DMSO solution. The reaction mixtures were worked up by pouring them onto ice and extracting with ethyl acetate. The ethyl acetate extracts were washed several times with water and the solvent removed without heat. The composition of the crude products was determined by nmr and is described below.

Reaction of 17 with Sodium Azide and Sodium *p*-Toluenesulfinate.—A mixture of 0.66 g of **17**, 0.88 g of sodium azide, and 0.53 g of sodium *p*-toluenesulfinate dihydrate in 30 ml of DMSO was allowed to react at room temperature for 20.5 hr. The reaction was worked up as described above and yielded 0.39 g of a semicrystalline mass. The nmr spectrum showed that this was 57% triazole **18** and 43% starting vinyl azide.

Reaction of 17 with Sodium *p*-Toluenesulfinate.—A mixture of 0.5 g of **17** and 0.4 g of sodium *p*-toluenesulfinate dihydrate in 30 ml of DMSO was allowed to react at room temperature for 22.5 hr. The reaction was worked up and yielded 0.28 g of crude product which nmr analysis shows to be 62% triazole **18**, and 38% vinyl azide **17**. The addition of ether to the crude product caused the precipitation of a white solid, mp 147–151°, having an identical infrared spectrum with that of authentic **18**.

Reaction of 17 with Potassium *t*-Butylate in DMSO.—A mixture of 0.32 g of **17** and 0.3 g of potassium *t*-butylate in 30 ml of DMSO was allowed to react for 18 hr at room temperature. The reaction turned deep red-brown at its initiation and bubbled. Acidification, of the reaction mixture and work-up yielded 0.3 g of the product which the nmr spectrum shows to be 50% of triazole **18** contaminated with DMSO. Crystallization of the material from water yielded 0.13 g of a white solid, mp 151–155° (**18**, mp 156–158°).

Deuterium Exchange of *trans*-2-Azidovinyl *p*-Tolyl Sulfone.—To a solution of 0.155 g of **17** in 0.5 ml of deuteriochloroform was added 1 drop of 6.27% sodium deuteroxide solution. The reaction was monitored by nmr. After 35 min there was no apparent change in the spectrum. After 6.5 hr there was 29% exchange, after 22 hr 50% exchange, and after 48 hr 70% exchange of the proton α to the sulfonyl group.

Preparation of 4(5)-*p*-Toluenesulfonyltriazole.—A mixture of 0.2 g of *p*-toluenesulfonylacetylene[14] and 0.54 g of trimethylsilyl azide[25] was heated on a steam bath (80°) in a glass-stoppered test tube for 20 hr. After heating, 15 ml of water was added and the solution was boiled for 5 min and filtered. The triazole crystallized on cooling yielding 0.119 g (48%) of colorless needles, mp 156–158°, mmp 156–158° with **18**. Infrared and nmr spectra were identical with those of the compound prepared by the reaction of 1 with sodium azide in dimethyl sulfoxide for 28 hr.

Registry No.—**1**, 15645-75-7; **2**, 15717-50-7; **4**, 15717-49-4; **8**, 15717-51-8; **12**, 15717-52-9; **14**, 15645-76-8; **18**, 14631-74-4; 1, 15645-78-0; 2, 15645-79-1; 3, 15717-53-0; 4, 15645-80-4; 5, 15717-54-1; 6, 15717-55-2; 7, 15717-56-3.

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(25) L. Birkofer and A. Ritter, *Angew. Chem. Intern. Ed. Engl.*, **4**, 417 (1965).

Small-Ring Epoxides. I. The Synthesis and Reactions of a 4-Methylene-1-oxaspiro[2.2]pentane Derivative

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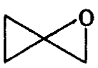
2,2,5,5-Tetramethyl-4-isopropylidene-1-oxaspiro[2.2]pentane (**4**) has been prepared by epoxidation of its dimethylenecyclopropane precursor **2**. Thermolysis of **4** gives the two ketones 2-isopropylidene-3,3,4,4-tetramethylcyclobutanone (**6**) and 2,5-dimethyl-4-isopropylidenehex-5-en-3-one (**7**). Solvolysis of **4** also generates **6** and **7** and, under mild conditions, a new alcohol, 2,5-dimethyl-4-isopropenyl-2,3-hexadien-5-ol (**13**), which is converted into **7** in acid. The mechanistic details of these thermal and solvolytic transformations are discussed in terms of related systems. The mass spectra of several of the compounds encountered in this work are interpreted.

The general subject of small-ring chemistry has received an increasingly large amount of attention in recent years. The advances achieved both in the synthetic and mechanistic aspects of this research area have been enormous and of considerable significance for other areas of organic chemistry. In connection with our interest in the effects of bond-angle strain on the properties and chemical reactivity of molecules, we have initiated a program designed to examine the oxygen analogs of various small-ring hydrocarbons. A comparison of the chemistry of these heterocycles with that of their parent carbocycles should provide further important information with regard to the chemical consequences of ring strain. The present paper is concerned with our initial studies on an interesting derivative of the oxaspiropentane skeleton (**1**).



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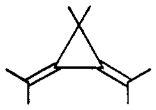

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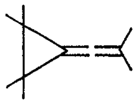

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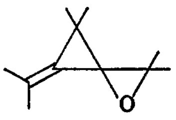
A convenient synthetic entry into this ring system is provided by our recent demonstration that alkenylidenecyclopropanes undergo smooth conversion into dimethylenecyclopropanes upon pyrolysis at reduced pressure in a flow system.[1] This reaction is illustrated by the synthesis of **2** from **3**. Precursor **3** is readily obtained from the base-catalyzed decomposition of 3-chloro-3-methyl-1-butyne[2] or, preferably, 1-bromo-3-methyl-1,2-butadiene[3] in the presence of tetramethylethylene.

The buffered peracetic acid oxidation[4] of **2** proceeded nicely to give monoepoxide **4** in excellent yield along with a small quantity of diepoxide **5** when equivalent amounts of reactants were used.[5] The structure of **4** rests on its mode of synthesis and its spectroscopic properties, particularly the presence of six equivalent sharp singlets with the expected chemical



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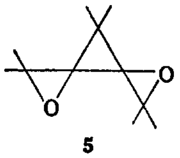

5

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(1) J. K. Crandall and D. R. Paulson, *J. Amer. Chem. Soc.*, **88**, 4302 (1966).

(2) H. D. Hartzler, *ibid.*, **83**, 4990 (1961).

(3) S. R. Landor, A. N. Patel, P. F. Whiter, and P. M. Greaves, *J. Chem. Soc., Sect. C*, 1223 (1966).

(4) M. Korach, D. Nielson, and W. Rideout, *J. Amer. Chem. Soc.*, **82**, 4328 (1960).

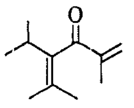
(5) The reactions of diepoxide **5** will be reported in a future publication.

shifts in the nmr spectrum. With a relatively simple synthesis of **4** in hand, a study of the chemistry of this interesting variant of system **1** was initiated.

Since the pyrolytic behavior of small-ring hydrocarbons has been a key feature in the study of their chemistry,[6] the first reaction of **4** to be examined in detail was its thermal isomerization. Compounds **6** and **7** were obtained as products upon flow pyrolysis at reduced pressure.

Compound **6** displays strong infrared bands of nearly equal intensity at 5.78 and 6.01 μ and ultraviolet absorption indicative of a conjugated chromophore (λ_{max}^{hexane} 244 mμ; ε 7750). Taken together these data suggest a conjugated cyclobutanone, probably constrained to a *cis* configuration.[7] The nmr spectrum shows two pairs of equivalent methyls on saturated carbon and two different methyl groups attached to olefinic carbon. A strong molecular-ion peak is observed in the mass spectrum of **6** at *m/e* 166. Compound **7** has a 5.93-μ carbonyl band and the appropriate group of absorptions for a disubstituted terminal olefin in its infrared spectrum, in addition to ultraviolet absorption indicative of a conjugated chromophore. The nmr spectrum suggests the presence of an isolated isopropyl group, a terminal methylene, and three methyls bonded to olefinic carbon. However illuminating, these data do not suffice to distinguish unequivocally between **7** and the alternate formulation illustrated by **8**.

A choice in favor of **7** was provided by lithium aluminum hydride reduction of the ketone to the corresponding alcohol. The compound obtained has spectral properties in general accord with **9** but not with structure **10**, the alcohol derived from **8**. In particular the nmr spectrum of **9** shows the methine proton on the hydroxyl-bearing carbon as a doublet at τ 5.99 with the large coupling constant of 9.5 cps. The isopropyl group appears as a pair of doublets spaced by 0.25 ppm because of its proximity to the neighboring asymmetric center which renders the two methyls magnetically nonequivalent.[8] It is interesting to note that, while **9** displays abnormally strong end absorption in the ultraviolet, a maximum is not apparent. This is consistent with severe steric distortion of the chromophoric system from planarity. Similar observations have been reported for other highly substituted 1,3-dienes.[9]



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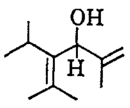

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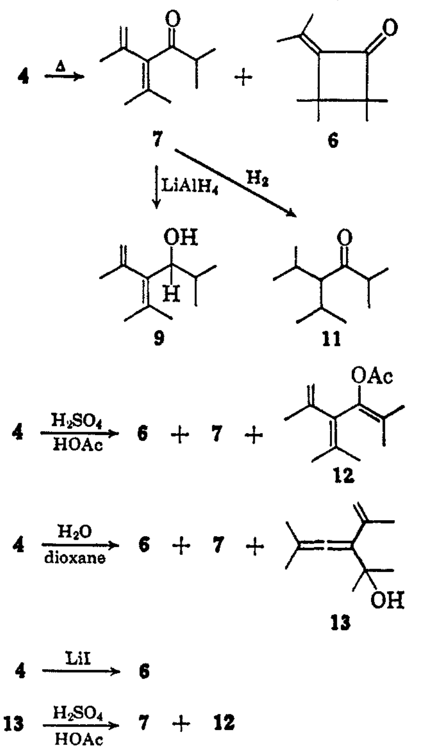
Catalytic hydrogenation of **7** produced the saturated ketone **11**. The nmr spectrum of this material shows complicated absorption for four protons in the methine region, a doublet centered at τ 8.99 for the methyls of the isopropyl group adjacent to the carbonyl, and two sets of doublets at τ 9.08 and 9.18 attributable to the magnetically nonequivalent[8] methyls of the two identical isopropyl groupings. A spectrum using benzene as solvent substantiated this interpretation since all six methyl signals were resolved under these conditions.

A control experiment established that **6** was not converted into **7** under the pyrolysis conditions. However, there was a marked dependence of the **6**–**7** product ratio ranging from 80:20 to 99:1 in various pyrolytic runs. When epoxide **4** was passed over Florisil at 200° in the pyrolysis unit, a 50% yield of **7** was obtained along with 5% of **6** and several other unidentified minor products.

Acid-catalyzed reactions in solution were also performed on **4** (Scheme I). Exposure to the protic medium provided by a sulfuric acid–acetic acid mixture produced **7** as the major material (76%) in the resulting mixture, the cyclobutanone **6** (12%), and a new compound (9%), identified as the enol acetate **12** on the basis of its spectral properties. Compound **12** shows strong bands in the infrared region at 5.70, 6.15, 8.3, and 11.1 μ while its nmr spectrum displays five separate methyls on olefin carbon atoms, an acetate methyl, and a disubstituted terminal methylene absorption. The enol acetate structure was confirmed by hydrolysis to ketone **7**. Cyclobutanone **6** was shown not to be converted into its acyclic isomer **7** in the sulfuric acid–acetic acid mixture.

Scheme I



A very interesting and informative transformation occurred when **4** was exposed to the weakly protic medium provided by a 3% solution of water in dioxane for 24 hr at reflux temperature. This reaction was found to give 49% of **6**, 16% of **7**, and 35% of a new crystalline compound which is assigned structure **13**. The infrared spectrum of this material shows hydroxyl

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[6] A recent review of the thermolysis of small-ring compounds is found in H. M. Frey, *Advan. Phys. Org. Chem.*, **4**, 147 (1966).

[7] Other 2-isopropylidenecyclobutanones show very similar spectral properties: see, for example, J. Conia and J. Sandrie, *Bull. Soc. Chim. France*, 744 (1963); G. B. Payne, *J. Org. Chem.*, **31**, 718 (1966); J. Gore, C. Djerassi, and J. Conia, *Bull. Soc. Chim. Fr.*, 950 (1967).

[8] R. H. Bible, "Interpretation of NMR Spectra," Plenum Press, New York, N. Y., 1962, p 75.

[9] W. F. Forbes, R. Shilton, and A. Balasubramanian, *J. Org. Chem.*, **29**, 3527 (1964); R. Criegee, U. Zirngibl, H. Furrer, D. Seebach, and G. Freund, *Chem. Ber.*, **97**, 2942 (1964).

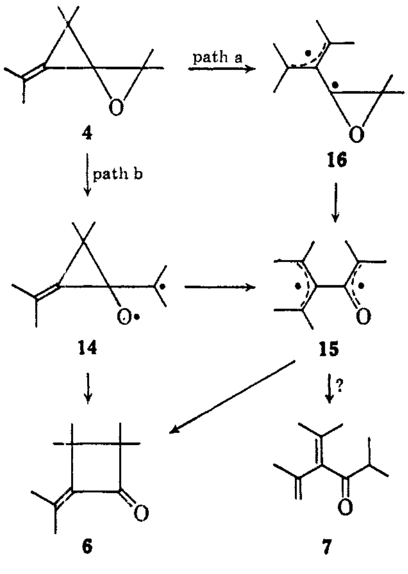
absorption, the terminal methylene bands, and a weak, but clearly perceptible allene peak at 5.15 μ. The ultraviolet spectrum (λ_{max}^{EtOH} 222 mμ, ϵ 13,600) is in reasonable accord with other examples of vinyl allenes.[10] The nmr spectrum has sharp singlets at τ 8.66 and 8.28 appropriate for methyls on a hydroxyl-bearing carbon and an olefinic center, respectively, an additional methyl on a double bond at 8.22 coupled weakly to the individual terminal methylene proton absorptions at 5.06 and 4.72, and a hydroxyl proton at 7.7. Finally, the mass spectrum displays a molecular-ion peak at *m/e* 166.

Hydrogenation of **13** in acidic methanol solution gave ketone **11** as the major product. This curious result is probably accountable by sequential acid-catalyzed rearrangement to the unsaturated ketone **7** and straightforward hydrogenation of the latter. In any event, subjecting **13** to sulfuric acid–acetic acid treatment gave ketone **7** as the only major product along with a small amount of enol acetate **12**.

Finally the effect of Lewis acids on **4** under aprotic conditions is typified by the reaction with anhydrous lithium iodide which yielded the cyclobutanone **6** as the major product. Ketone **7** was not among the trace amounts of other products formed.

Discussion.—The gas phase thermolysis of **4** to **6** is best described in terms of a homolytic bond-cleavage mechanism. Scheme II illustrates two pathways which adequately rationalize the observed conversion. Route a is initiated by bond breakage in the cyclopropane moiety whereas path b involves C–O homolysis of the epoxide ring. The initially formed diradical **14** in the latter sequence can conceivably rearrange directly to **6** in a concerted fashion or it might proceed *via* intermediate **15**. Comparison of the expected stabilities of **14** and **16**, however, strongly suggests that pathway a is the operative route to **6**. This conclusion is derived mainly from consideration of the relief of strain in the alternate bond-breaking steps. While a quantitative assessment of strain energies cannot be made for the complex system under discussion, qualitative considerations lead to the conclusion that reaction through the transition state leading to **16** should be preferred by a substantial margin. A crude estimate of the difference between the two modes of reaction can be obtained by comparison of the strain energies of ethylene oxide (13 kcal/mol)[11] and cyclopropane (27 kcal/mol).[12] The large differential between these values practically ensures a lower activation energy for the production of **16**, particularly since correction for other effects tends to increase the difference in energy between **14** and **16**. Thus, the extra strain imposed by the exocyclic methylene group[13] and the possibility of stabilizing resonance interaction of the developing radical centers of the transition state with the double bond[13,14] and the nonbonding orbitals on oxygen also favor **16**. The remaining details of path a are relatively straightforward. Rearrangement of the epoxy radical moiety of **16** to the α-keto radical **15** is in agreement with what is known about species of this nature.[15] Radical coupling of the latter interesting intermediate gives cyclobutanone **6** directly.

SCHEME II



Unfortunately, the carbocyclic analog of **4** is not known, preventing a comparison of the two systems. Nonetheless a parallel transformation would be predicted for this species. The resemblance of the rearrangement of **4** to the thermal conversion of spiropentane into methylenecyclobutane is probably only a formal one since the latter reaction appears to be initiated by peripheral C–C bond cleavage[16] as opposed to the radial bond cleavage in **4**.

It should be noted that **15** can also serve as a reasonable precursor for the production of **7** by way of an intramolecular 1,5-hydrogen migration. However, the apparent capriciousness of the **6**/**7** ratio in the pyrolysis of **4** and the predominance of **7** in the reaction over Florisil lead to the *tentative* conclusion that **7** arises by a *heterolytic* process catalyzed by active surface sites in the pyrolysis chamber. Circumstantial evidence supporting this notion is found in the resistance of **6** to thermal conversion into **7**.

In contrast to the preferred explanation for the thermolysis of **4**, its transformations promoted by acids in solution are believed to be initiated by C–O bond breaking. The rearrangement of **4** to **6** is the only important reaction observed with lithium iodide in ether. In nucleophilic, protonic solvents, this is still a major process. The conversion is depicted in Scheme III as involving coordination of the electrophilic catalyst (H^+ or Li^+) with the oxygen atom, followed by bond heterolysis and preferential pinacolic migration of an allylic carbon atom. It is possible that bond breaking and bond making at the cationic center are concerted, but the migrating group is poorly situated for backside displacement in the ground-state geometry and the large distortion necessary to achieve the transition-state conformation would appear to argue against a one-step mechanism. Cation **17** could also yield the acyclic ketone **7** by transformation

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[10] See, for example, E. R. H. Jones, H. H. Lee, and M. C. Whiting, *J. Chem. Soc.*, 341 (1960); F. T. Bond, *J. Org. Chem.*, **31**, 3057 (1966).

[11] R. A. Nelson and R. S. Jessup, *J. Res. Natl. Bur. Std.*, **48**, 206 (1952).

[12] R. B. Turner, P. Goebel, W. E. Doering, and J. F. Coburn, Jr., *Tetrahedron Lett.*, 997 (1965).

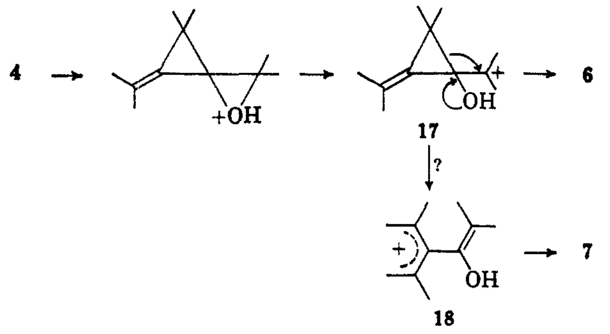
[13] J. P. Chesick, *J. Amer. Chem. Soc.*, **85**, 2720 (1963).

[14] W. E. Doering and J. C. Gilbert, *Tetrahedron Suppl.*, **7**, 397 (1966).

[15] T. J. Wallace and R. H. Gritter, *Tetrahedron*, **19**, 657 (1963).

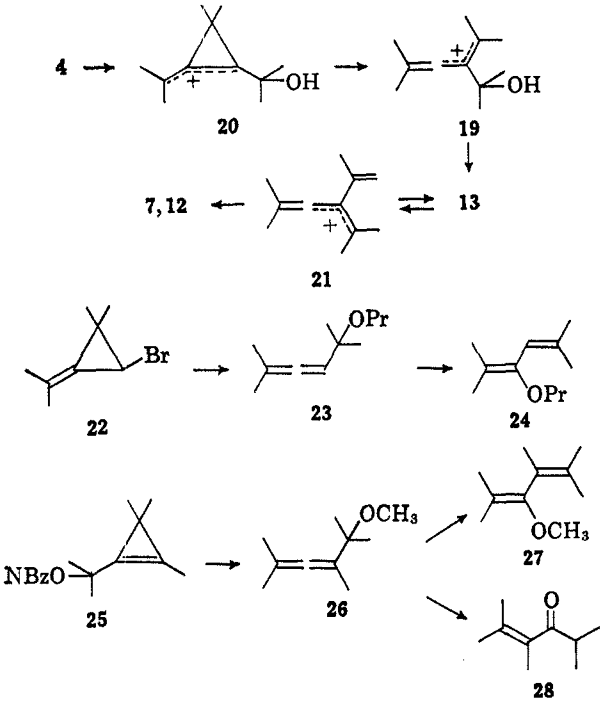
[16] A stimulating discussion of this point is included in ref 14.

Scheme III



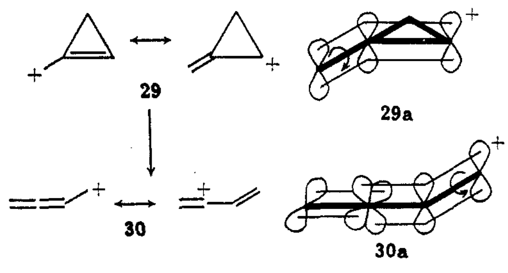
to **18** by a cyclopropylcarbinyl-type rearrangement[17] and subsequent deprotonation and tautomerization. The formation of enol acetate **12** is not particularly in accord with this mechanistic description, nor is the fact that acyclic ketone is not found in the lithium iodide experiment. This latter observation is somewhat difficult to reconcile with a common intermediate for **6** and **7**, since the cyclobutanone is found in all of the acid-catalyzed rearrangements, whereas **7** is observed only in the protonic solvent systems. In fact, the isolation of allene alcohol **13** from mild solvolysis conditions and demonstration that this material is converted into ketone **7** and enol acetate **12** in the sulfuric acid–acetic acid mixture provides strong positive evidence for a different mechanism. Thus, compound **13** is envisaged as arising from the alternate ring-opening possibility of protonated epoxide **4** which gives cation **19**, either directly or by way of **20** (*vide infra*), as shown in Scheme IV. Loss of a proton from **19** yields **13**. Reversible acid-catalyzed ionization of the hydroxy group of **13** then gives a related allenyl carbonium ion **21**, which serves as a precursor for **7** and **12**.

Scheme IV



Supporting evidence for this interpretation can be gleaned from related work. Meinwald and coworkers[18] report that treating **22** with silver propionate gave allene **23** which rearranged further on attempted silicic acid chromatography to enol ester **24**. Closs and Böll[19] found that methanolysis of *p*-nitrobenzoate **25** produced the allene derivative **26** which was converted into enol ether **27** by acid and yielded ketone **28** upon hydrolysis. Thus, these two systems, which might reasonably be expected to generate an intermediate similar to **20**, show a striking behavioral parallel. Generation of allene products from the solvolysis of derivatives corresponding to the two resonance contributors of generalized cation **29** suggests (but, of course, does not require) the intermediacy of such a reactive species. The atomic orbital representation **29a** aids in visualizing the transformation to the allenyl carbonium ion **30**. This change can be pictured as involving a 90° rotation about the exocyclic C–C bond which necessarily attenuates the allylic conjugation indicated in **29**, but thereby allows overlap of the p orbital on the exocyclic carbon atom with the σ bond of the cyclopropyl ring. Electronic reorganization at this point generates the allene moiety of **30**. If this explanation is correct, it is notable that allene products are preferred kinetically from **30** although the enol derivatives appear to be more stable.

While the intervention of the common ion **29** provides the most economical explanation for the apparent similarity of the 1-cyclopropenylcarbinyl and 2-methylenecyclopropyl systems, there is no direct evidence (such as the isolation of skeletally intact products) which demands this intermediate. Consequently other mechanisms for the formation of **13** and its further reaction products deserve consideration. One of these is a single-step transformation of protonated **4** to cation **19**. An analogous mechanism is thought to obtain for the solvolysis of most cyclopropyl derivatives, which apparently give allyl cations as first intermediates.[20] Closs[19] has recommended consideration of a bimolecular nucleophilic mechanism for the **25** to **26** conversion, but in the aqueous dioxane rearrangement of **4** the allene product **13** has lost a proton rather than combined with a nucleophile. In addition, nucleophilic attack at the heavily substituted tetrahedral carbons of **4**, **22**, and **25** is subject to question. Thus, although other rationalizations



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[17] See (a) R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver, and J. D. Roberts, *J. Amer. Chem. Soc.*, **81**, 4390 (1959); (b) R. Breslow in "Molecular Rearrangements," Part 1, P. deMayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp 259–280.

[18] J. Meinwald, J. W. Wheeler, A. A. Nimetz, and J. S. Liu, *J. Org. Chem.*, **30**, 1038 (1965).

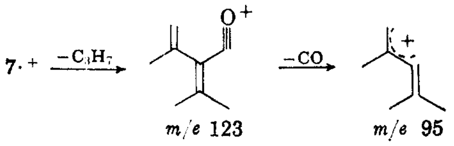
[19] Unpublished results cited in G. L. Closs, *Advan. Alicyclic Chem.*, **1**, 98 (1966).

[20] For a leading reference, see P. R. Schleyer, G. W. Van Dine, U. Schöllkopf, and J. Paust, *J. Amer. Chem. Soc.*, **88**, 2868 (1966).

are possible, the straightforward nature of the explanation utilizing intermediate **20** makes it more attractive at present. Direct evidence bearing on this point would, of course, be desirable.

Mass Spectra.—The mass spectral fragmentation of several of the key compounds obtained in this study deserve comment as examples of highly substituted molecules with a high concentration of functionality. In addition, the strained-ring compounds are of interest in determining whether correlations can be made between mass spectral and chemical behavior of such molecules.[21,22]

The mass spectrum of acyclic ketone **7** is relatively simple. In addition to a strong molecular ion, a small M − CH_3 peak, and the expected low-mass hydrocarbon fragments, there are only two important ions. The strong peaks at *m/e* 123 (M − C_3H_7) and 95 (M − C_3H_7CO) correspond to α cleavage at either side of the carbonyl group, but with the positive charge residing on the hydrocarbon fragment in the second case. Although direct fragmentation may lead to a portion of the *m/e* 95 ion, the observation of a metastable ion at *m/e* 73.5 demonstrates that at least some of *m/e* 95 arises by loss of carbon monoxide from the M − C_3H_7 ion. α cleavage of the unsaturated alkyl moiety (*m/e* 71) with retention of charge on the oxygen fragment amounts to 3% of the base peak at most.



An even simpler spectrum characterizes the saturated acyclic ketone **11**. Loss of the small isopropyl substituent by α cleavage gives an *m/e* 127 fragment (11%). Elimination of carbon monoxide from this ion yields an *m/e* 99 peak (19%) as substantiated by a metastable ion at *m/e* 77.3. The alternative α cleavage leads to a maximum of 6% abundance of an ion at *m/e* 71 (a portion of this peak may be derived from hydrocarbon fragments). The base peak appears at *m/e* 57 and is apparently a hydrocarbon fragment probably derived from loss of the neutral molecule propylene from the *m/e* 99 daughter ion. Perhaps the most suprising aspect of the mass spectrum of **11** is the almost complete absence of the expected fragment from a McLafferty rearrangement.[23] The 2% ion at *m/e* 128 is mainly attributable to isotopic contributions of the *m/e* 127 ion. Although there are six identical hydrogens appropriately situated for a McLafferty decomposition, apparently the rather severe nonbonded interactions present in **11** either retard this process by disfavoring the required conformations[24] or speed up the relative rate of competing α fragmentation. A subsequent efficient decomposition of the McLafferty ion could account for its absence,[25] although such a process leading to important ions in the spectrum is difficult to rationalize.[26,27] Further information on the effects of steric hindrance on the McLafferty rearrangement would be useful in understanding the fragmentation of **11**.

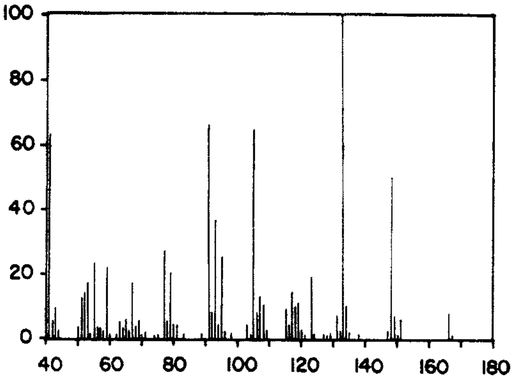
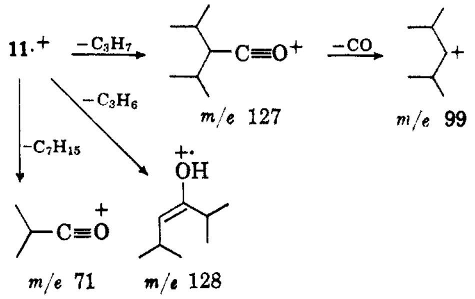
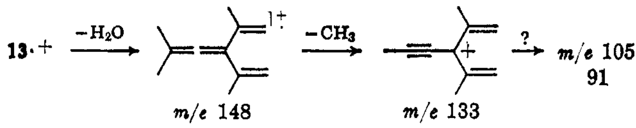


Figure 1.—The mass spectrum of **13**.



The mass spectrum of allene alcohol **13** possesses some interesting features. Examination of Figure 1 reveals that the ion distribution is heavily weighted toward the higher mass fragments indicative that highly stabilized ions are being formed. The *m/e* 148 ion (50%) is a result of the expected loss of water. Elimination of a methyl radical from this species gives the base peak at *m/e* 133 (metastable at *m/e* 119.6). A possible interpretation of this process is illustrated below. The virtue of the indicated fragmentation is the production of an especially stable carbonium ion. This ion may well undergo substantial structural reorganization before further decomposition. Thus, the abundant fragments at *m/e* 105 and 91 are thought to derive from the *m/e* 133 ion by the loss of ethylene and propylene, respectively, perhaps in a process akin to the decomposition of aromatic molecules. In any event, the spectrum of **13** is both unusual and highly characteristic.



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[21] Numerous workers have attempted to correlate photochemical reactions with mass spectral fragmentation: N. J. Turro, D. S. Weiss, W. F. Haddon, and F. W. McLafferty, *J. Amer. Chem. Soc.*, **89**, 3370 (1967); N. J. Turro, D. C. Neckers, P. A. Leermakers, D. Seldner, and P. D'Angelo, *ibid.*, **87**, 4097 (1964); A. L. Burlingame, C. Fenselau, W. J. Richter, W. G. Dauben, G. W. Shaffer, and N. D. Vietmeyer, *ibid.*, **89**, 3346 (1967); M. M. Bursey, L. R. Dusold, and A. Padwa, *ibid.*, 2649 (1967); F. W. McLafferty, *Anal. Chem.*, **31**, 82 (1959).

[22] P. Brown, J. Kossanyi, and C. Djerassi, *Tetrahedron Suppl.*, **8**, 241 (1966).

[23] F. W. McLafferty, "Interpretation of Mass Spectra," W. A. Benjamin, Inc., New York, N. Y., 1966, pp 123–131.

[24] A documented summary of factors which are known to affect the McLafferty rearrangement is included in C. Djerassi and L. Tökés, *J. Amer. Chem. Soc.*, **88**, 536 (1967).

[25] For example, diisobutyl ketone (API mass spectrum 832) shows only a small peak (2%) corresponding to the loss of a molecule of propene, but an additional fragment (33%) at M − 84 indicates that the initial ion undergoes a second McLafferty rearrangement.

[26] Tautomerization of the McLafferty fragment followed by further decomposition might be considered, but recent evidence indicates that tautomeric processes are not in general important in mass spectrometry.[27]

[27] J. K. MacLeod, J. B. Thomson, and C. Djerassi, *Tetrahedron*, **23**, 2095 (1967).

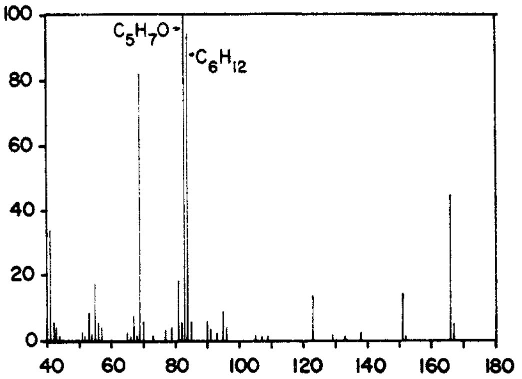


Figure 2.—The mass spectrum of 6.

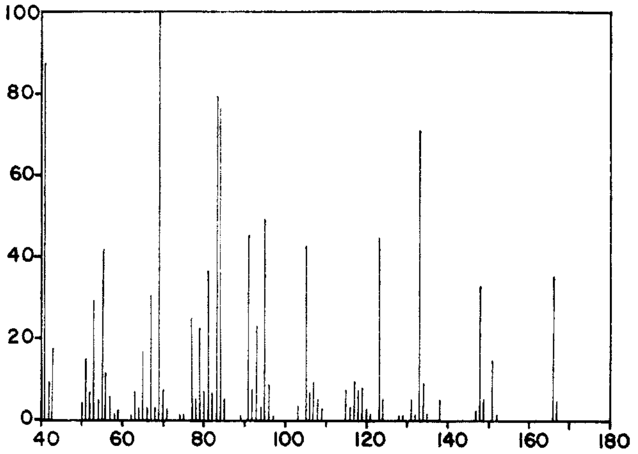
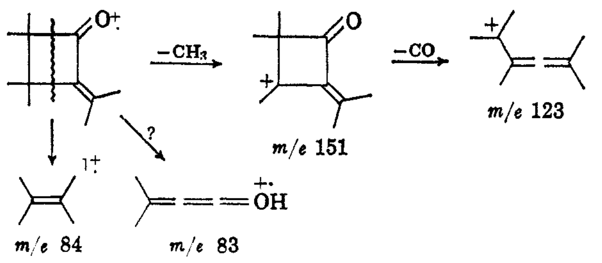


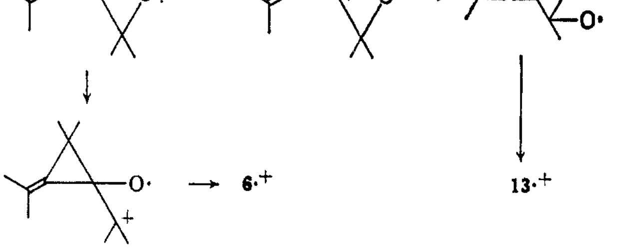
Figure 3.—The mass spectrum of 4.

Figure 2 displays the mass spectrum of cyclobutanone **6**. A molecular ion and an M − CH_3 peak are readily apparent. The fragment at *m/e* 123 probably arises by sequential loss of a methyl radical and carbon monoxide (or *vice versa*) from the molecular ion, perhaps as indicated to give an allenyl carbonium ion. The presence of an intense even-electron fragment at *m/e* 84 is striking. A metastable peak at 56.7 indicates that this ion decomposes further to *m/e* 69. Examination of the *m/e* 84 peak by high-resolution mass spectrometry indicated the constitution C_6H_{12} (*m/e* 84.0933) for the major contributor (93%) to this peak. This species is apparently the tetramethylethylene radical cation formed by fission of the cyclobutane ring in the manner observed for simple cyclobutanones.[28] Little of the ion in which the charge remains on the other fragment (*m/e* 82) is observed. Fragmentation in the alternate manner to give dimethylketene and tetramethylallene fragments is also not important. The *m/e* 83 base peak was also examined by high-resolution techniques and 97% of this peak was found to possess the empirical formula C_5H_7O (*m/e* = 83.0492). This amounts to the oxygen-containing moiety of the indicated ring fission *plus* a hydrogen atom, possibly to yield the indicated radical cation.



The spectrum of epoxide **4** (Figure 3) is rich in detail, possessing all of the peaks of both **6** and **13**. In fact, a reasonable facsimile of this spectrum can be generated by simply combining the spectra of **6** and **13** in an 8:7 ratio. While the synthetic spectrum thus produced is not an exact fit, the resemblance is nonetheless striking. Most of the peaks are of almost identical intensity with those of the experimental spectrum; there are no negative derivations that amount to as much as 10% of the base peak and positive variances appreciably larger than this are found only at *m/e* 69 and 95.

The significance of this comparison is by no means clear, but it is tempting to try to correlate the mass spectral behavior of **4** with its more normal chemistry. Thus, our tentative suggestion is that the molecular ion of the epoxide is undergoing rearrangement to the molecular ions of **6** and **13** and these isomeric species give rise to the observed spectrum. A relationship between pyrolytic behavior[29] and mass spectral fragmentation was originally sought, but the indication of *both* **6** and **13** tends to favor correlation with the acid-catalyzed chemistry. Similar explanations have been advanced previously to account for anomalous features of mass spectral fragmentations observed in other studies of epoxides.[22,30] One can argue that the epoxide molecular ion (indicated below with the charge localized on oxygen for convenience) is a reasonable model for a protonated epoxide and that mass spectral decomposition might parallel its solution chemistry. The suggested rearrangements indicated below are thus analogous to the carbonium-ion reactions of **4** discussed previously. (It should be noted, however, that the proposed production of the molecular ion of **13** does not have a complete parallel in the solution conversion of **4** into **13**, since an intramolecular hydrogen transfer is required. However, this structurally favorable process is viewed as occurring subsequent to the cationic skeletal rearrangement.) Further detailed study will be necessary to ascertain whether the notion of parallel mass spectral and solution carbonium-ion rearrangements of epoxides has any real merit and can be utilized in a predictive or correlative fashion.



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[28] H. Audier, J. M. Conia, M. Fétizon, and J. Goré, *Bull. Chim. Soc. Fr.*, 787 (1967).

[29] The inlet and source temperatures of the spectrometer were maintained such that thermal isomerization of **4** should not be important.

[30] S. Sasaki, Y. Itagaki, H. Moriyama, N. Nakanishi, E. Watanabe, and T. Aoyama, *Tetrahedron Lett.*, 623 (1966); Y. Ita gaki, T. Kurokawa, H. Moriyama, S. Sasaki, and Y. Watanabe, *Chem. Ind.* (London), 1654 (1965).

Experimental Section

General.—Infrared spectra were obtained with Perkin-Elmer Model 137 and 137G Infracord spectrophotometers. Unless otherwise specified these were taken in carbon tetrachloride solution. Nuclear magnetic resonance (nmr) spectra were obtained with a Varian Associates A-60 spectrometer in carbon tetrachloride solution. Chemical-shift data are given as τ values. Mass spectra were obtained with an AEI MS-9 mass spectrometer at 70 eV. Ultraviolet spectra were recorded on a Cary 14 spectrophotometer. Gas chromatography (glpc) was performed on Aerograph Model 600, Model 1200 (analytical, hydrogen flame detector), and A700 (preparative) chromatographs. The analytical column was 5 ft × $^1/_8$ in. of 15% Carbowax 20M on 60/80 Chromosorb W; preparative columns were 10 ft × $^3/_8$ in. of either 30% FFAP or 15% Carbowax 20M on 60/80 Chromosorb W. Percentage composition data were estimated by peak areas (uncorrected). Melting points were determined in sealed capillary tubes. Anhydrous magnesium sulfate was used for all drying operations. Microanalyses were performed by Midwest Microlabs, Inc.

1-(2-Methylpropenylidene)-2,2,3,3-tetramethylcyclopropane (3). A.—A mixture of 30 g of tetramethylethylene and 10 g of potassium *t*-butoxide was stirred under a nitrogen atmosphere for 10 min, after which 11.7 g of freshly distilled 1-bromo-3-methyl-1,2-butadiene was added over a 30-min period. The mixture was stirred at room temperature for 3 hr and 100 ml of pentane was added. The reaction mixture was suction filtered through a sintered-glass Buchner funnel containing Hyflow–Supercel filter aid. The pentane was distilled from the reaction mixture and the residue was eluted with hexane through a short column of Florisil. Removal of the hexane by flash evaporation gave 7.0 g (60%) of **3**. A recrystallized sample had mp 48–48.5° (lit.[2] mp 48.6–49.3°).

B.—Using the procedure of Hartzler,[2] yields of **3** on the order of 25–30% were obtained.

1,2-Bis(isopropylidene)-3,3-dimethylcyclopropane (2).—A 137-mg sample of **3** was pyrolyzed at 360° and 0.25 mm. The pyrolysis was carried out on a vacuum pyrolysis system consisting of a glass-helices packed Pyrex column, 10 mm × 130 mm, passing through an E. H. Sargent and Co. tube furnace. The sample was placed in a 5-ml flask attached at one end of the tube and a Dry Ice trap, 20 mm × 150 mm, was attached to the other end of the tube. Vacuum was applied at the trap and the pyrolysis product collected in the trap. The pyrolysis gave 131 mg (96%) of 1,2-bis(isopropylidene)-3,3-dimethylcyclopropane (**2**). The spectral properties of this product agree in detail with those reported by Bleiholder and Shechter.[31]

2,2,5,5-Tetramethyl-4-isopropylidene-1-oxaspiro[2.2]pentane (4).—To an ice-cold, mechanically stirred mixture of 2.01 g of **2** and 4.24 g of powdered, anhydrous sodium carbonate in 250 ml of methylene chloride was added dropwise 2.55 g of 40% peracetic acid which had been pretreated with a small amount of anhydrous sodium acetate. The mixture was stirred until the methylene chloride solution gave a negative starch–iodide test. The solid salts were removed by suction filtration and washed well with additional solvent. The solvent was removed from the filtrate by flash evaporation to give 2.13 g (96%) of product. Glpc analysis of the crude product showed 92% of **4** and 8% of **5**. Compound **4** has infrared bands at 5.65 (methylenecyclopropane),[32] 10.9 and 11.4 μ (epoxide). The nmr spectrum consists of equivalent sharp singlets at τ 8.86, 8.85, 8.62, 8.55, 8.26, and 8.21. Only end absorption was observed in the ultraviolet region (ϵ_{210} 13,000).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.62; H, 10.87.

Acid-Catalyzed Rearrangement of 4.—To a 200-mg sample of **4** dissolved in 75 ml of glacial acetic acid was added 30 drops of concentrated sulfuric acid and the mixture was stirred for 4 hr, poured into 200 ml of water, and extracted with six 25-ml portions of pentane. The pentane extracts were washed with two 25-ml portions of saturated sodium bicarbonate solution and dried. The solvent was removed by flash evaporation and the three products were isolated by preparative glpc as 76, 13, and 9% of the crude mixture.

The major material was 2,5-dimethyl-4-isopropylidenehex-5-en-3-one (**7**). The infrared spectrum of **7** displays bands at 3.22, 5.93, 6.15, and 11.1 μ. The nmr spectrum shows a six-proton doublet (J = 6.5 cps) at τ 9.00 ($CH(CH_3)_2$), a broad multiplet accounting for nine protons at 8.2 ($C{=}CCH_3$), a one-proton septet (J = 6.5 cps) centered at 7.24 ($CH(CH_3)_2$), and one-proton multiplets at 5.18 and 4.88 ($C{=}CH_2$). The ultraviolet spectrum (hexane) shows λ_{max} 239 mμ (ϵ 2000) and 211 (3600). The mass spectrum of **7** displays significant fragments at the following *m/e* values (percentage of the base peak given in parentheses): 166 (39), 151 (3), 123 (92), 95 (100), 71 (3), 67 (27), 55 (20), 43 (21), 41 (21).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.60; H, 10.93.

The second product is assigned as 2-isopropylidene-3,3,4,4-tetramethylcyclobutanone (**6**). This compound shows infrared bands at 5.78 and 6.01 μ. The nmr spectrum displays six-proton singlets at τ 9.01 and 8.79 ($C(CH_3)_2$) and three-proton singlets at 8.29 and 8.04 ($C{=}CCH_3$). The ultraviolet spectrum (hexane) shows λ_{max} 244 mμ (ϵ 7750).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.55; H, 10.98.

The third product is enol acetate **12**. The infrared spectrum shows peaks at 3.27, 5.70, 6.15, 8.3, and 11.1 μ. The nmr spectrum displays a six-proton singlet at τ 8.42 and a broad nine-proton band at 8.3 ($C{=}CCH_3$), a three-proton singlet at 8.04 (OAc), and one-proton multiplets at 5.40 and 5.09 ($C{=}CH_2$).

A small sample of enol acetate **12** was heated to 70° with 15 ml of glacial acetic acid, 5 ml of water, and 30 drops of concentrated sulfuric acid for 4 hr: the mixture was poured into water and extracted with several portions of pentane. After the combined extracts were dried, the solvent was removed to give a crude product containing **7** as the major component as established by glpc isolation and comparison with authentic material.

Control experiments with **6** and **7** demonstrated that these materials were not changed by the reaction conditions.

Reduction of 7.—A solution of 53 mg of ketone **7** in 10 ml of anhydrous ether was added to a stirred slurry of 50 mg of lithium aluminum hydride in 50 ml of ether. The reaction mixture was stirred for 30 min, 8 drops of water was added, and the mixture was stirred for 1 hr. The resulting mixture was suction filtered to remove the inorganic salts and the filtrate was dried. After removal of the solvent, a single product was isolated in almost quantitative yield. Alcohol **9** shows bands in its infrared spectrum at 2.86, 3.21, 6.04, 6.14, 9.88, and 11.2 μ. The nmr spectrum shows two three-proton doublets (J = 6.5 cps) centered at τ 9.25 and 9.00 (nonequivalent methyls of the isopropyl group), a broad six-proton signal at 8.31 and a broad three-proton signal at 8.16 ($C{=}CCH_3$), a one-proton peak at 7.8 (OH), a one-proton doublet (J = 9.5 cps) at 5.99 ($CHOH$), and one-proton multiplets at 5.44 and 4.99 ($C{=}CH_2$). The isopropyl hydrogen is obscured by the olefinic methyl resonances. The ultraviolet spectrum (hexane) shows no maximum, but strong end absorption is apparent: ϵ_{240} 275; ϵ_{220} 3590.

Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.65; H, 11.76.

Catalytic Hydrogenation of 7.—A solution of 100 mg of **7** in 25 ml of methanol was hydrogenated at atmospheric pressure using 30% palladium on charcoal as catalyst. After the uptake of 2 moles of hydrogen, the resulting mixture was filtered to remove the catalyst, the filtrate was poured into 100 ml of water, and extracted several times with 25-ml portions of pentane. The pentane extracts were combined and dried. After removal of the solvent, a single product was isolated in almost quantitative yield. Ketone **11** shows infrared bands at 5.85, 8.55, and 9.70 μ. The nmr spectrum displays a six-proton doublet (J = 6.5 cps) centered at τ 9.18, a six-proton doublet (J = 6.5 cps) centered at 9.06, a six-proton doublet (J = 6.9 cps) centered at 8.99, and a four-proton multiplet from 7.2 to 8.4. The nmr spectrum in benzene shows a six-proton doublet (J = 6.5 cps) centered at τ 9.18, a six-proton doublet (J = 6.5 cps) centered at 9.13, a six-proton doublet (J = 6.9 cps) centered at 9.02, and a four-proton multiplet from 7.3 to 8.2. The mass spectrum of **11** displays significant fragments at *m/e* (% base peak): 170 (3), 128 (2), 127 (11), 99 (20), 71 (7), 57 (100), 43 (41), 41 (12).

Anal. Calcd for $C_{11}H_{22}O$: C, 77.58; H, 13.02. Found: C, 77.77; H, 12.89.

Rearrangement of 4 in 3% Water–Dioxane.—A solution of 1.91 g of **4** in 100 ml of dioxane containing 3% water was refluxed for 24 hr and the resulting solution dried. Glpc analysis showed

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(31) R. F. Bleiholder and H. Schechter, *J. Amer. Chem. Soc.*, **86**, 5032 (1964).

(32) W. Rahman and H. G. Kuivila, *J. Org. Chem.*, **31**, 772 (1966).

the formation of three products as 16, 49, and 35% of volatile reaction product. The products were isolated by preparative glpc.

The first product was identified as ketone **7** and the second product as ketone **6**. The third component was a new compound whose structure is assigned as 2,5-dimethyl-4-isopropenyl-2,3-hexadien-5-ol (**13**), mp 35-36°. This material shows infrared absorption at 2.8, 5.15 (weak), 6.20, and 11.1 μ. The nmr spectrum displays a six-proton singlet at τ 8.66 ($C(CH_3)_2OH$), a six-proton singlet at 8.28 ($C{=}C{=}C(CH_3)_2$), a broad three-proton singlet at 8.22 ($C{=}CCH_3$), a one-proton signal at 7.7 (OH), and two one-proton multiplets at 5.05 and 4.72 ($C{=}CH_2$). The ultraviolet spectrum exhibits λ_{max}^{EtOH} 222 mμ (ϵ 13,600) and λ_{max}^{hexane} 218 mμ (ϵ 9000). The mass spectrum of **13** shows a parent ion at 166.1355 (calcd for $C_{11}H_{18}O$: 166.1358).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.35; H, 10.87.

Acid-Catalyzed Rearrangement of 13.—A small sample of allene **13** was stirred with 15 ml of glacial acetic acid containing 10 drops of concentrated sulfuric acid for 4 hr and the mixture was poured into water and extracted with several portions of pentane. After the combined extracts were dried, the solvent was removed to give a crude product containing **7** as the major component along with a small amount of enol acetate **12** as established by glpc isolation and comparison with authentic samples.

Rearrangement of 4 by Lithium Iodide.—A mixture of 26 mg of **4** and 0.5 g of anhydrous lithium iodide was heated to reflux in 30 ml of anhydrous ether for 56 hr. Glpc analysis indicated the formation of one major product (80%) which was collected by glpc and identified as ketone **6**.

Pyrolysis of 4.—A 102-mg sample of **4** was pyrolyzed in the flow system at 400° and 0.25 mm. This gave an 80% yield of two products in an 80:20 ratio. Isolation by glpc and comparison with authentic samples demonstrated that these materials were ketones **6** and **7**, respectively. In other runs the amount of **7** in the mixture varied from a trace to 20%.

Pyrolysis of 4 over Florisil.—A sample of epoxide **4** was pyrolyzed over Florisil (which had been dried at 200° and 0.25 mm for 4 hr) at 200° in the flow system at 0.25 mm. Glpc analysis indicated formation of 50% of **7** and 5% of **6** which were collected by preparative glpc and compared with authentic samples.

Hydrogenation of 13 in Acidic Methanol.—A 100-mg sample of **13** was dissolved in 10 ml of reagent grade methanol to which 10 drops of concentrated sulfuric acid had been added. This solution was hydrogenated at atmospheric pressure using 30% palladium on charcoal as catalyst. After the uptake of 2 mol of hydrogen, the resulting mixture was filtered to remove the catalyst, the filtrate was poured into 25 ml of water, and extracted several times with 25-ml portions of pentane. The pentane extracts were combined, washed with 25 ml of saturated sodium bicarbonate, and dried. After removal of the solvent by flash evaporation, the major product was isolated by preparative glpc and found to be ketone **11**.

Registry No.—**3**, 13303-30-5; **4**, 15448-69-8; **6**, 4868-12-6; **7**, 15448-71-2; **9**, 15448-72-3; **11**, 15448-73-4; **12**, 15448-74-5; **13**, 15448-75-6.

Acknowledgments.—Support of this research by the National Science Foundation in the form of a research grant (GP-6610) and an instrument grant (GP-5234) for purchase of the mass spectrometer used in this work is gratefully recorded. A Public Health Service Predoctoral Fellowship to D. R. P. is also acknowledged. Finally, the assistance of Mr. A. C. Clark in obtaining the mass spectral data is greatly appreciated.

Solvent Shifts of Proton Resonances Induced by Benzene and Pyridine in Epoxides and Ethers. An Aid to Structure Elucidation

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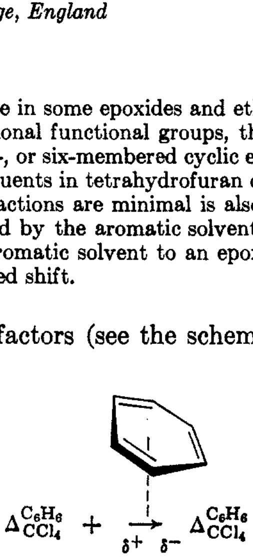
The solvent shifts of proton resonances induced by pyridine and benzene in some epoxides and ethers are reported. In the absence of severe steric effects or of effects due to additional functional groups, the benzene-induced shifts may be useful in differentiating an epoxide from a four-, five-, or six-membered cyclic ether. Different benzene-induced shifts are also observed for α- and β-methyl substituents in tetrahydrofuran derivatives. A preferred conformation for diisopropyl ether in which nonbonded interactions are minimal is also suggested by the solvent shifts. From a study of steric effects upon the shifts caused by the aromatic solvents in epoxyquinones, it is concluded that steric inhibition to the approach of bulk aromatic solvent to an epoxide proton flanked by a *t*-butyl group causes a deshielding contribution to the observed shift.

The solvent shifts of proton resonances induced by benzene relative to an "inert" solvent (solvent shift, $\Delta_{CCl_4}^{C_6H_6} = \delta_{CCl_4} - \delta_{C_6H_6}$ ppm) have proved to be of potential use in the elucidation of structural, stereochemical, and conformation problems; the empirical rules which have been deduced for ketones[1-6] may be cited as an example.

In general, it appears that benzene solvent molecules are transiently orientated by molecular or local solute dipoles, so that the benzene molecules solvate the positive end of the dipole while avoiding the negative end in a collision complex which may deviate from planarity due to steric factors (see the schematic representation 1).[7]



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It appeared probable that useful correlations might be made for solvent shifts in epoxides and ethers and representative members of these classes have therefore been studied. In this paper the solvent shifts induced by both benzene ($\Delta_{CCl_4}^{C_6H_6}$) and pyridine ($\Delta_{CCl_4}^{C_5H_5N}$) are reported. The $\Delta_{CCl_4}^{C_6H_6}$ values are given first for the appropriate proton with each structure, followed by the

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[1] D. H. Williams and N. S. Bhacca, *Tetrahedron*, **21**, 2021 (1965).

[2] G. D. Connolly and R. McCrindle, *Chem. Ind.* (London), 379 (1965).

[3] P. Laszlo and D. H. Williams, *J. Amer. Chem. Soc.*, **88**, 2799 (1966).

[4] C. Timmons, *Chem. Comm.*, 576 (1965).

[5] J. Ronayne, M. V. Sargent, and D. H. Williams, *J. Amer. Chem. Soc.*, **88**, 5288 (1966).

[6] D. H. Williams and N. S. Bhacca, *Tetrahedron*, **21**, 1651 (1965).

[7] J. Ronayne and D. H. Williams, *J. Chem. Soc., Sect. B*, 541 (1967).