TABLE II

EXPERIMENTAL DATA ON REACTIONS OF OLEFINS WITH TETRAFLUOROHYDRAZINE–NITRIC OXIDE MIXTURES

Olefin (mmoles)	N_2F_4 added, mmoles	NO added, mmoles	Time, hr	Pressure range, mm	Maximum temp, °C	N_2F_4 consumed, mmoles	NO consumed, mmoles
2-Butene (23.7)	62	62	69	690–500	26	21	36
2-Methyl-2-butene (143)	62	62	19	565–350	30	34	41
Isobutylene (23.7)	30	30	28	630–410	30	18	27
1-Pentene (100)	62	62	22	555–485	30	34	24
1-Hexene (100)	62	62	29	585–490	30	24	23
Cyclopentene (100)	62	62	72	520–295	30	48	46
Cyclohexene (100)	62	62	42	590–410	30	41	44
Methyl methacrylate (100)	62	62	21	573–285	30	43	23
Methacrylonitrile (117)	190	185	144	573–400	25	85	82

Reactions of 2-Methyl-2-butene with Tetrafluorohydrazine and Nitric Oxide.—To a 200-ml round-bottom flask was introduced 30.0 ml of dry chloroform and 10.0 g of 2-methyl-2-butene. The flask was attached to a vacuum manifold and deaerated by several freeze–thaw cycles. Into a separate evacuated flask attached to the manifold was condensed 6.43 g (62 mmoles) of tetrafluorohydrazine and 1.85 g (62 mmoles) of nitric oxide which was then allowed to expand into the reaction flask. The initial pressure was 569 mm. The reaction started within minutes with the formation of a greenish blue coloration and a decrease in pressure. The greenish blue color changed to a light yellow after 2–3 hr. The reaction was continued for a period of 19 hr with stirring (magnetic stirrer) to give a final pressure reading of 350 mm. The excess gas fraction was removed from the reactor and condensed into an expansion bulb and after expansion the mass spectrum of the gases was obtained. The gas fraction was made up of the following: 45.2% N_2F_4, 32.9% NO, 5.3% SiF_4, 6% N_2O, 4.4% $CHCl_3$, 4.6% N_2, and 1.6% N_2F_2. A total of 3.53 g (34 mmoles) of tetrafluorohydrazine (55%) and 1.24 g (41 mmoles) of nitric oxide (66%) was consumed in this reaction.

After thorough degassing[7] the flask containing the solution was opened to the air, removed from the manifold, and examined by gas chromatography. This product fraction consisted of several components. The major part of the solvent and excess 2-methyl-2-butene were removed on a rotary evaporatior at reduced pressure. The residue (9.63 g) was examined by gas chromatography and found to contain three major, one intermediate, and several minor components. The intermediate component was identified as 2-methyl-2,3-bis(difluoroamino)-butane by comparison of its retention time with that of an authentic sample.[2] The residue was fractionated through an 18-in. semimicro spinning band column to give 2.14 g (22.7%) of a mixture of *meso*- and *dl*-3-(2-methyl-2-fluorobutyl)-N′-fluorodiimide N-oxides, bp 52–59° (13 mm), and 5.21 g (33.8%) of 3-(2-methyl-2-difluoroaminobutyl)-N′-fluorodiimide N-oxide, bp 73–74° (12 mm). Some decomposition of the latter compound was noted to occur during the distillation (see Table I for characterization data). In most cases the products in the crude residue after removal of solvent and excess olefin were separated by gas chromatography using an Aerograph gas chromatographic instrument, Model A-110-C, with a 5-ft dinonyl phthalate column at 50–100°.

(7) This step is critical since mixtures of air, hydrocarbons, and N_2F_4 are highly explosive.

Registry No.—Tetrafluorohydrazine, 10036-47-2; **1**, 14296-41-4; **2**, 14296-42-5; **3**, 14296-43-6; **4**, 14296-44-7; **5**, 14362-58-4; **6**, 14296-45-8; **7**, 14296-46-9; **8**, 14296-47-0; **9**, 14296-48-1; **10**, 14362-59-5; **11**, 14296-49-2; **12**, 14296-50-5; **13**, 14296-51-6; **14**, 14296-52-7; **15**, 14296-53-8; **16**, 14296-54-9; **17**, 14296-55-0; **18**, 14296 28-7; **19**, 14296-29-8.

Acknowledgment.—The interpretation of the F^{19} nmr spectra were carried out by Mrs. Carolyn Haney. The technical support of Mr. J. O. Woods is greatly appreciated.

Derivatives of Thiacyclobutene (Thiete). II.[1] Reactions of 7-Thiabicyclo[4.2.0]-1(8)-octene 7,7-Dioxide[2-4]

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7-Thiabicyclo[4.2.0]-1(8)-octene 7,7-dioxide (**1**) is isomerized to the endocyclic olefin, 7-thiabicyclo[4.2.0]-1(6)-octene (**2**) by treatment with potassium hydroxide in tetrahydrofuran. Treatment of the exocyclic compound **1** with potassium *t*-butoxide in *t*-butyl alcohol gave principally 2-methylsulfonylcyclohexanone (**3**), a small amount of *endo* sulfone **2**, and isobutylene. Treatment of the *exo* sulfone with potassium ethoxide gave 1-ethoxy-7-thiabicyclo[4.2.0]octane 7,7-dioxide (**7**). *endo* sulfone **2**, but not the *exo* sulfone **1**, could be aromatized to benzothiete sulfone **8**.

The synthesis of the first bicyclic thiete sulfone, 7-thiabicyclo[4.2.0]-1(8)-octane 7,7-dioxide (**1**) has been reported previously[5] and the preparations of several monocyclic thiete sulfones[6,7] and fused aromatic derivatives of thiete sulfone[5b,8] have been described.

(1) Part I: D. C. Dittmer and M. E. Christy, *J. Am. Chem. Soc.*, **84**, 399 (1962).

(2) This work was aided by National Science Foundation Grants GP 726 and GP 5513.

(3) Reported in part at the 148th National Meeting, American Chemical Society, Chicago, Ill., Sept 1964.

(4) Taken from the Ph.D. Thesis of F. A. Davis, Syracuse University, 1966.

(5) (a) D. C. Dittmer and F. A. Davis, *J. Org. Chem.*, **29**, 3131 (1964); (b) L. A. Paquette, *ibid.*, **30**, 629 (1965).

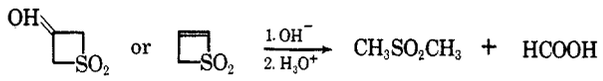
(6) See references given in ref 5a for earlier work.

(7) J. N. Wells and F. S. Abbott, *J. Med. Chem.*, **9**, 489 (1966); G. Opitz and H. Schempp, *Z. Naturforsch.*, **19b**, 78 (1964); G. Opitz and H. Schempp, *Ann.*, **684**, 103 (1965); R. H. Hasek, R. H. Meen, and J. C. Martin, *J. Org. Chem.*, **30**, 1495 (1965).

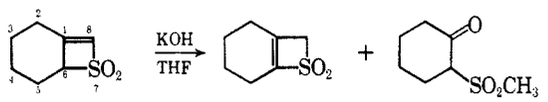
(8) D. C. Dittmer and N. Takashina, *Tetrahedron Letters*, 3809 (1964); L. A. Paquette and T. R. Phillips, *J. Org. Chem.*, **30**, 3883 (1965).

Isomerization of Sulfones

When thiete sulfone or 3-hydroxythietane sulfone was treated with barium hydroxide, dimethyl sulfone was obtained.[1] The reaction was interpreted as the addition of hydroxide ion to the carbon–carbon double bond followed by a reverse aldol reaction.

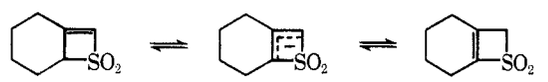


Treatment of 7-thiabicyclo[4.2.0]-1(8)-octene 7,7-dioxide (**1**) with potassium hydroxide in tetrahydrofuran gave a quite different result. A 90% yield of the endocyclic isomer, 7-thiabicyclo[4.2.0]-1(6)-octene (**2**), was obtained plus a small yield (5%) of 2-methylsulfonylcyclohexanone (**3**). The completeness of the



1 **2** **3**

isomerization of **1** to **2** agrees with the idea of endocyclic double bonds in the cyclohexane system being more stable than exocyclic double bonds.[9,10] If the assumption is made that the isomerization of **1** to **2** proceeds *via* the carbanion **4**, then resonance structure **5** may make more of a contribution to the anion **4** than



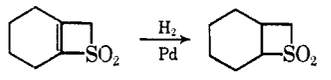
1 **4** **2**

structure **6** since the alkyl substituent (the cyclohexane

5 **6**

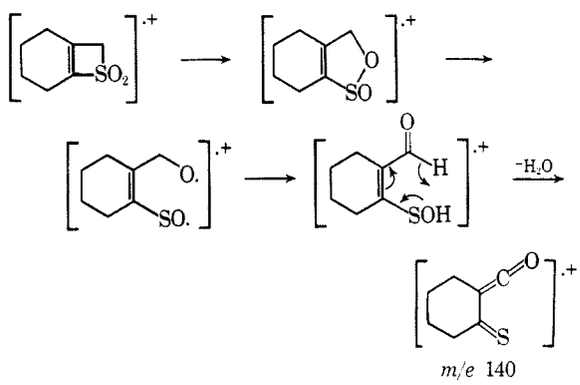
ring) being electron supplying would tend to repel electrons, a factor which appears to be important in the isomerization and protonation of allylic anions.[11] Tertiary carbanions are less stable than secondary carbanions[12] because of the unfavorable inductive effects of alkyl groups and because of steric hindrance to solvation of the tertiary anion.

The structure of sulfone **2** is supported by analysis for elements, its infrared spectrum, its mass spectrum, nmr spectrum, and its conversion to the known saturated compound[5a] on hydrogenation. Whereas **1** showed



2

absorption in the infrared region for a carbon–carbon double bond at 1608 cm^{-1}, the *endo* sulfone showed absorption at 1650 cm^{-1}, the intensity of the latter being about half that of the former, indicating a more highly substituted double bond.[13] *exo* sulfone **1** shows a strong infrared absorption at 800 cm^{-1} which is missing in the spectrum of *endo* sulfone **2**; this absorption may be caused by the out-of-plane bending vibrations of the olefinic hydrogen. The nmr spectrum of **2** showed absorption at δ 4.3, 2.3, and 1.8 (relative areas 2:4:4) in agreement with the structure given. The mass spectra of the sulfones **1** and **2** are similar[14] but there are differences which can be attributed to their respective structures. The mass spectrum of each compound shows a parent peak (P) at *m/e* 158 and a base peak at *m/e* 79 (P − CH_2SO_2H). The most significant difference in the mass spectra of **1** and **2** is at *m/e* 140 (P − H_2O). The exocyclic olefinic sulfone **1** shows no appreciable amount of a fragment at this mass but the endocyclic isomer **2** has a strong peak (55% of base). It is not difficult to write a scheme (eq 1) for the loss of water from the parent radical ion of the *endo* isomer (two hydrogens are on a carbon adjacent to the sulfone group), but it is considerably more difficult to do so for the *exo* isomer. A cyclic sulfinate intermediate has been proposed as an intermediate in the pyrolysis and in the mass spectrum of dibenzothiophene sulfone[15] and such an intermediate has actually been isolated in good yield in a pyrolysis of a thiete sulfone.[16] Differences in intensities between the two isomers also are observed at *m/e* 38, 39, 58, 67, 68, 69, 77, 81, 82, 84, 105 and 107.



m/e 140 (1)

Base-Catalyzed Ring Opening of Thiete Sulfones

The formation of the small amount of 2-methylsulfonylcyclohexanone (**3**) in the isomerization with potassium hydroxide in tetrahydrofuran may proceed by addition of hydroxide ion to the double bond followed by a reverse aldol condensation with ring opening analogous to the reaction of thiete sulfone with hydroxide ion.

(9) H. C. Brown, J. H. Brewster, and H. Schechter, *J. Am. Chem. Soc.*, **76**, 467 (1954).

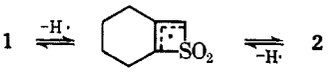
(10) Brown, *et al.*,[9] consider differences in nonbonded interactions as the major cause of the preference for a double bond to be *endo* instead of *exo* in the cyclohexane system. Alternatively, the preference may be ascribed to differences in the two isomers in the numbers of various kinds of bonds between differently hybridized carbons: M. J. S. Dewar, "Hyperconjugation," The Ronald Press Co., New York, N. Y., 1962.

(11) S. W. Ela and D. J. Cram, *J. Am. Chem. Soc.*, **88**, 5777 (1966).

(12) Indicated by the work of A. I. Shatenshtein on hydrogen–deuterium exchange of saturated hydrocarbons in liquid ammonia reviewed in *Advan. Phys. Org. Chem.*, **1**, 175 (1963).

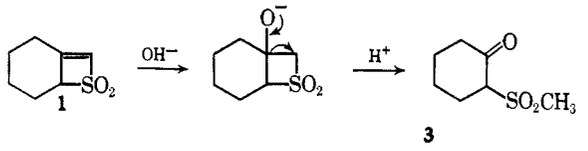
(13) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, p 38.

(14) Once a hydrogen atom is lost from either of the isomers a common intermediate is obtained, accounting for the similar spectra.

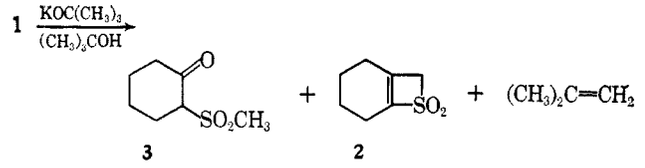


(15) (a) E. K. Fields and S. Meyerson, *J. Am. Chem. Soc.*, **88**, 2836 (1966); (b) Q. N. Porter, *Australian J. Chem.*, **20**, 103 (1967).

(16) D. C. Dittmer, R. S. Henion, and N. Takashina, Abstracts of Papers, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, 101 O.

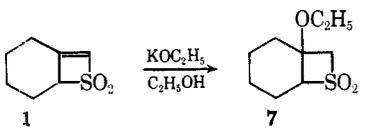


Treatment of the *exo* isomer **1** with potassium *t*-butoxide in *t*-butyl alcohol for 12 hr gave 2-methylsulfonylcyclohexanone, **3** (60–66%), and the *endo* sulfone **2** (10%). Isobutylene was evolved. The low yield of isomerized sulfone **2** may reflect steric hindrance to removal of the tertiary proton by the bulky base, *t*-butoxide ion. Solvation of the *t*-butoxide ion by the protic solvent may also inhibit the proton removal from carbon.



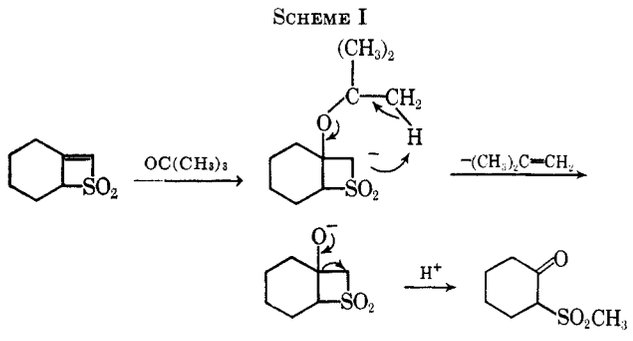
Treatment of the *endo* sulfone **2** with potassium *t*-butoxide in *t*-butyl alcohol for 12 hr gave only a 30% yield of 2-methylsulfonylcyclohexanone and 57% of the starting sulfone was recovered. If the reaction time was 48 hr, the yield of keto sulfone increased to 50% and only 12% of the starting material was recovered.

When sulfone **1** was treated with potassium ethoxide in ethanol, ether **7** was obtained in 95% yield, no keto sulfone being formed.



These results can be rationalized by Scheme I involving attack of *t*-butoxide ion on the double bond of sulfone **1** to yield a sterically hindered ether in which strain is relieved by abstraction of a proton from the *t*-butyl group, elimination of isobutylene, and formation of the keto sulfone. The ethoxy group being smaller and with statistically fewer protons is stable in the adduct.

SCHEME I

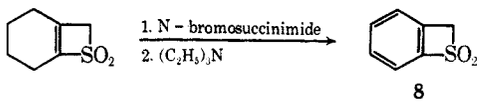


Addition of *t*-butoxide anion to the double bond of the *endo* sulfone is inhibited by the greater instability of the anion formed;[12] *i.e.*, it is a tertiary carbanion whereas with the *exo* sulfone a secondary carbanion is formed. The *endo* sulfone may be isomerized to the *exo* sulfone which then reacts with *t*-butoxide ion; the slower reaction time for the *endo* compound is consistent with a slow isomerization step preceding the addition of the *t*-butoxide anion. Alternatively, the *endo* sulfone may directly yield the keto sulfone but by a more difficult path than the *exo* sulfone is required to take, so that a longer reaction time is necessary to obtain yields comparable with those from the *exo* sulfone.

An analogy for the elimination of isobutylene in the reaction described above is its base-catalyzed elimination from O,O-diethyl S-(*t*-butyl)phosphorodithioate.[17]

2H-Benzo[*b*]thiete 1,1-Dioxide

The first synthesis of the parent member of the family of benzothiete sulfones started with the endocyclic olefinic sulfone, 7-thiabicyclo[4.2.0]-1(6)-octene 7,7-dioxide (**2**).[18a] We observed as did others[5b] that the exocyclic thiete sulfone **1** could not be aromatized by treatment with N-bromosuccinimide followed by elimination of hydrogen bromide.[18b] Treatment of *endo* sulfone **2** with N-bromosuccinimide in carbon tetrachloride at 60° gave a quantitative yield of succinimide and an oil. Treatment of the oil with triethylamine gave 2H-benzo[*b*]thiete 1,1-dioxide (**8**) in low yield.



The infrared spectrum of benzothiete sulfone **8** showed absorption at 3036 cm^{-1} caused by aromatic C–H stretching, at 1445 cm^{-1} caused by aromatic ring vibrations, as well as absorptions at 1300, 1190, and at 1120 cm^{-1} for vibrations of the sulfone group.

The ultraviolet spectrum in acetonitrile showed three maxima at 260 (ϵ 8540), 267 (ϵ 13,600), and 274 mμ (ϵ 13,600), further indications of the presence of an aromatic ring. Methyl phenyl sulfone has absorption in the ultraviolet region at 260 (ϵ 640), 264 (ϵ 940), and 272 mμ[19] (ϵ 830). The greater intensities of the absorptions of the benzothiete sulfone over those of methyl phenyl sulfone may be attributed in part to the distortion of the benzene ring by the fused ring; the symmetry is altered and the electronic excitation may be accompanied by a particularly favorable vibrational excitation which distorts the symmetry further and leads to increased intensity of absorption.[20] The intensity of the absorption of benzocyclobutene in the ultraviolet long wavelength region (analogous to the $^1B_{2u} \leftarrow {}^1A_{1g}$ absorption of benzene) is about ten times that for *o*-xylene;[21] the intensity of absorption for benzothiete sulfone **8** is about 15 times that of methyl phenyl sulfone. Irrespective of whether a vibrational excitation accompanies the electronic excitation, the reduced symmetry of benzothiete sulfone **8** (point group S_1) as compared with methyl phenyl sulfone (point group C_{2v}) could lead to an intensification of the absorption of the former;[22] the absorbance of methyl *o*- and

(17) W. E. Bacon and W. M. LeSuer, *J. Am. Chem. Soc.*, **76**, 670 (1954).

(18) (a) An early attempt to aromatize the Diels–Alder adduct of thiete sulfone and butadiene was not successful: N. Takashina, unpublished results. (b) We observed the evolution of sulfur dioxide. Loss of sulfur dioxide has been reported to result from the treatment of bis(2-phenethyl) sulfone with N-bromosuccinimide: F. J. Lotspeich, *J. Org. Chem.*, **30**, 2068 (1965).

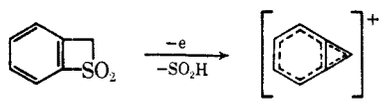
(19) A. Mangini, *Gazz. Chim. Ital.*, **88**, 1063 (1958).

(20) H. H. Jaffé and M. Orchin, "Theory and Application of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, pp 129 ff.

(21) M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, **80**, 2255 (1958); D. D. Tunnicliff, R. R. Brattain, and L. R. Zumwalt, *Anal. Chem.*, **21**, 890 (1949).

(22) See ref 20, p 122.

m-tolyl sulfone (S_1) at long wavelength is somewhat greater than that for methyl *p*-tolyl sulfone (C_{2v}).[23] Nmr absorption of benzothiete sulfone in $CDCl_3$ occurred at δ 5.10 (relative area 2) and at 7.55 (relative area 4) in agreement with the proposed structure. The mass spectrum of the new sulfone showed the parent peak at *m/e* 154; the base peak was at *m/e* 89 corresponding to an ion formed by loss of SO_2 and a proton. This ion may be the benzocyclopropenium cation which has been suggested to occur in the mass spectra of benzo[*b*]thiophene[15b] and certain bisbenzyl isoquinoline alkaloids.[24]



Experimental Section

Isomerization of *exo* Sulfone 1 to *endo* Sulfone 2.—7-Thiabicyclo[4.2.0]-1(8)-octene 7,7-dioxide (1.95 g, 0.012 mole), prepared as previously described,[5a] in 50 ml of tetrahydrofuran (distilled from lithium aluminum hydride) was added by syringe to powdered potassium hydroxide (3.26 g, 0.05 mole) in a 100-ml, three-necked flask equipped with a magnetic stirring bar, inlet tube for nitrogen, and a syringe cap. The reaction mixture, which was yellow after 1 hr, was stirred for about 12 hr at room temperature, water (100 ml) was added, and the mixture was extracted three times with 50-ml portions of chloroform. The chloroform extracts were dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure to give 1.75 g (0.01 mole, 90% yield) of an oil which gradually solidified. Recrystallization from ether gave white needles, mp 80–81°.

Anal. Calcd for $C_7H_{10}SO_2$: C, 53.14; H, 6.37; S, 20.27. Found: C, 53.24; H, 6.19; S, 20.39.

The *endo* sulfone 2 had the following properties: infrared (KBr), 2940 (s), 2860 (sh), 1650 (w), 1430 (m), 1280 (s), 1180 (m), 1155 (s), 1120 (m), 1095 (m), and 850 cm^{-1} (m); nmr ($CDCl_3$), δ 4.3 (closely spaced multiplet in which five lines are resolved, 2 H), 2.3 (complex, 4 H), and 1.8 (complex, 4 H); mass spectrum[25] (Hitachi RMU 6D), *m/e* 158 (parent ion, 5.6%[26]), 140 (P − H_2O, 55.3%), 107 (10.8%), 105 (10.2%), 93 (P − SO_2H, 11.3%), 84 (14.3%), 82 (21.5%), 81 (P − C_6H_5, 34.3%), 80 (15.4%), 79 (100%), 77 (51.7%), 67 (61.5%), 55 (10.8%), 54 (21.0%), 53 (26.7%), 52 (19.5%), 51 (27.1%), 50 (13.8%), 41 (24.1%), 39 (11.8%).

The *exo* sulfone 1 has the following properties: infrared (KBr), 3040 (w), 2933 (s), 2841 (sh), 1608 (m), 1443 (m), 1328 (m), 1292 (s), 1225–1200 (s), 1170 (s), 1140 (s), 1070 (m), 1042 (w), 927 (m), 800 cm^{-1} (s); nmr ($CDCl_3$), δ 2.0 (complex, 8 H), 4.5 (triplet with evidence of further splitting, 1 H), 6.2 (doublet, J = 2 cps, 1 H); mass spectrum, *m/e* 158 (parent ion, 0.1%), 93 (P − SO_2H, 12.6%), 82 (2.5%), 81 (8.6%), 80 (7.9%), 79 (100%), 77 (12.4%), 67 (9.4%), 55 (7.7%), 54 (11.1%), 43 (18.3%), 52 (11.7%), 51 (13.6%), 50 (6.2%), 41 (16.2%), 39 (46.5%).

The yellow aqueous solution left after the extraction with chloroform described above was acidified with 10% hydrochloric acid. Extraction with chloroform and removal of the chloroform after drying gave a yellow oil (0.17 g). Sublimation (0.4 mm, 70°) gave a white solid, mp 71–72°, in 6% yield whose infrared spectrum was identical with that of an authentic sample of 2-methylsulfonylcyclohexanone (see below).

Hydrogenation of *endo* Sulfone.—Hydrogenation of 7-thiabicyclo[4.2.0]-1(6)-octene 7,7-dioxide (2) (3.0 g, 0.019 mole) in 50 ml of absolute ethanol at 40 psi over 50 mg of 10% palladium on charcoal for 4 days yielded a clear oil whose infrared spectrum was identical with that of an authentic sample of 7-thiabicyclo-[4.2.0]-octane-7,7-dioxide.[5a]

Treatment of *exo* Sulfone 1 with Potassium *t*-Butoxide.—7-Thiabicyclo[4.2.0]-1(8)-octene 7,7-dioxide (1) (3.0 g, 0.019 mole) in 20 ml of *t*-butyl alcohol was added by syringe to a solution of potassium *t*-butoxide (prepared by dissolving 0.97 g of potassium in 30 ml of *t*-butyl alcohol) in a 100-ml, three-necked flask equipped with a magnetic stirring bar, inlet for nitrogen, syringe cap, and thermometer. After 12 hr, water (50 ml) was added and the mixture was extracted twice with 50-ml portions of chloroform, which were dried over anhydrous sodium sulfate. Removal of the chloroform under reduced pressure left 0.3 g (10%) of 7-thiabicyclo[4.2.0]-1(6)-octene 7,7-dioxide (2) which was identified by comparison with an authentic sample. The aqueous solution was acidified with 10% hydrochloric acid and extracted with chloroform three times. The chloroform extract was dried and the chloroform removed under reduced pressure to give 2.2 g (66%) of an oil which gave white crystals, mp 71–72°, on sublimation at 75° and 0.25 mm.

Anal. Calcd for $C_7H_{12}O_3S$: C, 47.71; H, 6.86; S, 18.20. Found: C, 47.57; H, 6.87; S, 18.40.

A 2,4-dinitrophenylhydrazone was prepared, mp 194–196° (lit.[27] melting point of the 2,4-dinitrophenylhydrazone of 2-methylsulfonylcyclohexanone, 195–196°).

If nitrogen was passed through the reaction mixture and through two traps cooled by Dry Ice–acetone and by liquid nitrogen, respectively, isobutylene could be isolated from the trap cooled by liquid nitrogen. Identification of the isobutylene was made by comparison of its infrared spectrum with that of an authentic sample. If the sulfone was omitted from the reaction mixture, no isobutylene was formed.

Treatment of *endo* Sulfone 2 with Potassium *t*-Butoxide.—7-Thiabicyclo[4.2.0]-1(6)-octene 7,7-dioxide (2) (1.13 g, 0.0074 mole) in 15 ml of *t*-butyl alcohol was added by syringe to a solution of potassium *t*-butoxide (prepared by dissolving 0.40 g of potassium in 20 ml of *t*-butyl alcohol) in a 100-ml, three-necked flask equipped with magnetic stirring bar, inlet tube for nitrogen, syringe cap, and thermometer. After the reaction mixture was stirred for 12 hr at room temperature and 1 hr at 70°, water was added and the aqueous mixture extracted with chloroform. Removal of the chloroform under reduced pressure gave starting sulfone (0.64 g, 0.0042 mole, 57%) identified by its melting point and infrared spectrum. The aqueous solution was acidified with 10% hydrochloric acid and extracted with chloroform. Removal of the chloroform under reduced pressure gave 0.39 g (30%) of 2-methylsulfonylcyclohexanone. When the reaction time was extended to 48 hr, only 12% (0.11 g) of starting material was recovered and 58% (0.75 g) of 2-methylsulfonylcyclohexanone was obtained.

Treatment of *exo* Sulfone 1 with Potassium Ethoxide.—7-Thiabicyclo[4.2.0]-1(8)-octene 7,7-dioxide (1.0 g, 0.0063 mole) in 20 ml of absolute ethanol was added by syringe to a solution of potassium ethoxide (prepared by dissolving 0.5 g of potassium in 30 ml of absolute ethanol) in a 100-ml, three-necked flask equipped with a magnetic stirring bar, inlet tube for nitrogen, and syringe cap. The reaction mixture was stirred for 12 hr at room temperature and for 1 hr at 70°. Water (100 ml) was added and the aqueous mixture extracted twice with chloroform. Removal of the chloroform yielded 1.14 g (0.0057 mole, 90%) of a yellow oil. Chromatography on a Florisil column gave a pure sample.

Anal. Calcd for $C_9H_{16}O_3S$: C, 52.99; H, 7.91; S, 15.72. Found: C, 53.10; H, 7.67; S, 15.67.

The 1-ethoxy-7-thiabicyclo[4.2.0]octane 7,7-dioxide (7) had the following properties: infrared (thin film), 2940 (s), 2870 (sh), 1440 (m), 1390 (w), 1300 (s), 1210 (m), 1190 (s), 1160 (s), 1130 (m), 1100 (m), 1080 (s), 850 (w), 760 (w), 710 cm^{-1} (w); nmr ($CDCl_3$), δ 1.2 (triplet, 3 H), 1.8 (complex, 8 H), 3.4 (quadruplet, 2 H), 4.1 (complex, 3 H).

2H-Benzo(b)thiete 1,1-Dioxide (8).—N-Bromosuccinimide

(23) W. E. Truce and C. W. Vriesen, *J. Am. Chem. Soc.*, **75**, 5032 (1953).

(24) J. Baldas, Q. N. Porter, I. R. C. Bick, and N. J. Vernengo, *Tetrahedron Letters*, 2059 (1966).

(25) We wish to thank Dr. Richard Enrione, Mr. I. Stamos, and Mrs. Anna Willis for assistance in obtaining the mass spectra.

(26) Percentages are relative to the intensities of the base peaks. All ionizing voltages were about 70 ev.

(27) W. E. Truce and R. H. Knospe, *J. Am. Chem. Soc.*, **77**, 5063 (1955). A sample of the 2,4-dinitrophenylhydrazone kindly was supplied by Professor Truce. Although the melting point of the 2-methylsulfonylcyclohexanone reported here (71–72°) differs from that reported by Truce and Knospe (57–58°), the infrared and proton nmr spectra of our sample and a sample prepared by the method of Truce and Knospe were identical. Repeated sublimation of the material originally melting at 57–58° caused the melting point to increase to 64–65°. Possibly different crystalline forms are responsible for the different melting points. The behavior of the melting points is analogous to that of the 2,4-dinitrophenylhydrazone of *cis*-2-keto-10-methyldecalin which melted sharply but differently after each recrystallization: R. B. Woodward, F. Sondheimer, D. Taub, K. Heusler, and W. M. McLamore, *J. Am. Chem. Soc.*, **74**, 4238 (1952).

(2.24 g, 0.0126 mole) and a few milligrams of dibenzoyl peroxide were added to a solution of 7-thiabicyclo[4.2.0]-1(6)-octene 7,7-dioxide (2) (1.0 g, 0.0063 mole) in 50 ml of carbon tetrachloride. The reaction mixture was heated at 60–65° in a oil bath until all of the N-bromosuccinimide had been converted to succinimide (1–2 days). The succinimide (1.3 g) was removed by filtration and the carbon tetrachloride was washed successively with water, 5% aqueous sodium thiosulfate, and water and then dried over anhydrous sodium sulfate. Removal of the carbon tetrachloride under reduced pressure gave a clear oil which was treated for 12 hr at room temperature with 20 ml of triethylamine in benzene followed by a 3-hr period at the temperature of refluxing solvent. The triethylamine hydrobromide was removed by filtration and the benzene removed under reduced pressure to give 1.0 g of a brown oil. The oil was dissolved in chloroform, treated twice with decolorizing charcoal, and chromatographed on a column of Florisil. Elution with chloroform gave 0.6 g of a colorless oil which was sublimed (30°, 0.25 mm) to yield a white solid, mp 100–120°. Recrystallization from ether gave needles, mp 126–128°. The over-all yield to recrystallized product was about 3%.

Anal. Calcd for $C_7H_8O_2S$: C, 54.52; H, 3.92. Found: C, 54.58; H, 3.97.

The benzothiete sulfone had the following properties: infrared (KBr), 3025 (w), 2940 (w), 1465 (m), 1445 (m), 1300 (s), 1195 (s), 1175 (m), 1150 (m), 1125 (s), 720 (s), 710 cm^{-1} (s); nmr ($CDCl_3$), δ 5.1 (singlet, 2 H), 7.55 (singlet, 4 H); ultraviolet (CH_3CN), 260 (ϵ 8540), 267 (ϵ 13,600), 274 mμ (ϵ 13,600); mass spectrum, *m/e* 154 (parent ion, 14.8%), 137 (P − OH, 19.0%), 93 (15.8%), 91 (22.1%), 90 (P − SO_2; 56.8%), 89 (P − SO_2H, 100%), 77 (14.2%), 64 (19.5%), 63 (43.8%), 62 (17.9%), 51 (23.1%), 50 (15.3%), 39, (37.5%).

Reactions of *gem*-Dihalocyclopropanes with Electrophilic Reagents. Formation of Allyl Derivatives and/or Dienes

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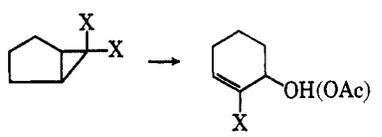
The reaction of *gem*-dihalocyclopropanes with silver acetate–acetic acid yields $R_1R_2C{=}CBrCR_3R_4OAc$ and/or $R_1R_2C{=}CBrCR_3{=}CR_4R_5$. The distribution of the two products depends on the number of methyl groups. Tetramethyldibromocyclopropane yields 3-bromo-2,4-dimethyl-2,4-pentadiene as the sole product. Reaction of both *cis*- and *trans*-1,1-dibromo-2,3-dimethylcyclopropane gave *trans*-3-bromo-2-acetoxy-3-pentene.

Ring-opening rearrangement reactions of *gem*-dihalocyclopropanes have been effected by the use of solvents with either electrophilic or nucleophilic reagents,[2] thermally[2,3] or by means of alkali or alkaline earth metals.[2,4] Solvolysis and thermal rearrangement give allyl derivatives, dienes, or alkynes; metals and organometallics give allenes (Scheme I). The use of boiling quinoline or pyridine leads largely to ring opening concurrent with dehydrohalogenation.[5]

The purpose of the present paper is to report some of the detailed data that were only briefly described in our earlier communication on *gem*-dihalocyclopropane ring expansions.[2f]

Results

Electrophilic Rearrangement of 6,6-Dichlorobicyclo[3.1.0]hexane and 6,6-Dibromobicyclo[3.1.0]hexane.—The experimental data in Table I indicate that the electrophilic rearrangement can be carried out under mild conditions with aqueous silver nitrate, silver perchlorate, silver acetate–acetic acid, mercuric acetate–acetic acid, and sodium acetate–acetic acid to give good yields of 2-chloro-3-hydroxycyclohexene (I), 2-bromo-3-hydroxycyclohexene (II), or their actate derivatives such as 2-bromo-3-acetoxycyclohexene (III). Under



X = Br or Cl

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(2) (a) W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **76**, 6162 (1954); (b) W. E. Parham and H. E. Reiff, *ibid.*, **79**, 1177 (1955); (c) W. E. Parham, H. E. Reiff, and P. Swartzentruber, *ibid.*, **78**, 1437 (1956); (d) W. E. Parham and R. R. Twelves, *J. Org. Chem.*, **22**, 730 (1957); (e) W. E. Parham and C. D. Wright, *ibid.*, **22**, 147 (1957); (f) P. S. Skell and S. R. Sandler, *J. Am. Chem. Soc.*, **80**, 2024 (1958); (g) P. S. Skell, R. E. Glick, S. R. Sandler, and L. Gatlin, Fourth Report of the Petroleum Research Fund, 1959, p 82; (h) S. R. Sandler, *Dissertation Abstr.*, **21**, 61 (1960); (i) E. E. Schweizer and W. E. Parham, *J. Am. Chem. Soc.*, **82**, 4085 (1960); (j) W. R. Moore and H. R. Ward, *Chem. Ind.* (London), 594 (1961); (k) W. E. Parham, D. A. Bolan, and E. E. Schweizer, *J. Am. Chem. Soc.*, **83**, 603 (1961); (l) S. Winstein and J. Sonnenberg, *J. Org. Chem.*, **27**, 748 (1962); (m) E. Bergman, *ibid.*, **28**, 2210 (1963); (n) for a review of ring opening reactions of *gem*-dihalocyclopropanes, see W. E. Parham and E. E. Schweizer, *Org. Reactions*, **13**, 55 (1963); (o) A. J. Birch, J. M. Brown, and F. Stansfield, *J. Chem. Soc.*, 5343 (1964); (p) L. Gatlin, R. E. Glick, and P. S. Skell, *Tetrahedron*, **21**, 1315 (1965); (q) S. J. Cristol, R. M. Sequeira, and C. H. DePuy, *J. Am. Chem. Soc.*, **87**, 4007 (1965); (r) C. W. Jefford and R. Medary, *Tetrahedron Letters*, **19**, 2069 (1966); (s) L. Skattebøl, *J. Org. Chem.*, **31**, 1554 (1966); (t) L. Skattebøl and B. Boulette, *ibid.*, **31**, 81 (1966); (u) W. E. Parham and R. J. Sperley, *ibid.*, **32**, 924 (1967).

(3) (a) A. P. ter Borg and A. F. Bickel, *Proc. Chem. Soc.*, 283 (1958); (b) H. Winberg, *J. Org. Chem.*, **24**, 264 (1959); (c) S. M. McElvain and P. L. Weyna, *J. Am. Chem. Soc.*, **81**, 2579 (1959); (d) N. P. Neureiter, *J. Org. Chem.*, **24**, 2044 (1959); (e) N. P. Neureiter, U. S. Patent 2,951,878 (1960); (f) E. E. Schweizer and W. E. Parham, *J. Am. Chem. Soc.*, **82**, 4085 (1960); (g) A. P. ter Borg and A. F. Bickel, *Rec. Trav. Chim.*, **80**, 1 (1960); (h) W. E. Parham, R. W. Soeder, and R. M. Dodson, *J. Am. Chem. Soc.*, **84**, 1755 (1962); (i) W. R. Moore, W. R. Moser, and J. E. LaPrude, *J. Org. Chem.*, **28**, 2200 (1963); (j) R. C. DeSelms and C. M. Combs, *ibid.*, **28**, 2206 (1963); (k) G. C. Robinson, *ibid.*, **29**, 3433 (1964); (l) C. W. Jefford, S. Mahajan, J. Waslynm, and B. Waegell, *J. Am. Chem. Soc.*, **87**, 2183 (1965); (m) O. M. Nefedov and N. N. Novitskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (2) 395 (1965); (n) K. Dimroth, W. Kinzelau, and M. Soyka, *Ber.*, **99**, 2351 (1966); (o) D. C. Duffey, J. P. Minyard, and R. H. Lane, *J. Org. Chem.*, **31**, 3865 (1966).

(4) (a) W. von E. Doering and P. L. LaFlamme, *Tetrahedron*, **2**, 75 (1958); (b) W. von E. Doering and P. L. LaFlamme, U. S. Patent 2,933,544 (1960); (c) W. R. Moore and H. R. Ward, *J. Org. Chem.*, **25**, 2073 (1960); (d) L. Skattebøl, *Tetrahedron Letters*, 167 (1961); (e) L. Skattebøl, *Acta. Chem. Scand.*, **17**, 1683 (1961); (f) T. J. Logan, *Tetrahedron Letters*, 173 (1961); (g) P. D. Gardner and M. Narayana, *J. Org. Chem.*, **26**, 3518 (1961); (h) W. J. Ball and S. R. Landor, *Proc. Chem. Soc.*, 143 (1961); (i) L. Skattebøl, *Chem. Ind.* (London), 2146 (1962); (j) W. R. Moore and H. R. Ward, *J. Org. Chem.*, **27**, 4179 (1962); (k) K. G. Untch, D. J. Martin, and N. T. Castellucci, *ibid.*, **30**, 3572 (1965); (l) C. L. Osborn, T. C. Shields, B. A. Shoulders, J. F. Krause, H. V. Cortez, and P. D. Gardner, *J. Am. Chem. Soc.*, **87**, 3158 (1965); (m) L. Skattebøl, *J. Org. Chem.*, **31**, 2789 (1966).

(5) (a) W. E. Parham, R. W. Soeder, J. R. Throckmorton, K. Kuncl, and R. M. Dodson, *J. Am. Chem. Soc.*, **87**, 321 (1965); (b) W. E. Parham and R. J. Sperley, *J. Org. Chem.*, **32**, 926 (1967).