 25°, the benzene was evaporated at 60 mm to leave 6.7 g of residue. Glpc analysis (no calibration factors used) showed 18% residual **8**, 29% enyne **9**, 43% of a major product (55% efficiency), and 11% other material. Short-path distillation gave 5.2 g, bp 65–95° (30 mm), of similar composition from which the major product was isolated by preparative glpc. It was assigned as the adduct 2,3,3,6-tetramethyl-4-heptyn-2-yl trifluoroacetate (**10c**) on the basis of spectral properties: ir 1785 cm^{-1} (CF_3CO_2–); mass spectrum (70 eV) *m/e* (rel intensity) 264 (<1), 150 (21), 135 (30), 109 (100) ($(CH_3)_2CHC{\equiv}C{-}C^+(CH_3)_2$?), and 67 (55); mass spectrum (13 eV) *m/e* (rel intensity) 150 (100), (P − CF_3CO_2H); nmr (see Table II).

A separate run was carried out similarly with 2.25 g (19.8 mmol) of trifluoroacetic acid in 5 ml of benzene and 3.05 g (20.3 mmol) of allene **8** in 7 ml of benzene. Evaporation of one-half of this final solution gave 2.35 g of residue (trifluoroacetic acid would have been largely lost) which by more careful glpc analysis showed 2.5% residual **8**, 27% enyne **9**, 7% triene **15**, 49% adduct **10c**, 7% unknown A, and 7% unknown B; A and B had retention times reasonable for monoadducts. Preparative glpc gave product A contaminated by 15% triene **15**: ir 1790 (s) (CF_3CO_2–) and 1750 cm^{-1} (shoulder) (methylenecyclopropane ?); nmr δ 2.57 (seven lines, *J* ~ 7 Hz, 1) ($(CH_3)_2CH$–), 1.25 (s, 6), 1.13 (s, 6), and 1.13 (d, *J* = 6.75 Hz, 6) ($(CH_3)_2CH$–) plus extra lines appropriate for **15**. Hydrolysis of 30 μl of this material in a solution of one pellet of sodium hydroxide in 1 ml of ethanol–water (10:1) at reflux for 1.5 hr, flooding with water, extraction with ether, and evaporation gave a crude residue whose glpc analysis showed that triene **15** had survived but product A had been replaced by a material with retention time equal to that of isopropyl 2,2,3,3-tetramethylcyclopropyl ketone (**23**). Therefore A is assigned as 1-(tetramethylcyclopropylidene)-2-methyl-1-propyl trifluoroacetate (**22c**). Product B could not be obtained pure by preparative glpc. The second half of the original reaction mixture was evaporated and the residue refluxed for 2 hr in a solution of 0.58 g of sodium hydroxide in 13 ml of ethanol–water (10:1). Glpc analysis of the residue after the usual recovery procedure showed residual **9** and **15** but total loss of adducts **10c**, **22c**, and B; the major new materials were alcohol **10a** (see below), ketone **23**, and a new material presumably derived from B in a ratio of 8.5:1.0:1.2 compared to the initial ratio of **10c**:**22c**:B of 7.0:1.0:1.0. Enough of ketone **23** was collected by preparative glpc to confirm the glpc assignment spectrally.

Isopropyl 2,2,3,3-Tetramethylcyclopropyl Ketone (23). Reaction of diazomethane (*ca.* 2.8 g) and isobutyryl chloride (2.34 g, 22 mmol) in ether gave crude isopropyl diazomethyl ketone.[27] A solution of this ketone in 10 ml of tetramethylethylene was added dropwise to a stirred mixture of 250 mg of copper powder and 250 mg of freshly prepared cuprous chloride in 30 ml of tetramethylethylene.[26] Exothermic reaction and gas evolution began halfway through the addition. After addition was complete, the mixture was refluxed 20 min, filtered, and evaporated. Distillation of the residue through a small Vigreux column gave 0.7 ml of product: bp 85–87° (23 mm); $n^{20}D$ 1.4442; ir 1695 cm^{-1}. Minor impurities could be removed by preparative glpc to give a pure sample of **23**: nmr δ 2.55 (seven lines, *J* = 7 Hz, 1) ($(CH_3)_2CHCO$–), 1.42 (s, 1) (α-keto cyclopropyl H), 1.20 (s, 6), 1.18 (s, 6), and 1.02 (d, *J* = 7 Hz, 6), ($(CH_3)_2CH$–); mass spectrum (70 eV) *m/e* (rel intensity) 168 (10), 153 (30), 125 (39) (P − C_3H_7), and 97 (100) (P − C_3H_7CO).

Reaction of Allene 8 with Acetic Acid. A solution of allene **8** in acetic acid was stable for extended periods at 25°. However, heating a solution of 2.13 g of **8** in 40 ml of acetic acid containing 20 drops of concentrated sulfuric acid at 80° led to consumption of **8** after 1 hr. Flooding with water, extraction with methylene chloride, drying, and evaporation gave 1.70 g of residue which showed enyne **9** and two new products C and D in a ratio of 37:15:48 by glpc analysis. Each was isolated by preparative glpc. Product C was alcohol **10a** (see below). Major product D is assigned as 2,3,3,6-tetramethyl-4-heptyn-2-yl acetate (**10b**):[11] ir 1740 cm^{-1}; nmr (Table II).

Reaction of Allene 8 with Methanol. A solution of 2.27 g o allene **8** in 40 ml of methanol containing 7 drops of sulfuric acid was refluxed for 1.25 hr. Isolation by flooding with water and extraction with methylene chloride in the usual fashion gave 2.21 g of residue whose glpc analysis showed 10% enyne **9** and 80% of a major product isolated by preparative glpc. It was assigned 2,3,3,6-tetramethyl-4-heptyn-2-yl methyl ether (**10d**): ir no bands in 1800–1600-cm^{-1} region; nmr (Table II). A second reaction mixture containing 1.03 g of **8**, 200 mg of toluene standard, 83 mg of TSA, and 25 ml of methanol was refluxed for 70 min. Glpc analysis both before and after treatment with water showed mainly adduct **10d**, minor amounts of rearrangement products **9** and **15** (1.5:1.0), and a small extra peak in the adduct region, but no ketone **23**. The isolated crude product mixture was treated with 5 ml of CH_3OH–H_2O (10:1) containing 3 drops of sulfuric acid for 50 min at reflux. Both **10d** and the minor unidentified peak survived and no ketone **23** appeared.

Reaction of Allene 8 with Water. A mixture of 5.0 g of allene **8**, 3 ml of water, 40 ml of THF, and 0.16 g of sulfuric acid was refluxed 6 days; a very small second denser layer persisted throughout the reaction. Flooding with water, extraction with methylene chloride, and evaporation gave 4.14 g of residue whose glpc analysis showed 15% residual **8**, 22% enyne **9**, 11% triene **15**, 43% of a major product, 3% of material with retention time equal to that of ketone **23**, and three minor products totaling 5%. This residue was chromatographed over Florisil. Hexane eluted the $C_{11}H_{18}$ isomers in the general order triene **15** before allene **8** before enyne

9 but no clean separation was achieved; nmr spectra confirmed the glpc assignments. Benzene eluted the major product (1.6 g, 80% pure) which was further purified by bulb-to-bulb distillation and assigned as 2,3,3,6-tetramethyl-4-heptyn-2-ol (**10a**):[11] ir 3450 cm^{-1}; nmr (Table II); mass spectrum (50 eV) *m/e* (rel intensity) 168 (54), 153 (28), 125 (25) (P − C_3H_7), 110 (16) (P − CH_3COCH_3),[46] and 70 (100); mass spectrum (12 eV) *m/e* (rel intensity) 168 (100), 153 (4), 125 (2), 110 (9), and 70 (3).

Anal. Calcd for $C_{11}H_{20}O$: C, 78.56; H, 11.90. Found: C, 78.53, H, 11.97.

As a control experiment for the stability of ketone **23** under acidic conditions, a mixture of alcohol **10a** and ketone **23** (ratio 8.7:1) was treated with a mixture of 4 ml of THF, 0.3 ml of water, and 0.02 ml of sulfuric acid. After 48 hr at reflux the ratio of **10a**:**23** had increased to 11.9.

Chlorination of Allene 8. Chlorine (300 μl, 7.0 mmol) was condensed at −78° and slowly swept with an oxygen stream into a stirred solution of 1.83 g (12.2 mmol) of allene **8** in 10 ml of carbon tetrachloride containing suspended sodium carbonate. After flushing with oxygen for 5 min, the mixture was filtered. Glpc analysis showed only one peak besides residual **8** and direct nmr analysis showed no significant bands besides those of **8** and the ultimately isolated product; no rearranged **9** was formed. Parallel reaction of 2.20 g (14.6 mmol) of **8** with an equimolar amount of chlorine gave, after evaporation of most of the solvent at reduced pressure, 2.53 g of residue, 87% product **24** by glpc analysis (80–85% crude yield). The product was not very stable thermally but distillation at 0.5 mm and 35° bath temperature gave 1.15 g of 6-chloro-2,3,3,6-tetramethyl-1-hepten-4-yne (**24**): $n^{23}D$ 1.4569; ir 2230 (w) (C≡C), 1640 (m), and 895 cm^{-1} (s) ($R_2C{=}CH_2$); uv only end absorption; nmr (Table I); mass spectrum (70 eV) *m/e* (rel intensity) 184 (24) with correct isotopic cluster for one Cl and 149 (100) (P − Cl).

Brominations of Allene 8. A solution of 0.291 g (1.82 mmol) of bromine in 1 ml of methylene chloride was added dropwise to a solution of 0.545 g (3.63 mmol) of allene **8** in 2 ml of methylene chloride and immediate decoloration occurred. The nmr spectrum was very complex but showed *no* remaining **8**. Use of suspended sodium carbonate failed to eliminate the more than stoichiometric consumption of **8**.

A solution of 1.02 g (6.4 mmol) of bromine in 5 ml of methanol was added dropwise at 0° to a solution of 1.08 g (7.2 mmol) of allene **8** in 60 ml of methanol–water (10:1). Flooding with water, extraction with methylene chloride, drying, and evaporation gave 1.27 g of residue whose glpc analysis showed residual **8** (19%) and two major products E (13%) (retention time 5.5 min) and F (62%) (retention time 15 min) besides two other trace products. Collection of E and F by preparative glpc and comparison of their individual spectra with that of the residue indicated that no other significant products not detected by glpc had been formed; neither E nor F contained bromine as judged by the Beilstein copper wire test. Major product F is assigned as 2,5,5,6-tetramethyl-6-methoxy-3-heptyn-2-yl methyl ether (**27**): ir 2230 (vw) (RC≡CR′) and 1080 cm^{-1} (C–O–C) with no C=C absorptions; nmr δ 3.22 (s, 3) (OCH_3), 3.18 (s, 3) (OCH_3), 1.33 (s, 6), 1.22 (s, 6), and 1.17 (s, 6); mass spectrum (70 eV) *m/e* (rel intensity) 197 (<1) (P − CH_3) and 73 (100) ($(CH_3)_2C^+OCH_3$) with no other peaks >10% intensity. Minor product E is assigned as 2,5,5,6-tetramethyl-6-hepten-3-yn-2-yl methyl ether (**30**): ir 2230 (vw) (RC≡CR′), 1645 (w) (C=C), 1080 (s) (C–O–C), and 895 (s) cm^{-1} ($R_2C{=}CH_2$); nmr (Table I). The yield of **27** was thus 55–60% and that of **30** was 10–15%.

A solution of 2.15 g (13.4 mmol) of bromine in 10 ml of methanol was added dropwise at 25° to a solution of 2.03 g (13.5 mmol) of allene **8** in 35 ml of methanol. After 1 hr, the mixture was evaporated at reduced pressure to give a residue consisting of a major yellow layer and a minor brown layer. The latter (0.6 g) remained after addition of carbon tetrachloride and was discarded; evaporation of carbon tetrachloride gave 2.9 g of residue whose glpc analysis showed a major "component" G (retention time 10 min, 75% of the observed peaks). Collection of this peak, however, gave a material H with spectral properties different from those of the injected residue: ir 2220 (w) (conj RC≡CR′), 1615 (m) (conj C=C), 1075 (s) (C–O–C), and 890 cm^{-1} (m) ($R_2C{=}CH_2$); uv λ_{max} 223 nm (ε 12,400) and λ_{max} 232 nm (ε 10,400) (C=C–C≡C);[28] nmr δ 5.05 (m, 2) ($R_2C{=}CH_2$), 3.17 (s, 3) (OCH_3), 1.82 (m, 3) (=C–CH_3), 1.22 (s, 6), and 1.17 (s, 6). H is thus assigned as 2,3,3,6-tetramethyl-6-hepten-4-yn-2-yl methyl ether (**25**), a dehydrobromination product of G which must then be 6-bromo-2,3,3,6-tetramethyl-4-heptyn-2-yl methyl ether (**26**). Consistent with this assignment were spectral properties of the original residue rich in G: ir 2230 (w) (RC≡CR′), 1110 (s), and 1075 cm^{-1} (m) (C–O–C), but no C=C absorptions; nmr δ 3.17 (s, 3) (OCH_3), 1.93 (s, 6) ($(CH_3)_2C$–Br), 1.20 (s, 6), and 1.14 (s, 6) which accounted for two-thirds of the total proton area of the spectrum. Part of this residue rich in **26** (0.87 g) was refluxed 2 hr in 18 ml of methanol. Evaporation gave 0.94 g of a two-layer residue; the major layer (*ca.* three-fourths of the total) had spectral properties fully consistent with those of diether **27**. Glpc analysis showed 61% **27**, 18% of material with retention time equal to that of methoxyeneyne **25** (either present as such or as thermal precursor **26**), and several minor components.

A bromination conducted at −15° with 2.32 g of bromine in 10 ml of methanol and 2.18 g of **8** in 110 ml of methanol followed by evaporation at <25° again gave a two-layer residue containing comparatively more of the dark layer. This total product was chromatographed over Florisil. Hexane eluted 0.13 g of material whose glpc spectrum showed major bands at 4 min (I, 25%) and 18 min (J, 58%); very small peaks of these retention times had also been observed in the residue from the previous bromination in methanol at 25°. The ir spectrum of this eluate had bands at 2220 (vw) (conj C≡C), 1645 (w) (C=C), 1615 (m) (conj C=C), and 895 cm^{-1} (s) ($R_2C{=}CH_2$); the nmr spectrum showed olefinic protons mainly at δ 5.15, allylic methyl groups, and saturated methyl groups but very little methoxyl absorption. *Tentative* assignments for I (the most volatile bromination product isolated) and J (the least volatile) are 2,3,3,6-tetramethyl-1,6-heptadien-4-yne (**28**) and 6-bromo-2,5,5,6-tetramethyl-1-hepten-3-yne (**29**). 2% benzene–hexane eluted 0.46 g, >95% enyne **25**, $n^{21}D$ 1.4682.

Immediately after completion of a second bromination at −15° using 2.20 g (13.7 mmol) of bromine and 2.08 g (13.8 mmol) of **8**, the reaction mixture was treated at −15° with a solution prepared from 0.63 g (27.4 mmol) of sodium in 10 ml of methanol. After 15 min at −15° and 30 min at 25°, the mixture was partially evaporated at reduced pressure, flooded with water, and extracted with methylene chloride. Evaporation of the dried extract gave 2.3 g of residue whose glpc analysis showed 63% diether **27**, 23% methoxyenyne **30**, and 10% methoxyenyne **25**; preparative glpc and spectral analysis confirmed these glpc assignments.

Reaction of Allene 8 with Chlorosulfonyl Isocyanate. A solution of 3.55 g (23.7 mmol) of allene **8** in 5 ml of ether was added dropwise at 0° to a stirred solution of 2.20 ml (23.8 mmol) of freshly distilled chlorosulfonyl isocyanate in 5 ml of ether. After 1 hr the mixture was poured onto ice and the ether layer was washed with water. Evaporation of the dried ether layer gave a semisolid which was triturated with hexane to leave 3.44 g of crystalline product, mp 70–81°. Crystallization from hexane gave pure 1-chlorosulfonyl-3,3-dimethyl-4-(tetramethylcyclopropylidene)-2-azetidinone (**33**): mp 87.5–89.5°; ir 1855 (m), 1800 (s), 1775 cm^{-1} (s); nmr δ 1.44 (s, 6) and 1.25 (s, 12).

Anal. Calcd for $C_{12}H_{18}ClNO_3S$: C, 49.39; H, 6.22; N, 4.80; Cl, 12.15. Found: C, 48.87; H, 6.51; N, 4.76; Cl, 12.29.

Reductive Cleavage of Sulfonyllactam 33. A solution of 1.51 ml (1.2 equiv) of pyridine in 3 ml of acetone was added dropwise at −25° (carbon tetrachloride slush bath) to a stirred solution of 4.48 g of crude **33**, mp 70–80°, and 3.46 g (2 equiv) of thiophenol in 25 ml of acetone. After an additional 30 min, the mixture was warmed to room temperature and stirred for 20 min with 10 ml of added water. This two-phase system was then flooded with water and extracted with ether. The residue from the dried ether extract was chromatographed over Florisil in benzene. Benzene eluted 3.3 g (96%) of diphenyl disulfide. Ether eluted successive fractions of 1.01, 0.71, 0.36, and 0.18 g; the last three fractions had very similar ir spectra whereas the first had some extra bands, particularly at 1800 cm^{-1}. Crystallization of the last three fractions combined, mp 95–100°, from benzene gave a pure sample of 3-(2′,2′,3′,3′-tetramethylcyclopropyl)-2,2-dimethyl-3-oxopropionamide (**34**): mp 103–104°; ir (CCl_4) 3480, 3340, 3180, 1675 (broad), and 1605 cm^{-1}; ir (KBr) 3440, 3410, 3180, 1695 (cyclopropyl ketone), 1660 (amide carbonyl), and 1615 (primary amide) cm^{-1}; nmr δ 7.2–5.7 (very broad, 2) ($CONH_2$), 1.60 (s, 1) (α-keto cyclopropyl H), 1.27 (s, 6), and 1.17 (s, 12); mass spectrum (70 eV) *m/e* (rel intensity) 211 (11), 196 (40), 168 (16) (P − HNCO), 125 (100) (P − $(CH_3)_2CCONH_2$), 97 (65) (P − $(CH_3)_2(H_2NCO)C$–CO–), 87 (55), and 83 (100).

(46) See H. Budzikiewicz, C. Djerassi, and D. H. Williams ("Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, p 103) for a possibly analogous loss of a carbonyl fragment from Δ^3 alcohols.

Anal. Calcd for $C_{12}H_{21}NO_2$: C, 68.25; H, 9.95; N, 6.64. Found: C, 68.35; H, 10.00; N, 6.82.

Hydrolysis of Ketoamide 34. Barium hydroxide octahydrate (1.0 g) was added to a solution of 0.21 g of **34** in a mixture of 8 ml of ethanol and 5 ml of water. The resulting suspension was stirred overnight and then refluxed 6 hr. Addition of 1.5 *N* hydrochloric acid in ethanol–water (1:1) until the mixture was acidic gave a clear solution from which the organic material was recovered by flooding with water and extraction with methylene chloride. Evaporation gave an oil (0.18 g) whose ir spectrum showed characteristic –COOH absorption. The oil was refluxed for 4 hr in a mixture of 5 ml of ethanol and 5 ml of water. Analogous recovery of the organic material gave 0.15 g of oil whose glpc spectrum showed a major peak with retention time appropriate for ketone **23**. Nmr analysis showed the oil to be a mixture of ketone **23** and unchanged starting ketoamide **34**, slightly richer in the former; no extraneous bands were observed.

Epoxidation of Allene 8.[11] A solution of 3.59 g (17.8 mmol based on 85% assay) of *m*-chloroperbenzoic acid in 200 ml of methylene chloride was added slowly at 0° to a stirred solution of 3.26 g (21.7 mmol) of allene **8** in 25 ml of methylene chloride containing 2.50 g of suspended sodium carbonate. The mixture was brought to room temperature, washed with water, dried, and evaporated at 1 mm to leave 4.81 g of residue (84% crude yield calculated as **36**) which solidified on cooling. Crystallization from hexane gave 0.9 g, mp 66–68°, and 1.2 g, mp 64–68°. Infrared spectral comparison of the crude and crystallized products showed no major differences and, in particular, no hydroxyl absorption occurred in either. The product is assigned as 1-(2′,2′,3′,3′-tetramethylcyclopropyl)-2-methyl-1-oxo-2-propyl *m*-chlorobenzoate (**36**): ir 1730 (ester) and 1700 cm^{-1} (cyclopropyl ketone); nmr (CD_3COCD_3) δ 7.4–8.1 (m, 4) (ClC_6H_4–), 1.73 (s, 1) (cyclopropyl hydrogen), 1.57 (s, 6), 1.22 (s, 6), and 1.08 (s, 6); mass spectrum (70 eV) *m/e* (rel intensity) 322 (3) with correct isotopic cluster for one Cl, 139 (34) (ClC_6H_4CO), 125 (100) ($C_7H_{13}CO$), 111 (14) (ClC_6H_4), and 97 (31) (C_7H_{13}).

Anal. Calcd for $C_{16}H_{23}ClO_3$: C, 66.97; H, 7.13; Cl, 11.02; O, 14.88. Found: C, 65.94; 65.88; H, 7.06, 7.17; Cl, 11.07; O, 15.10.

Hydrolysis of ester **36** (0.54 g) in a mixture of 0.18 g of sodium hydroxide, 4 ml of ethanol, and 0.4 ml of water for 4 hr at reflux gave, after extraction with methylene chloride, 0.27 g of residue, homogeneous to glpc analysis, with ir bands at 3440 and 1685 cm^{-1}, and nmr singlets at δ 3.90 (broad), 1.65, 1.27, 1.23, and 1.21 in a ratio of 1:1:6:6:6 as expected for the parent alcohol, but no further characterization was performed.

Methoxymercuration of Allene 8. A solution of 1.94 g (12.9 mmol) of allene **8** in 40 ml of methanol was added gradually at room temperature to a stirred solution of 3.8 g (11.9 mmol) of mercuric acetate in 50 ml of methanol. Addition of 2 g of solid sodium carbonate after 5 min gave no yellow color. Solids were removed by filtration and the filtrate was evaporated. The residue was taken up in benzene, solids were again removed by filtration, and the filtrate was evaporated to give the crude oily mercuriacetate which was then shaken with a solution of 2.08 g of sodium chloride in 20 ml of water. The aqueous phase was decanted from the precipitated solid which was washed with water. Crystallization of this residue (4.0 g) from ethanol–water gave 1.9 g, mp 84–86°, and 0.35 g, mp 74–78°. Further crystallization gave pure 1-(tetramethylcyclopropylidene)-2-methoxy-2-methyl-1-propylmercuric chloride (**39**): mp 87–88°; ir transparent from 2500 to 1500 cm^{-1} except for a weak broad band at 1740 cm^{-1}; Raman spectrum transparent in same region except for similar weak band at 1730 cm^{-1}; nmr (C_6H_6) δ 2.97 (s, 3), 1.14 (s with satellites corresponding to $J_{^{199}Hg-^1H}$ = 11.4 Hz, 6), 1.02 (s with satellites corresponding to $J_{^{199}Hg-^1H}$ = 19.5 Hz, 6), and 0.98 (s with no observable satellites, 6) [in CCl_4 the singlets occurred at δ 3.17, 1.30, 1.22, and 1.20 with similar *J* values]; mass spectrum (70 eV) *m/e* (rel intensity) 418 (1.3) with appropriate isotopic cluster for 1 mercury plus 1 chlorine and 73 (100) ($(CH_3)_2C^+OCH_3$).

Anal. Calcd for $C_{12}H_{21}ClHgO$: C, 34.53; H, 5.07; O, 3.83. Found: C, 34.02; H, 4.96; O, 4.06.

Attempted Reductions of Mercurichloride 39. A solution of 0.132 g (3.48 mmol) of sodium borohydride in 4 ml of 2.5 *M* sodium hydroxide solution was added dropwise at room temperature to a stirred suspension of 1.9 g (4.55 mmol) of mercurichloride **39** in 35 ml of 1 *M* sodium hydroxide solution; a dark grey color developed immediately. After 25 min additional, the suspension was extracted with carbon tetrachloride and the extract filtered. Evaporation gave a semisolid residue which could be purified by sublimation at 90° (1 mm) to give 0.62 g (49%) of bis[1-(tetramethylcyclopropylidene)-2-methoxy-2-methyl-1-propyl]mercury (**42**): mp 100–102°; ir very similar to that of **39** except for the virtual absence of the 1740-cm^{-1} band; nmr (C_6H_6) δ 3.20 (3, s), 1.38 (s with satellites appropriate for $J_{^{199}Hg-^1H}$ = 4.6 Hz, 6), 1.28 (s, 6), and 1.19 (s with satellites appropriate for $J_{^{199}Hg-^1H}$ = 7.7 Hz, 6);[47] mass spectrum (70 eV) *m/e* (rel intensity) 564 (0.75) with appropriate isotopic cluster for 1 Hg, 202 (15) with appropriate isotopic cluster for 1 Hg, and 73 (100).

A solution of 717 mg (1.27 mmol) of mercurichloride **39** in 10 ml of ether was added dropwise to a stirred suspension of 115 mg (3.0 mmol) of lithium aluminum hydride in 5 ml of ether. After 2 hr at reflux, the mixture was worked up with water and aqueous base. Evaporation of the ether gave 209 mg of oil which quickly crystallized and which was shown by spectral analysis to be largely allene **8**.

An attempt to hydrogenate **39** with an equal weight of prereduced Adam's catalyst in ethanol at 25° and 1 atm led to no consumption of hydrogen.

Bromodemercuration of Mercurichloride 39. A solution of 1.35 g (8.44 mmol) of bromine in 6 ml of pyridine was added dropwise to a stirred solution of 3.48 g (8.37 mmol) of mercurichloride **39** in 30 ml of pyridine. The reaction was noticeably exothermic and after 5 min a starch–iodide test was negative. Ether (100 ml) was added and the mixture washed with 150-ml portions of water. During the second washing solids appeared and were removed by filtration. The dried ether layer was evaporated and the semisolid residue was triturated with pentane. Evaporation of the pentane fraction gave 1.38 g (62%) of oil: ir 1740 cm^{-1} (m) (methylenecyclopropane ?); nmr δ 3.07 (s, 3), 1.33 (s, 6), 1.21 (s, 6), and 1.18 (s, 6); mass spectrum (70 eV) *m/e* (rel intensity) 260 (<0.1) with appropriate isotopic cluster for 1 bromine, 87 (22), and 85 (100). A solution of 443 mg (2.61 mmol) of silver nitrate in 70 ml of methanol was added to a solution of 564 mg (2.16 mmol) of this product in 12 ml of methanol. Precipitation of silver bromide began immediately but was not complete after 30 min at room temperature. After 3 hr, filtration gave 370 mg (91%) of silver bromide and a clear filtrate. The filtrate was treated with solid sodium carbonate and evaporated. The resulting residue was triturated with carbon tetrachloride. Evaporation of carbon tetrachloride gave 330 mg (73%) of a liquid whose ir and nmr spectra were fully consistent with those of diether **27**. To further rule out structure **44**, this product was refluxed for 2 hr with a mixture of 4 ml of methanol, 1 ml of water, and 3 drops of sulfuric acid. Recovery of the organic material in the usual fashion gave unchanged material. The most reasonable assignment for the bromodemercuration product based on the spectral and chemical results is 1-bromo-2-methyl-1-(tetramethylcyclopropylidene)-2-propyl methyl ether (**43**).

(47) Note that the $J_{^{199}Hg-^1H}$ values for **42** are approximately one-half those of **39** as expected for the change from RHgCl to R_2Hg (ref 31).