10% hydrochloric acid and water. Two similar cyclizations were carried out with 2.0 and 2.5 g of the fluorenone XIV, and the products were combined and chromatographed on silica gel (400 g) with 80:20 benzene–petroleum ether (bp 60–68°) as the initial solvent. The first product eluted was benz[*a*]indeno[1,2-*c*]fluorene-9,14-dione (V) (0.12 g). Recrystallization from benzene gave orange needles melting at 244–247°. Further elution gave 1.54 g of V contaminated with the starting material XIV. This sample was purified by recrystallization from benzene.

The third component (0.3 g) isolated was recrystallized from benzene and gave benz[*de*]indeno[2,1-*b*]anthracene-8,10-dione (XV), mp 323–330°. Further purification by chromatography and recrystallization from benzene gave a sample melting at 330–331.5°: ir (KBr) 5.84 (C=O), 6.07 μ (C=O).

Anal. Calcd for $C_{24}H_{12}O_2$: C, 86.73; H, 3.64. Found: C, 86.69; H, 3.85.

Cyclization of 5-(*o*-Chlorobenzoyl)benzo[*c*]fluorene (XIII).—The fluorene XIII (1.5 g) was heated with sodium hydroxide (0.78 g) in water (3.75 ml) and quinoline (3.75 ml) in a bomb at 260° for 6 hr. The resulting product was extracted with benzene and ether and the extract was washed with hydrochloric acid. Removal of the solvent gave a solid which was chromatographed on silica gel (200 g) using 8:2 benzene–petroleum ether (bp 60–68°) as the initial solvent. The first compound eluted was 14-hydrobenz[*a*]indeno[1,2-*c*]fluoren-9-one (XVI) (0.6 g). Recrystallization from benzene gave orange needles melting at 236–237°, ir (Nujol) 5.90 μ (C=O).

Anal. Calcd for $C_{24}H_{14}O$: C, 90.54; H, 4.43. Found: C, 90.83; H, 4.68.

The second component (0.76 g) eluted from the silica gel was recrystallized from benzene and gave 10-hydrobenz[*de*]indeno[2,1-*b*]anthracen-8-one (XVII). The yellow needles melted at 214–215°. Sublimation raised the melting point by 1°; ir (Nujol) showed 6.08 μ (C=O).

This sample did not give a satisfactory C and H analysis.

Benz[*de*]indeno[2,1-*b*]anthracene-8,10-dione (XV).—A solution of the indene XVII (0.25 g) and potassium dichromate (0.42 g) in acetic acid (4 ml) was refluxed for 1.5 hr. Analysis by tlc of the product indicated that the major product was starting material. Further oxidation of the material gave a brown precipitate which was dissolved in benzene. Chromatography on silica gel (2 g) with benzene as the initial solvent gave as the second component benz[*de*]indeno[2,1-*b*]anthracene-8,10-dione (XV). Recrystallization from benzene gave orange needles (0.01 g) melting at 332–333.5°.

Registry No.—I, 27915-35-1; II, 27915-36-2; III, 27915-37-3; IV, 27915-38-4; V, 27921-55-7; VI, 27915-39-5; VIIa, 27915-40-8; VIIb, 27971-71-7; VIII, 27915-41-9; IX, 27915-42-0; X, 27971-72-8; XII, 205-12-9; XIII, 27921-57-9; XIV, 27921-58-0; XV, 27921-59-1; XVI, 27921-60-4; XVII, 27921-61-5; sulfuric acid, 7664-93-9; ethyl 3,3-diphenyl-3-hydroxypropanoate, 894-18-8; *cis*-spiro[2,2-dibromoindan-1-one-3,10′-[4b,9a]dihydro-4b-phenylindeno[1,2-*a*]inden-9-one, 27915-43-1; *trans*-spiro[indan-3,10′(9′*H*)-4b,9a-dihydro-4b-phenylindeno[1,2-*a*]indan], 27915-44-2; 9-(*o*-chlorobenzoyl)benzo[*c*]fluorene, 27921-62-6; 5,9-di-(*o*-chlorobenzoyl)benzo[*c*]fluorene, 27921-63-7.

Stable Carbonium Ions. CIV. Protonated Alicyclic Ethers and Sulfides[1]

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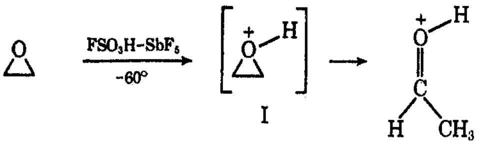
Three-, four-, five-, and six-membered protonated alicyclic ethers and sulfides have been studied in FSO_3H–SbF_5–SO_2 solution generally at −60° by pmr spectroscopy.[3] At low temperatures the onium ions were observed with negligible exchange rates and, with exception of the three-membered ring compounds, without ring opening followed by polymerization. Comparison of alicyclic protonated ethers and sulfides with ethylene and tetramethylene halonium ions show regular changes in the series of related onium ions.

The protonation of alkyl ethers[3a] and sulfides[3b] in superacid solutions has been investigated. We report now the observations of protonated alicyclic ethers and sulfides in the superacid systems FSO_3H–SbF_5 ("magic acid") and HF–SbF_5.

Results and Discussion

Protonated Oxiranes.—The observation of protonated oxiranes was attempted in superacid solutions, *e.g.*, FSO_3H–SbF_5, HF–SbF_5, at low temperatures. The results of the protonation of ethylene oxide (oxirane) in "magic acid" or HF–SbF_5 at temperatures between −10 and +95° (in SO_2ClF) are not conclusive as the reaction products cannot be easily identified owing to competing polymerization reactions. A broad nmr signal is observed at approximately δ 5.00 which by comparison with the methylene absorptions of the ethylenebromonium ion as well as protonated aziridine could be due to protonated oxirane. When samples were left standing at 0° for a few days, the spectral features of protonated acetaldehyde II were observed.



I

II

Other attempted routes to protonated oxirane also proved difficult. The reaction of 2-iodo- and 2-chloroethanol in "magic acid" yields quantitatively the corresponding ethylenehalonium ion III.[4]

III

Propylene oxide (2-methyloxirane) in "magic acid" solution at −60 to −78° yields an nmr spectrum which indicates the presence of a minor amount of protonated propionaldehyde and a species [rather broad nmr ab-

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[1] Part CIII: G. A. Olah, D. P. Kelly, and R. G. Johanson, *J. Amer. Chem. Soc.*, **92**, 4137 (1970).

[2] Taken in part from the Ph.D. dissertation of P. J. Szilagyi, Case Western Reserve University, 1969.

[3] (a) G. A. Olah and D. H. O'Brien, *J. Amer. Chem. Soc.*, **89**, 1725 (1967); (b) G. A. Olah, D. H. O'Brien, and C. U. Pittman, Jr., *ibid.*, **89**, 2996 (1967).

[4] G. A. Olah, J. M. Bollinger, and J. Brinich, *ibid.*, **90**, 2587 (1968); G. A. Olah and J. M. Bollinger, *ibid.*, **89**, 4744 (1967); **90**, 947 (1968).

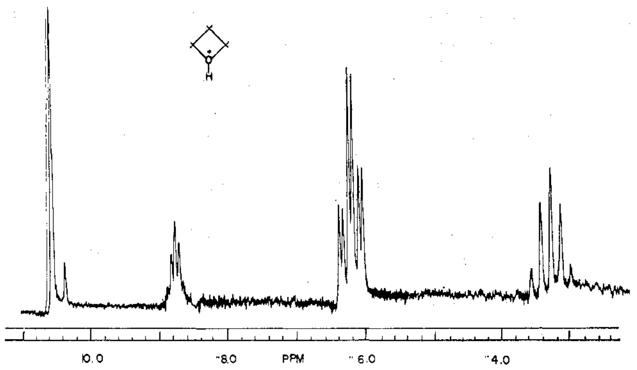
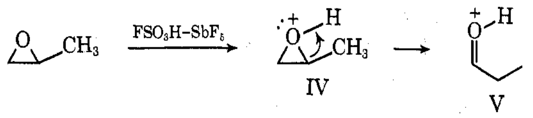
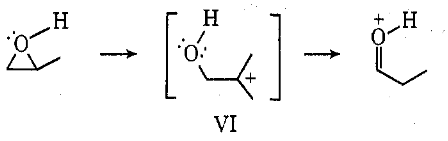


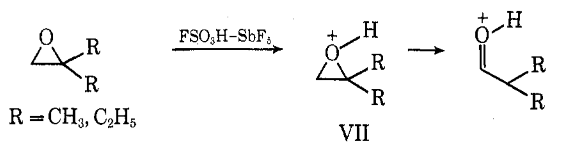
Figure 1.—Oxetane in 1:1 FSO_3H-SbF_5 diluted with SO_2 at −60°.

sorptions at δ 1.53 (methyl), 5.20 (methylene), and 5.8 (methine)] which slowly disappeared, while the amount of protonated propionaldehyde present increased. The reaction could be complete in 17 min at 20° if it was carried out in sealed tube, yielding protonated propionaldehyde (V) as the only spectroscopically observable species. The spectra are usually very poorly resolved and thus the multiplicities could not be determined. The exclusive production of protonated propionaldehyde from the reaction of propylene oxide with "magic acid" in SO_2 at low temperatures indicates, however, that a protonated intermediate oxiranium ion (IV) is undergoing ring opening reaction[5] followed by a 1,2-hydride shift. This shift is further assisted by the contribution of the lone electron pair of oxygen placing the positive charge on the thermodynamically most favorable position. Attempts to observe the proposed secondary carbonium ion intermediate (VI) have failed.

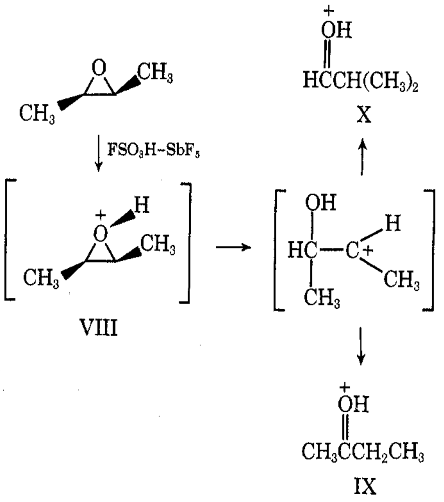




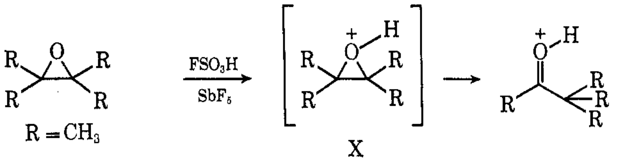
2,2-Dimethyl- and 2,2-diethyloxiranes in "magic acid" solution at −60° also resulted in products, which slowly (at 0°, in matter of days) yielded the corresponding protonated aldehydes. In the case of protonated 2,2-dimethyloxirane (VII), the methyl protons are at δ 1.63 and the methylene protons at δ 5.20, respectively. The nmr spectrum of the protonated 2,2-diethyloxirane could not be assigned owing to the complexity of the spectrum, but after standing protonated isobutyraldehyde is formed.



Upon protonation of both *cis*- and *trans*-2,3-dimethyloxiranes in the super acid solution, protonated methyl ethyl ketone (IX) and isobutyraldehyde (X) were formed. The intermediate oxiranium ion (VIII) could not be observed in pure form before at least partial cleavage has occurred.

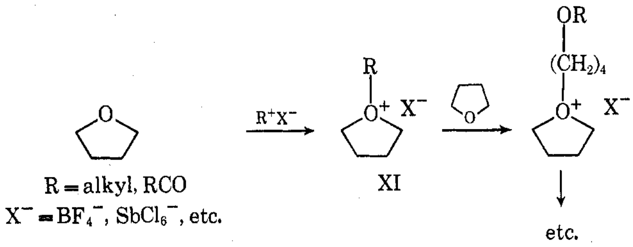


2,3-Dimethylbutylene oxide and 2-methylbutylene oxide in "magic acid" solution yielded only the corresponding protonated ketones, without giving a stable oxiranium ion intermediate prior to at least partial cleavage. One can rationalize this observation as due to increased strain, and an additional driving force could be the stability of resulting tertiary carbonium ions when ring openings occur.



Meerwein's outstanding studies on oxonium ions included the isolation of many O-alkylated alicyclic oxonium salts[6] particularly those of tetrahydrofuran and pyran. No direct observation of the related protonated alicyclic ethers was, however, previously achieved.

Three-, four-, and five-membered ring oxonium salts are easily polymerized.[7,8] Meerwin and his coworkers investigated the polymerization of tetrahydrofuran by Lewis acids, protic acids, carbonium ions, and acyl cations. Both the intermediate oxonium salts (XI) and the polymeric products were isolated and analyzed.[7]



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[5] For a review of formation of aldehydes and ketones from epoxides, see R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 737 (1959).

[6] For a summary, see H. Meerwein in "Houben-Weyl Methoden der Organischen Chemie," E. Müller, Ed., 4th ed, Vol. VI/3, Georg Thieme Verlag, Stuttgart, 1965, pp 325.

[7] H. Merrwein, D. Delfs, and H. Morschel, *Angew. Chem.*, **72**, 927 (1960).

[8] G. A. Latremouille, G. T. Merrall, and A. M. Eastham, *J. Amer. Chem. Soc.*, **82**, 120 (1960).

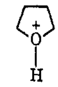
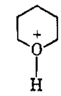
Klages[9] studied the preparation of dialkyloxonium salts and also described impure tetramethylenoxonium hexachloroantimonate without, however, being able to isolate it in pure form or characterize it by physical measurements.

Protonation of four-, five-, and six-membered cyclic ethers was effected in 1:1 FSO_3H–SbF_5 solution diluted with SO_2 at −60 to −78°. The protonated ethers gave well-resolved spectra, showing only slow exchange rates at this temperature range and no or only very little polymerization. Upon quenching of the solutions in the cold with sodium hydrogen carbonate the starting alicyclic ethers were recovered unchanged.

The nmr parameters of protonated oxetane (XII), tetrahydrofuran (XIII), and tetrahydropyrane (XIV) are summarized in Table I. The proton on oxygen in the protonated alicyclic ethers is more deshielded than that in aliphatic ethers[3] but more shielded than that in protonated alcohols.[10] The coupling constant, $J_{H\text{-}OH^+}$, is also consistent with those reported for the protonated alcohols (2.9–3.7 Hz) and aliphatic ethers (3.4–4.1 Hz). Figures 1 and 2 show the representative spectra. The stability of protonated alicyclic ethers is intermediate between the very stable protonated alicyclic amines and alicyclic sulfides. The amines were found to be stable in the strongly acidic solutions up to +40°, at which temperature the proton on nitrogen is exchanged rapidly, but no polymerization or ring opening is detected with the exception of protonated azetidine. Alicyclic sulfides on the other hand are quite readily decomposed in strong acid media above −60°. The half-life of protonated alicyclic sulfides at −60° is estimated in the order of about 10 min. Protonated alicyclic ethers at low temperatures (−60°) decompose in a matter of hours; leaving the samples at 0° overnight, only small amounts of the protonated ether was found left in the sample the next day.

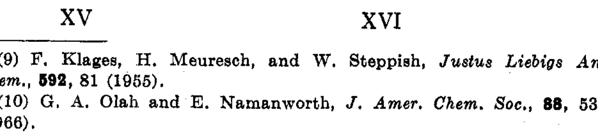
TABLE I

NMR PARAMETERS OF PROTONATED ALICYCLIC ETHERS[a]

Compd	H_1	H_2–H_3, ppm	OH^+	$J_{H\text{-}OH^+}$, Hz
 XII	6.20 (dtr)	3.30 (p)	8.80 (p)	3.8
 XIII	4.91 (dtr)	2.50 (p)	9.00 (p)	3.0
 XIV	5.00 (dtr)	2.00–2.20 (m)	9.40 (p)	2.0–2.5

[a] Chemical shifts in ppm from external cappillary TMS. Figures in parenthesis represent multiplicity of peaks: (p) pentet, (m) multiplet, (dtr) doublet of triplets.

Bicyclo[2.2.1]oxaheptane (XV) was also protonated in HSO_3F–SbF_5 solution at −78° and gave the protonated ketone (XVI) which is, however, unstable even at low temperatures and decomposes with a half-life of about 5 min at −60°. The ring-opened decomposition products have not been identified.



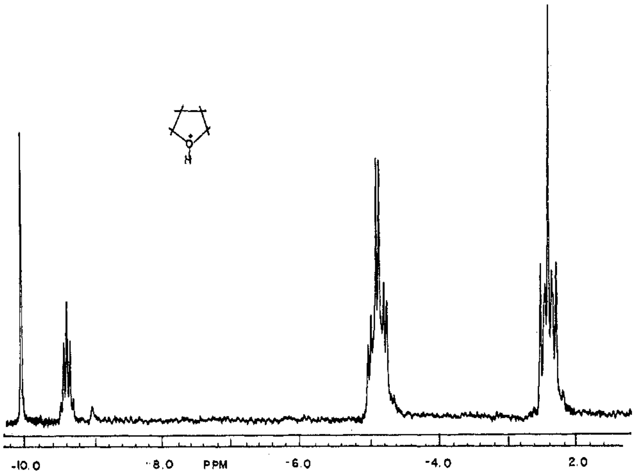
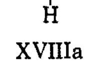


Figure 2.—Tetrahydrofuran in 1:1 FSO_3H–SbF_5 diluted with SO_2 at −60°.

The nmr spectrum of protonated 2,5-dimethyltetrahydrofuran (a mixture of cis and trans isomers) showed two different OH^+ triplets at δ 8.90 and 9.22 and a pair of methyl doublets at δ 1.75 and 1.80 due to the trans and cis isomers. The ring methylene protons are centered at δ 2.50 as a complex multiplet, while the methine proton absorptions center at δ 5.50.

When a solution of protonated *cis*-2,5-dimethyltetrahydrofuran (XVII) was allowed to warm to −20°, the formation of the trans isomer was observed. Further warming of the solution and rapid cooling resulted in the formation of an equilibrium mixture of cis and trans isomers.[11] The mixture consists of 58% of the cis and 42% of the trans isomer. The half-life of isomerization of cis to trans was found to be 10 min at −20°. Pmr data obtained for the protonated 2,5-dimethyltetrahydrofuran are comparable to those reported previously for 2,5-dimethyltetramethylenehalonium ions[12] (see subsequent discussion).



Protonated Thiaranes.—Reaction of ethylene sulfide and propylene sulfide with FSO_3H–SbF_5 yielded, when the reagents were mixed at −60° in SO_2 solution, only polymeric products insoluble in SO_2. When the reaction mixture was prepared by extracting the thiaranes from *n*-pentane into the "magic acid" –SO_2 solution at

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[9] F. Klages, H. Meuresch, and W. Steppish, *Justus Liebigs Ann. Chem.*, **592**, 81 (1955).

[10] G. A. Olah and E. Namanworth, *J. Amer. Chem. Soc.*, **88**, 5327 (1966).

[11] The first observation of this isomerization was made by Dr. J. Sommers in our laboratories some years ago but was not reported before.

[12] G. A. Olah and P. E. Peterson, *J. Amer. Chem. Soc.*, **90**, 4675 (1968).

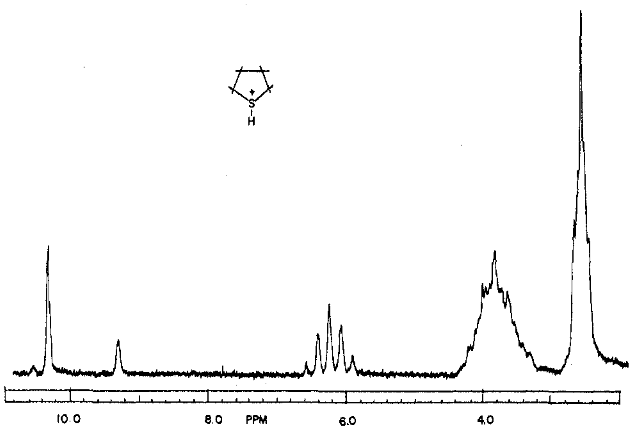
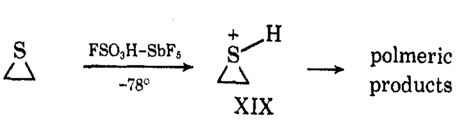


Figure 3.—Tetrahydrothiophene in FSO_3H–SbF_5–SO_2 at −60°.

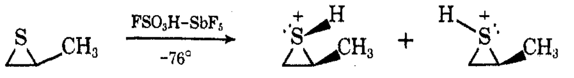
−78° or lower temperatures, the solution exhibited nmr spectra indicating the protonated thiarane (XIX).



XIX

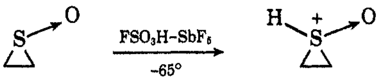
The nmr spectrum of thiarane in FSO_3H–SbF_5–SO_2 is composed of a complex symmetrical spectrum (A_2B_2X) centering at δ 3.63 considerably deshielded from thiarane itself (δ 2.33). On standing, the solution produced a broad diffused absorption band due to polymerization.

Similarly, the spectrum of propylene sulfide in FSO_3H–SbF_5 (XX–XXI) could be best interpreted as that of the protonated thiarane. The methyl groups exhibit two doublets at δ 1.63 ppm and 1.76 suggestive of the two conformations XX and XXI. The ring protons are assigned to the complex bands centered at δ 3.66 and 4.4, respectively. (No attempt was made to analyze the complex $ABCX_3$ type system.) It is suggested that the SH proton is underlying the low field peak. Theoretically, each proton signal should consist of at least 16 lines.



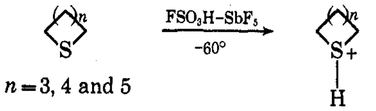
XX XXI

As a model compound for thiaranium ions the protonation of ethylene sulfoxide XIII was also carried out. The spectrum indicates that protonation takes place on the sulfur atom (XXIII) showing the methylene multiplet absorption peak at δ 3.87 (deshielded from δ 2.47 from that of the A_2B_2 type multiplet in ethylene sulfoxide itself) and also the SH proton at δ 5.27.



XXII XXIII

The protonation of four-, five-, and six-membered alicyclic sulfides was carried out in FSO_3H–SbF_5–SO_2 solution. Although the protonation took place without exchange at −60°, some difficulty was experienced due to frequent polymerizations which yielded insoluble gummy materials. This could be prevented by extracting the alicyclic sulfide slowly from *n*-pentane or petroleum ether into an acid mixture with vigorous stirring below −60°.

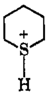


XXIV

The nmr pattern of ring protons is more complicated than in the case of the related protonated alicyclic ethers, although the proton on sulfur in most cases is well resolved. The SH^+ proton absorption in the protonated alicyclic sulfides (XXIX) is at consistently higher field (average 6.30 ppm) than the corresponding SH^+ absorption in protonated aliphatic sulfides (average 7.61 ppm). Chemical shifts and coupling constants of the protonated alicyclic sulfides are summarized in Table II. The representative spectrum of tetrahydrothiophene in FSO_3H–SbF_5–SO_2 at −60° is shown in Figure 3. Due to rapid skeletal inversion of tetrahydrothiophene, only an average value can be obtained for the coupling constants between the nonequivalent α protons and sulfur proton.

TABLE II

NMR PARAMETERS OF PROTONATED ALICYCLIC SULFIDES[a]

	H_1	H_2–H_3	SH	$J_{H_1-SH^+}$, Hz
	4.40 to 3.20 (m)		7.40 (m)	
	3.80 (m)	2.60 (m)	6.25 (p)	10 ($J_{cis} + J_{trans}/2$)
	3.75 (m)	2.80–2.00 (m)	6.30 (m)	$J_1 = 12.5$ $J_2 = 4.5$

[a] Chemical shifts from external TMS in ppm.

2,5-Dimethyltetrahydrothiophene (XXV) was also protonated in FSO_3H–SbF_5 solution at −65°. The resulting spectrum indicating that both cis and trans isomers are present consisted of two doublet of doublets due to the methyl protons at δ 1.92 and 1.75 and a complex pattern due to the methylene protons at δ 2.20. The methine proton absorptions were centered at δ 4.20, while the SH^+ protons were at δ 5.8. Warming the sample to −15° and keeping it at this temperature for 30 min caused no change in the nmr spectra.

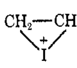
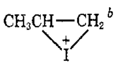
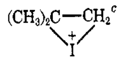
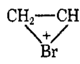
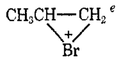
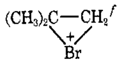
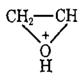
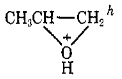
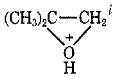
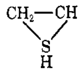
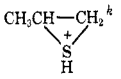
Conclusions

Four-, five-, and six-membered alicyclic ethers and sulfides form stable protonated intermediates in strongly acidic solution which may be observed at low temperatures and characterized by nmr spectroscopy. Further support for the structural assignments comes from the fact that starting ethers and sulfides can be recovered by quenching solutions of the onium ions.

The fate of the three-membered ring ethers and sulfides in superacids is more uncertain. The more highly substituted oxiranes show no evidence of forming any long-lived intermediate at the temperature range studied. This is not unexpected, considering the strained structures and that ring opening leads to more stable tertiary carbonium ions.

TABLE III

COMPARISON OF PMR SHIFTS IN ETHYLENE, PROPYLENE, AND 1,1-DIMETHYLETHYLENEHALONIUM IONS AND THE CORRESPONDING PROTONATED ETHYLENE OXIDES AND SULFIDES

	δ_{CH_2}		δ_{CH}	δ_{CH_2}	δ_{CH_3}		δ_{CH_2}	δ_{CH_3}
 [a]	5.77	 [b]	7.73	5.77	3.32	 [c]	5.72	3.45
 [d]	5.53	 [e]	7.48	5.86	2.98	 [f]	5.55	3.32
 [g]	~5.00	 [h]	~5.8	5.20	1.53	 [i]	5.20	1.63
 [j]	~3.63	 [k]	~4.4	3.66	1.63 1.76			

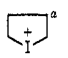
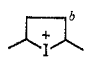
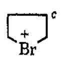
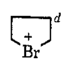
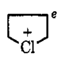
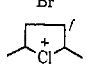
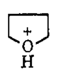
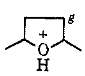
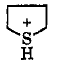
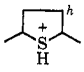
Registry no. for the above compounds: [a] 157-15-3; [b] 20174-89-4; [c] 27705-43-7; [d] 20174-90-7; [e] 20174-91-8; [f] 27705-46-0; [g] 27659-85-4; [h] 27659-86-5; [i] 27569-87-6; [j] 27659-88-7; [k] 27659-89-8.

Ethylene oxide, propylene oxide, and the dimethyloxiranes show at low temperature in superacids spectra, which can be interpreted as the oxiranium intermediates contaminated, however, with polymers and undergoing rapid exchange processes. This interpretation seems justified, because the observed intermediate species upon standing yield only protonated aldehydes and ketones. No dioxanes and dioxalene intermediates could be assigned to the spectra.

Further substantiation can be obtained when we compare the nmr parameters of previously studied three- and five-membered halonium ions[4,12] with those of the presently studied three- and five-membered oxonium and sulfonium ions (no four-membered halonium ions were so far observed; thus no comparison with the four-membered oxonium and sulfonium ions is possible). Tables III and IV show the comparative data for the three and five-membered systems, respectively.

TABLE IV

COMPARISON OF PMR SHIFTS OF TETRAMETHYLETHYLENE AND 2,5-DIMETHYLTETRAMETHYLETHYLENEHALONIUM IONS AND THE CORRESPONDING PROTONATED ETHERS AND SULFIDES

	$\delta_{\alpha CH_2}$	$\delta_{\beta CH_2}$		δ_{CH}	δ_{CH_2}	δ_{CH_3}
 [a]	50	2.80	 [b]	6.50	2.83	2.12, 2.16
 [c]	5.20	2.85	 [d]	6.43	2.90	2.15, 2.16
 [e]	5.20	2.73	 [f]	6.32	2.80	2.08, 2.08
	4.91	2.50	 [g]	5.50	2.50	1.75, 1.80
	3.80	2.60	 [h]	4.20	2.20	1.85, 1.90

Registry no. for the above compounds: [a] 22211-91-2; [b] 27705-48-2; [c] 22211-90-1; [d] 22211-95-6; [e] 22211-89-8; [f] 22211-94-5; [g] 27659-90-1; [h] 27659-91-2.

Whereas no direct correlation exists between electronegativities of heteroatoms, charge densities in onium ions, and nmr chemical shifts (the latter being effected by other factors like shielding and anistropy effects), the regularities observed in the series of halonium, oxonium, and sulfonium ions shown in Tables III and IV seem to be significant. They suggest that the data obtained for the difficult to handle three-membered ring systems at least qualitatively follow the same pattern as the well-defined five-membered ring ions. The study of protonated alicyclic ethers has particular importance with regard to their intermediacy in the cationic polymerizations of alicyclic ethers.

Experimental Section

Materials.—Ethylene oxide, propylene oxide, 2,2′-dimethyloxirane, 2,2′-diethyloxirane, 2,3-dimethyloxirane, styrene oxide, *trans*-stilbene oxide, tetrahydrofuran, and 2,5-dimethyltetrahydrofuran were commercially available materials and were used usually without further purification. 2,3-Dimethyl-2-butylene oxide was prepared from 2,3-dimethylbutene by oxidation with perbenzoic acid in 61% yield.[13,14] 2-Butylene oxide was prepared by a similar method in 54.5% yield and the fraction boiling at 74–75° was used.[15] 2,3-Dimethyloxiranes were separated by distillation through a spinning-band column. The major product, *trans*-2,3-dimethyloxirane, boiled at 53.5° and the *cis*-2,3-dimethyloxirane boiled at 59.7°.

Ethylene sulfide (thiarane) was prepared from ethylene carbonate and potassium thiocyanate in 50–64% yields.[16] The crude product was fractionated and the fraction with bp 54.0–54.5° was used. Propylene sulfide and ethylene sulfoxide (Dow Chemical Co.) were used without further purifications.

Antimony pentafluoride and fluorosulfuric acid were obtained from the Allied Chemical Co. and were purified by distillation. Sulfur dioxide (Matheson Coleman and Bell, anhydrous grade) was used without purification.

2,5-Dimethyltetrahydrothiophene.—2,5-Dimethyltetrahydrothiophene was prepared according to a modification of the procedure of Gryszkiewitz-Trochimowski.[17] Sodium sulfide (24.0 g, 0.1 mol) (as the nonahydrate) is refluxed overnight with 24.4 g (0.1 mol) of 2,5-dibromohexane in 500 ml of methanol. The resulting solution was decanted from the solid material and the title compound distilled off at 140–142°. The yield was 6.1 g or approximately 50%.

Separation of *cis*- and *trans*-2,5-Dimethyltetrahydrofuran.—The commercially available material (Aldrich Co.) was separated by vpc on a 20-ft Carbowax column at 80°, flow rate 10 ml sec^{-1}, injecting 200 μl at a time. In 2 hr, about a 1-ml sample of each of the cis and trans isomers was collected, with a retention time of 17 and 19 min, respectively.

Protonation of Alicyclic Ethers and Sulfides and Their Nmr Study.—The spectra of protonated alicyclic ethers and sulfides were observed in 1:1 solution of FSO_3H-SbF_5 diluted with SO_2. The samples were prepared in a Dry Ice–acetone bath at temperatures below −60°. The alicyclic compounds were usually extracted from *n*-pentane. A 5–10% weight solution of the

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[13] G. Braun, "Organic Syntheses," Collect Vol. I, Wiley, New York, N. Y., p 431.

[14] E. R. Eliel and M. N. Rerick, *J. Amer. Chem. Soc.*, **82**, 1362 (1960).

[15] W. J. Hickinbottom, D. Peters, and D. G. M. Wood, *J. Chem. Soc.*, 1360 (1955).

[16] S. Searles, E. F. Lutz, H. R. Hays, and H. E. Mortensen, *Org. Syn.*, **42**, 59 (1962).

[17] E. Gryszkiewitz-Trochimowski, *J. Russ. Phys. Chem. Soc.*, **48**, 901 (1916).

oxonium compounds was generally prepared for pmr observation. External capillary TMS was used for reference. A Varian Associates Model A-56/60A spectrometer with a variable temperature probe was used for all spectra.

Registry No.—XII, 27659-92-3; XIII, 27659-93-4; XIV, 27659-94-5; XXIV (n = 3), 27659-95-6; XXIV (n = 4), 27659-96-7; XXIV (n = 5), 27659-97-8; 2,5-dimethyltetrahydrothiophene, 1551-31-1.

Acknowledgment.—Support of this work by a grant from the National Institutes of Health is gratefully acknowledged.

Preparation and Chemistry of Vinyl Sulfonium Ylides. New Synthetic Intermediates[1]

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Diphenylsulfonium vinyl ylides are conveniently generated by treatment of allylsulfonium salts with an organolithium. Base treatment of allyldimethylsulfonium salts leads exclusively *via* [3,2]-sigmatropic rearrangement to homoallylmethyl sulfides. These ylides show no tendency to undergo α elimination thermally as evidenced by lack of cyclopropene formation. Alternatively, cyclopropene is produced upon photolytic decomposition at −78°. Accompanying such α elimination is 1,2- and 1,4-phenyl migration in the photolysis of diphenylsulfonium allylide. Detection of cyclopropene by formation of its Diels–Alder adduct with various dienes as well as some chemistry of these adducts is discussed. Vinyl ylides undergo epoxide formation with saturated ketones; with cyclohexanones, equatorial attack is preferred over axial attack. With Michael systems, reaction proceeds with exclusive generation of cyclopropanes.

Our initial investigations into the chemistry of vinyl sulfonium ylides were prompted by both mechanistic and synthetic considerations. From a mechanistic standpoint, it was desired to construct a system which would answer unambiguously the question of carbene formation in the thermal decomposition of sulfur ylides (eq 1).

$$\underset{-}{\mathrm{RCH}}\text{—}\underset{+}{\mathrm{S}}\mathrm{R_2'} \longrightarrow \mathrm{RCH{:}} + \mathrm{SR_2'} \longrightarrow \text{carbene-derived products} \qquad (1)$$

Several authors have claimed carbene-derived products from the thermal decomposition of sulfonium ylides.[3] Notably, Johnson and coworkers[4] have reported the formation of *cis*- and *trans*-stilbene from diphenylsulfonium benzylide. These workers also claim that, when acenaphthylene is added to solutions of diphenylsulfonium benzylide or *n*-butylide, cyclopropanes are formed. However, there are other possible interpretations of the experimental data which is presented by the authors.

Franzen and coworkers[5] determined that, in the generation of diphenylsulfonium *n*-butylide with tritylsodium, triphenyl-*n*-butylmethane is produced, assertedly by insertion of *n*-propylcarbene into the C–H bond of triphenylmethane. Of greater significance, perhaps, is Franzen's claim that diphenylsulfonium isobutylide yields both 1-butene and methylcyclopropane. However, the authors present only vpc evidence for the formation of methylcyclopropane.

Although these results are all commensurate with carbene intermediacy, none of the products which have been proven to be produced demand a carbene mechanism. Other processes, among which may be nucleophilic substitution, can easily account for their formation. Moreover, it is significant that none of the researchers have reported the trapping of an ylide-derived carbene with an undisputed carbene trapping agent such as cyclohexene.

In contrast to the confusion that persists with regard to thermally induced elimination, the photolytic and metal cation induced α elimination of stable sulfur ylides is documented.[6] Recently, Corey has reported that ultraviolet irradiation of an α-ketosulfoxonium ylide leads to Wolff rearrangement products derived from an α-ketocarbene.[6b] We reported the formation of 7-benzoylnorcarane when dimethylsulfonium phenacylide, in the presence of cyclohexene, is photolyzed or reacted with the salts of transition metals.[6c] Johnson and Amel also reported photolytic decomposition of the same ylide.[6d] Kunieda and Witkop have demonstrated C–H bond insertion with a carbene generated from the photolysis of a sulfoxonium ylide.[6e]

One major source of ambiguity in the interpretation of the decomposition products of sulfur ylides is that if a carbene is formed, it may react almost exclusively with the very nucleophilic starting ylide. Even if an olefin is employed as solvent, the ylide, being much more nucleophilic, may react preferentially with the carbene. The product of such a process is usually an olefin, the formal carbene dimer. This reaction of the carbene with the ylide is thus indistinguishable from the product of nucleophilic substitution by the ylide on the sulfonium salt and from the more unlikely process, carbene dimerization.

We chose to study vinyl sulfonium ylides since trapping of the vinyl carbene would occur as an intramolec-

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[1] Preliminary accounts of portions of this work have appeared: B. M. Trost and R. LaRochelle, *Tetrahedron Lett.*, **29**, 3327 (1968); B. M. Trost and R. LaRochelle, *J. Amer. Chem. Soc.*, **92**, 5804 (1970).

[2] National Institutes of Health Predoctoral Fellow.

[3] A. W. Johnson, "Ylide Chemistry," Academic Press, New York, N. Y., 1966, pp 304–306.

[4] A. W. Johnson, V. J. Hruby, and J. L. Williams, *J. Amer. Chem. Soc.*, **86**, 918 (1964).

[5] V. Franzen, H. J. Schmidt, and C. Mertz, *Chem. Ber.*, **94**, 2942 (1962).

[6] (a) L. Horner and E. Spetschka, *ibid.*, **85**, 225 (1952); (b) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **86**, 1640 (1964); (c) B. M. Trost, *ibid.*, **89**, 138 (1967); (d) A. W. Johnson and R. T. Amel, *J. Org. Chem.*, **34**, 1240 (1969); (e) T. Kunieda and B. Witkop, *J. Amer. Chem. Soc.*, **91**, 7751 (1969).