Evidence of Reversible Zwitterion Formation in the Reaction of 7-Ketonorbornane and Dimethyloxosulfonium Methylide[1]

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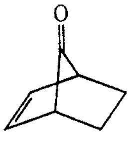
Dimethyloxosulfonium methylide reacts with excess 7-ketonorbornane in dimethyl sulfoxide at room temperature to produce a complex mixture containing spiro[norbornan-7,2′-oxacyclopropane], methyl 7-(7-hydroxynorbornyl)carbinyl sulfoxide, bis[7-(7-hydroxynorbornyl)carbinyl] sulfoxide and no unreacted ketone. We attribute this unusual and heretofore unobserved reaction type to steric crowding by the *exo*-2,3 hydrogens of the ketone which forces the betaine-type intermediate to adopt a conformation from which hydride transfer rather than intramolecular displacement is the dominant reaction. When the reaction is stopped prior to completion, a metastable intermediate can be isolated which reacts with 7-ketonorbornene to produce spiro[norborn-2-en-*anti*-7,2′-oxacyclopropane] in addition to the other products. It is suggested that this reversibly formed insoluble intermediate is the betaine-type zwitterion derived from the addition of bis[7-(7-hydroxynorbornyl)carbinyl]oxosulfonium methylide to 7-ketonorbornane.

In the course of a recent investigation into the reactivity of some unsaturated bicyclic ketones toward dimethyloxosulfonium methylide,[2] we examined the competitive reaction of equimolar quantities of 7-ketonorbornene (**1**) and 7-ketonorbornane (**3**) with a less than stoichiometric amount of ylide. Contrary to the individual behavior of **1**,[3] of dehydronorcamphor (**2**), and of norcamphor (**4**) with this ylide, the mixture produced large amounts of a sulfur-containing solid. Although a high yield of spiro[norborn-2-en-*anti*-7,2′-oxacyclopropane] (**5**) was also obtained, very little spiro[norbornane-7,2′-oxacyclopropane] (**6**) was formed and almost no unreacted **3** could be recovered. With the expectation that it could provide a better insight into some aspects of ketone–ylide reactions which are not yet fully understood,[4] we undertook a more thorough investigation of the anomalous behavior of 7-ketonorbornane (**3**) toward dimethyloxosulfonium methylide. The results of this study are reported here.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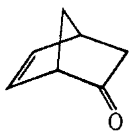
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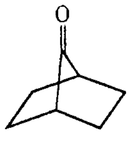
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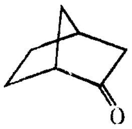
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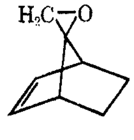
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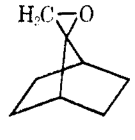
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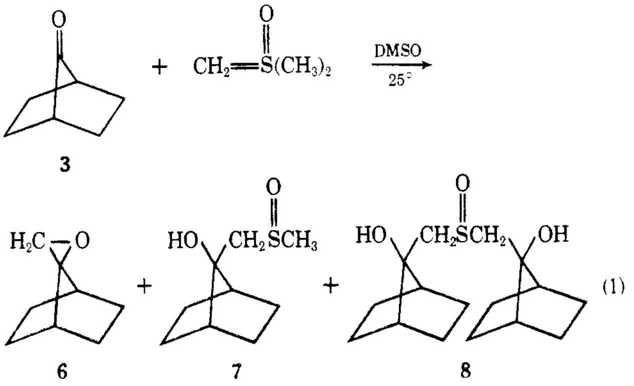
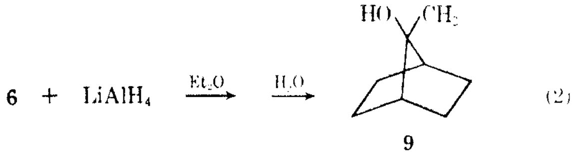
Results

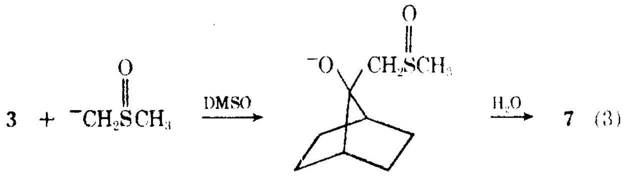
The reaction of 7-ketonorbornane (**3**) with dimethyloxosulfonium methylide in dimethyl sulfoxide (DMSO) at 25° ultimately produces spiro[norbornan-7,2′-oxacyclopropane] (**6**), methyl 7-(7-hydroxynorbornyl)carbinyl sulfoxide (**7**), and bis[7-(7-hydroxynorbornyl)carbinyl] sulfoxide (**8**), *e.g.*, eq 1.



The structure of the epoxide, **6**, was established by reduction with lithium aluminum hydride to the known 7-methyl-7-hydroxynorbornane (**9**, eq 2).[3] That of



7 follows from the fact that it can also be prepared from **3** and methylsulfinyl carbanion (eq 3).[5]



The structure of **8** is suggested by spectral and analytical data. The infrared (ir) spectrum exhibits hydroxyl and sulfoxyl absorptions but no carbon–carbon double bond or carbonyl bands. The proton magnetic resonance (pmr) spectrum (Figure 1) shows a complex multiplet at δ 1.1–2.2 (relative area, 10), two singlets at 3.22 and 3.26 (relative area, 2), and a concentration-dependent singlet at ~3.5 (relative

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[1] Portions of this work have been presented at the 40th Annual Meeting of the South Carolina Academy of Science, Greenville, S. C., April 1967 [*Bull. S. Carolina Acad. Sci.*, **29**, 51 (1967)], and at the 19th Southeastern Regional Meeting of the American Chemical Society, Atlanta, Ga., Nov 1967, Abstract 236.

[2] R. S. Bly, C. M. DuBose, Jr., and G. B. Konizer, *J. Org. Chem.*, **33**, 2188 (1968).

[3] R. K. Bly and R. S. Bly, *ibid.*, **28**, 3165 (1963).

[4] *Cf.* E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1353 (1965).

[5] E. J. Corey and M. Chaykovsky, *ibid.*, **87**, 1345 (1965).

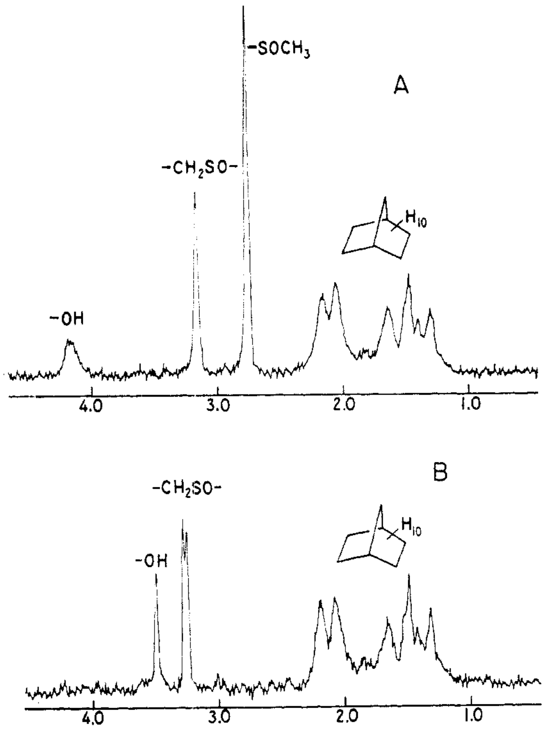
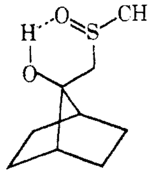


Figure 1.—The 60-MHz pmr spectra of (A) methyl 7-(7-hydroxynorbornyl)carbinyl sulfoxide and (B) bis[7-(7-hydroxynorbornyl)carbinyl] sulfoxide determined in deuteriochloroform and reported in parts per million with tetramethylsilane (δ 0.00) as internal standard.

area, 1). The high-field multiplet is essentially superimposable on the corresponding region in the spectrum of **7** and exhibits the characteristic splitting pattern of the ten hydrogens on a 7,7-disubstituted norbornyl skeleton. The singlets at δ 3.22 and 3.26 can be assigned to the nonequivalent methylene hydrogens adjacent to a sulfoxyl group[6] and the singlet at 3.5 to a hydroxyl proton. Since the elemental analysis corresponds to an empirical formula of $C_{16}H_{26}O_3S$, each molecule must contain two magnetically equivalent structural units of this type (*cf.* Figure 1). Hence **8** is clearly bis[7-(7-hydroxynorbornyl)carbinyl] sulfoxide.

The hydroxyl hydrogens of both **7** and **8** form strong



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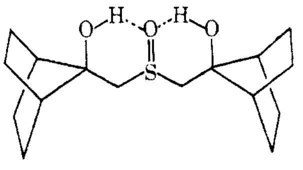

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intramolecular hydrogen bonds with the sulfoxyl oxygen. In a 0.005 *M* solution in carbon tetrachloride, the O–H stretch of **7** appears as a single sharp absorption at 3430 cm^{-1}. The spectrum of **8** exhibits a strong, bonded-hydroxyl peak at 3440 cm^{-1} and a much weaker nonbonded one at 3620 cm^{-1}.[7]

The relative amounts of **6**, **7**, and **8** produced are dependent upon the time of reaction and upon the mole ratio of 7-ketonorbornane (**3**) to dimethyloxosulfonium methylide, ketone/ylide (K/Y). Product analyses from a series of experiments in which these factors were varied are summarized in Table I. Since the isolated product balance in each of these heterogeneous reactions is at best ~70%, the data do not permit an evaluation of such factors as a change in the rate of stirring or addition of ketone, a variation in concentration of the reactants, or small differences in temperature. However, certain general trends appear to be significant.

TABLE I

PRODUCTS OF THE REACTION OF 7-KETONORBORNANE (**3**) WITH DIMETHYLOXOSULFONIUM METHYLIDE

Run no.	Mole ratio of ketone/ ylide	Reaction time, hr	Weight, mg (yield, %) **6**	**7**	**8**	3	**10**
1	0.92	1	296 (52)	78 (9)	48 (7)	0	0
2	0.92	27	272 (48)	65 (7)	39 (6)	0	0
3[a]	0.92	1	305 (54)	100 (11)	29 (4)	0	0
4	1.84	1	142 (25)	48 (5)	55 (8)	0	212[b]
5	1.84	24	209 (37)	75 (9)	170 (35)	10 (~2)	Trace
6	2.80	1	82 (9)	25 (2)	83 (8)	5 (~1)	644[b]

[a] Ketone was added over a 10-min period. [b] Probably contains a small amount of **8**.

The optimum yield of epoxide **6** is obtained when approximately equimolar amounts of ketone and ylide are used (K/Y = 0.92). An increase in K/Y results in a decrease in the relative amount of **6**, an increase of **8**, and no significant change in the amount of **7**.

Increasing K/Y also has the effect of retarding the rate of appearance of the three final products. When K/Y = 0.92, the over-all yield of **6**, **7**, and **8** after 1 hr is 69%. The yield under these conditions decreases slightly at longer reaction times, perhaps because of further side reactions between the products and the excess ylide. When K/Y = 1.84 the over-all yield of **6**, **7**, and **8** after 1 hr drops to 38%, when K/Y = 2.80, to 9% (*cf.* runs 1, 4, and 6, Table I). These decreases in **6**, **7**, and **8** are accompanied by the appearance of a new material, **10**, which precipitates from the reaction mixture together with **8** when water is added. This new material is apparently an intermediate in the overall reaction, for with increasing reaction times less **10** and more of **6**, **7**, and **8** can be isolated. For example, when the reaction where K/Y = 1.84 is allowed to proceed for 24 hr, instead of being stopped after 1 hr, the total yield of **6**, **7**, and **8** increases to 71% and no **10** is obtained.

We have as yet been unable to isolate the intermediate **10** in sufficiently pure form to allow a rigorous structure proof. While the solid can be stored at −20° for several days it decomposes readily when heated either dry or as a heterogeneous mixture in an organic solvent. The material is too insoluble in cold water or in organic solvents to permit the determination of a meaningful nmr spectrum. Its ir spectrum (KBr) has strong hydroxyl and sulfoxyl bands but shows only a weak and very broad absorption in the carbonyl region (~1800 cm^{-1}). An elemental analysis, performed on the crude material, indicates that more than two 7-ketonorbornane moieties are associated with each sulfoxyl unit. Since the ir spectra of samples obtained from reactions with differing ketone to ylide ratios show only minor dif-

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(6) K. Mislow, M. M. Green, P. Laur, J. T. Melillo, T. Simmons, and A. L. Ternay, Jr., *J. Amer. Chem. Soc.*, **87**, 1958 (1967).

(7) L. P. Kuhn, *ibid.*, **74**, 2492 (1952).

ferences, it appears that **10** consists largely of a single compound, but we cannot rule out the possibility of one or more minor contaminants. Possible structures for this intermediate are considered in the Discussion.

In order to establish the nature of its decomposition product(s), a sample of **10** was suspended in benzene and heated at the boiling point for 3 hr (eq 4). The volatile products were sublimed and analyzed by gas-liquid partition chromatography (glpc). The sublimate constituted ~50 wt % of the recovered products and consisted of the epoxide **6** and the starting ketone, **3** (mole ratio, 0.9:1.0). An nmr analysis of the nonvolatile products confirmed the presence of the two sulfoxides **7** and **8** (mole ratio, 2:1). Both the volatile and the nonvolatile fractions contained traces of DMSO which may have been a contaminant in the starting material.

$$\mathbf{10} \xrightarrow[\text{benzene}]{80^\circ} \mathbf{3} + \mathbf{6} + \mathbf{7} + \mathbf{8} + \text{DMSO (?)} \qquad (4)$$

The proportion of products produced during the decomposition of **10** is apparently dependent upon the temperature and/or reaction time for, when a suspension of the intermediate in DMSO is stirred for 6 days at room temperature, **6** and **3** are produced in a mole ratio of 1.8:1.0 while **7** and **8** are formed in the ratio of 1.3:1.0.

Additional products are produced when the decomposition is accomplished by stirring a suspension of **10** for 6 days at room temperature, in a DMSO solution containing two molecular equivalents of the more reactive[8] ketone **1** (eq 5). A glpc and spectral analysis

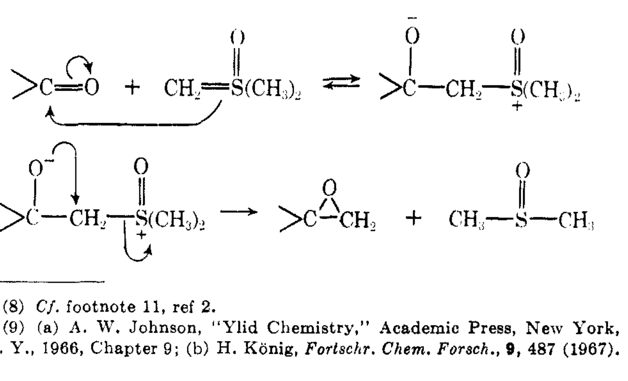
$$\mathbf{10} + \mathbf{1} \xrightarrow[\text{DMSO}]{25^\circ} \mathbf{3} + \mathbf{5} + \mathbf{6} + \mathbf{7} + \mathbf{8} \qquad (5)$$

of the volatile components reveals the presence of the unsaturated oxide, **5**,[3] as well as **6** and **3** (mole ratio, 1.7:1.0:4.0) and some unreacted **1**. An nmr analysis of the nonvolatile components again demonstrates the presence of both **7** and **8** (mole ratio, 1.0:1.5) as well as a trace of one or more unsaturated materials.

Discussion

The reaction of a ketone with dimethyloxosulfonium methylide is usually thought of as a two-step reaction:[9] a nucleophilic attack by the ylide on the carbonyl carbon to give an intermediate betaine-type zwitterion followed by the intramolecular nucleophilic displacement of dimethyl sulfoxide to produce the epoxide (Scheme I). The first step is frequently considered reversible and rate limiting since this has been demonstrated in the case of group V ylides,[10] the latter step irreversible and rapid since epoxides are normally stable in DMSO. In fact, however, there appears to have been no conclusive demonstration that a betaine-type zwitterion is actually an intermediate in the reaction of an oxosulfonium ylide much less that its formation is reversible.[4]

Scheme I



Clearly the reaction of dimethyloxosulfonium methylide with 7-ketonorbornene (**3**) represents a case which cannot be fully explained on the basis of Scheme I. While such a reaction path could still account for the formation of the observed oxide **6**, a different process is necessary to explain the formation of the sulfoxides **7** and **8**. It is unlikely that this process involves an alkylsulfinyl carbanion, $RSOCH_2^-$, for such intermediates are appreciably more basic than oxosulfonium ylides,[5,11,12] or betaines and appear to be formed in significant concentration only at a considerably higher temperature[5] than is required for the transformations which we observe.

We believe the reaction of dimethyloxosulfonium methylide with 7-ketonorbornane (**3**) to proceed as outlined in Scheme II. In essence the proposal is that the initially formed zwitterion **11**, though fairly stable, is hampered from attaining the preferred *trans* coplanar conformation for intramolecular displacement of DMSO by steric crowding between the *exo*-2,3 hydrogens of the norbornane ring and the sulfoxyl methyl groups and in order to minimize such steric interactions adopts instead the cyclohexanelike conformation shown. In this conformation 1,5-hydrogen transfer to produce the new ylide **12** becomes the dominant reaction. Once formed, **12** may add another molecule of ketone to produce a second betaine-type intermediate, **13**, which is then either converted into methyl 7-(7-hydroxynorbornyl)carbinyl sulfoxide (**7**) and the epoxide **6** by an intramolecular nucleophilic displacement or undergoes another 1,5-hydrogen shift to produce a third ylide, **14**. Attack by a third molecule of ketone then yields the intermediate **15** which decomposes to bis[7-(7-hydroxynorbornyl)carbinyl] sulfoxide (**8**) and another molecule of epoxide **6**.

Though as far as we are aware intramolecular proton transfers from carbon to oxygen to re-form an ylide have not previously been observed in oxosulfonium ylide reactions, the acidic nature of the methyl hydrogens in trimethyloxosulfonium salts has been demonstrated by deuterium-exchange studies[12] and such shifts are known to occur in other cases.[13]

The effects produced by varying the ratio of ketone to ylide are in accord with the reaction sequence proposed in Scheme II. Since each intramolecular displacement would produce equimolar amounts of sulfoxide and saturated epoxide, at least half of the ultimate products of the over-all reaction should consist of epoxide **6**. Within the experimental limitation of our inability to determine the amount of dimethyl sulfoxide formed, this appears to be so. As more ketone is

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[8] *Cf.* footnote 11, ref 2.

[9] (a) A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966, Chapter 9; (b) H. König, *Fortschr. Chem. Forsch.*, **9**, 487 (1967).

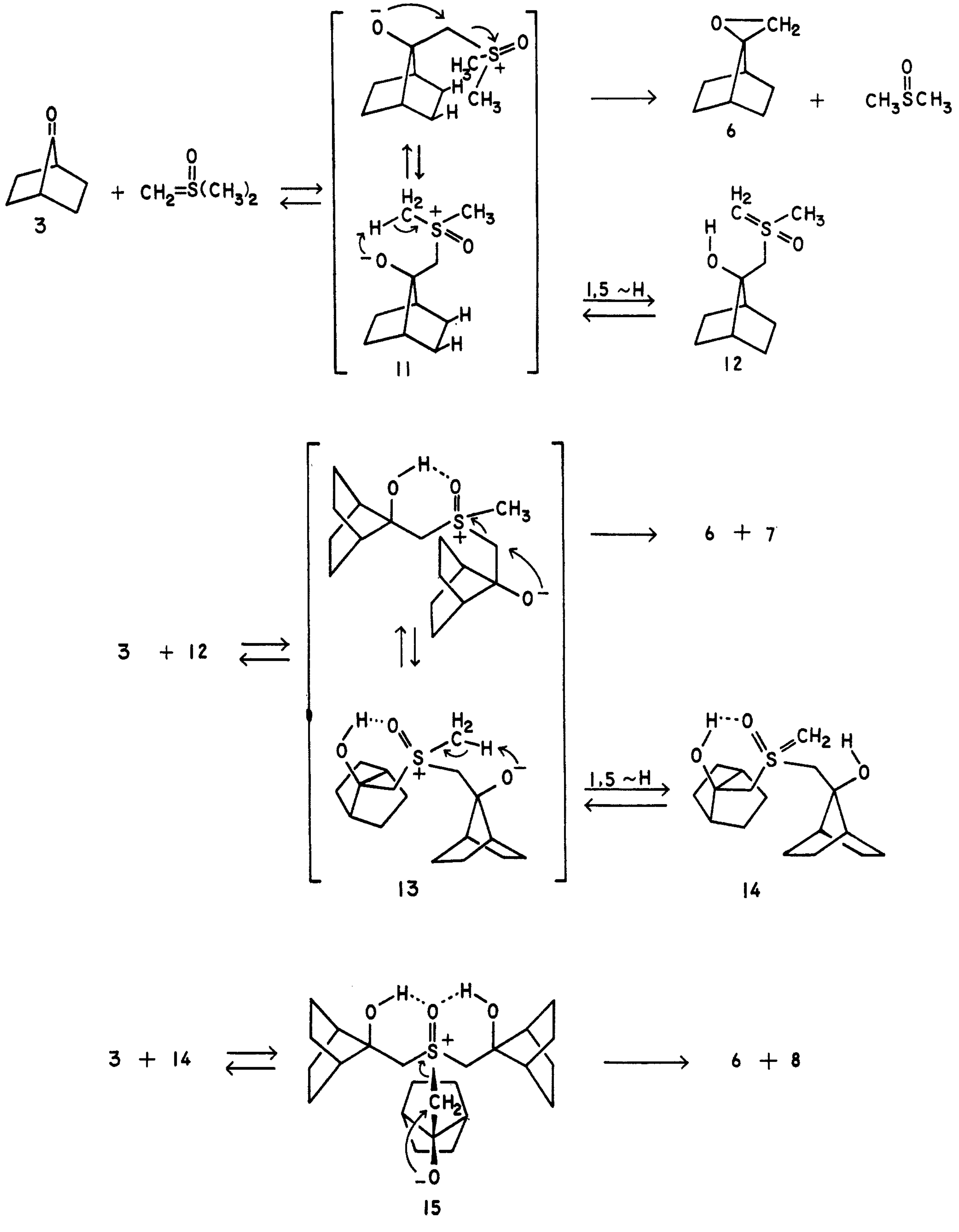
[10] (a) A. Maercker, *Org. Reactions*, **14**, 305 (1965), and references cited therein; (b) see also Chapters 7 and 8, ref 9a.

[11] E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **84**, 867 (1962).

[12] (a) W. von E. Doering and A. K. Hoffman, *ibid.*, **77**, 521 (1955); (b) S. G. Smith and S. Winstein, *Tetrahedron*, **3**, 317 (1958).

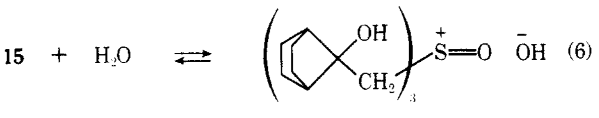
[13] (a) A. G. Hartmann, *J. Amer. Chem. Soc.*, **87**, 4972 (1965); (b) A. W. Johnson and R. B. LaCount, *ibid.*, **83**, 417 (1961).

SCHEME II



allowed to react with a given amount of ylide, a larger fraction of the total products are formed from the most sterically crowded trisubstituted zwitterion **15**, and both the over-all rate and the ratio of **7** to **8** in the products (*cf.* Table I) are decreased.

In view of the fact that it seems to contain three norbornyl units per sulfur atom, it is likely that the insoluble metastable intermediate, **10**, is either the zwitterion **15** or perhaps tris[7-(7-hydroxylnorbornyl)-carbinyl]oxosulfonium hydroxide (**16**), produced from



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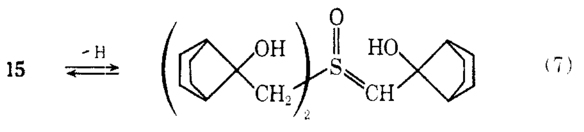
15 upon the addition of water, *viz.*, eq 6. The ylide **17**, which might be formed from **15** by a further proton shift, appears to be a less likely alternative since no



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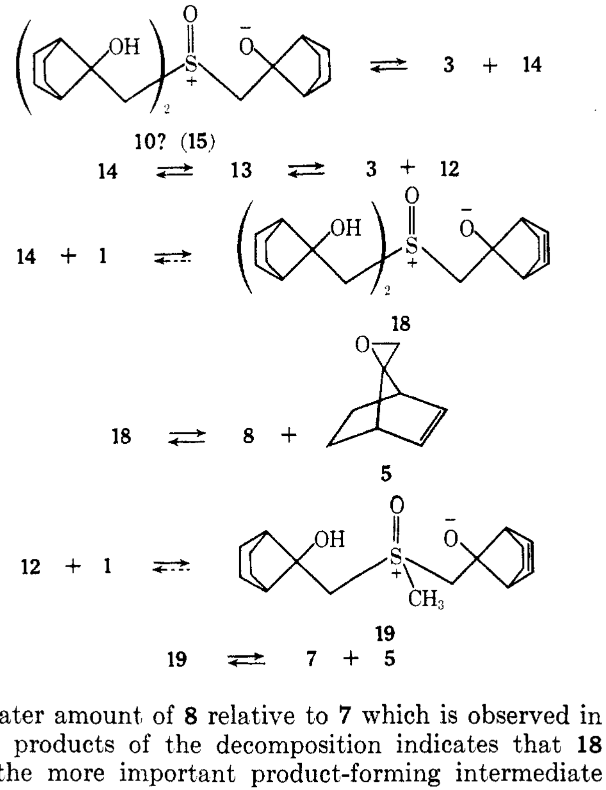
products which might have resulted from the further reaction of such an ylide with more ketone have been observed.

The thermal dissociation of **10** in the absence of excess ketone to regenerate **3** in addition to appreciable amounts of **6**, **7**, and **8**, clearly indicates that the ketone–ylide addition steps can be reversed. That they are in fact reversible under the reaction conditions is established by the observation that the addition of the more reactive 7-ketonorbornene (**1**) to a suspension of **10** in DMSO produces large amounts of the unsaturated epoxide, **5**, as well as the saturated ketone, **3**. The probable route for the formation of **5** from the reaction of **10** and **1** is shown in Scheme III. The greater amount of **8** relative to **7** which is observed in the products of the decomposition indicates that **18** is the more important product-forming intermediate in this case. This observation and the absence of appreciable amounts of unsaturated sulfoxides support our earlier suggestion that both the initial addition of ylide and subsequent displacement of sulfoxide are facilitated by the double bond of **1**.[2]

Scheme III



Among the ketones whose reactions with dimethyloxosulfonium methylide have been studied, 7-ketonorbornane (**3**) is unique. Its strain-induced bias for nucleophilic addition[3] and the steric effect of its *exo* hydrogens combine to render it an ideal substrate with which to demonstrate and study the reversible formation of zwitterionic intermediates.

Experimental Section[14]

The Preparation of Methyl 7-(7-Hydroxynorbornyl)carbinyl Sulfoxide (7).—A mixture of 0.122 g (5.1 mmol) of sodium hydride (0.225 g of a 54% suspension in mineral oil) and 10 ml of DMSO was heated with stirring under a nitrogen atmosphere at 65–70° until no more hydrogen was evolved. The mixture was cooled to room temperature and a solution of 0.505 g (4.6 mmol) of 7-ketonorbornane (**3**) in 5 ml of DMSO was added. Stirring was continued for 1 hr after which the reaction mixture was poured into 30 ml of water. The aqueous solution was washed with pentane and extracted with five ~15-ml portions of chloroform. The chloroform extract was washed with saturated sodium chloride, dried (Na_2SO_4), and distilled at atmospheric pressure. The residue was washed with a small amount of pentane and filtered to give 708 mg (75.3%) of crude product. Recrystallization from pentane gave 463 mg of pure **7**: mp 111.5–112.5°; ir (KBr) 3380 (O—H), 1040, 1050 (C—O), 1015 cm^{-1} (S=O); nmr (*cf.* Figure 1A) ($CDCl_3$) δ 4.0 (s, concentration dependent, 1 OH), 3.13 (s, 2 >CCH_2SO-), 2.73 (s, 3 -$SOCH_3$), 2.2–1.1 (m, 10 >CH + >CH_2).

Anal. Calcd for $C_9H_{16}O_2S$: C, 57.41; H, 8.57; S, 17.03. Found: C, 57.44; H, 8.53; S, 17.31.

The Reaction of 7-Ketonorbornane with Dimethyloxosulfonium Methylide. A. Isolation and Identification of Products.—Trimethyloxosulfonium iodide (2.20 g, 10.0 mmol) was added in one portion to a nitrogen-blanketed suspension of 0.243 g (10.1 mmol) of sodium hydride (0.450 g of a 54% suspension in mineral oil) in 10 ml of DMSO. The mixture was stirred at room temperature until no more hydrogen was evolved. A solution of 1.10 g (10.0 mmol) of 7-ketonorbornane (**3**) in 15 ml of DMSO was added during ~10 min. The reaction mixture was stirred for 1 hr, poured into 40 ml of ice-water, and extracted with five 25-ml portions of pentane (fraction 1). A white solid remained suspended in both the aqueous layer and the pentane extract. Filtration of both layers gave a total of 0.188 g of insoluble product (fraction 2). The aqueous solution was extracted with five 25-ml portions of chloroform (fraction 3).

Fraction 1 was washed with 10 ml of saturated sodium chloride, dried (Na_2SO_4), and concentrated to ~1 ml. Sublimation of the residue at 70° (20 mm) gave 0.655 g of spiro[norbornan-7,2′-oxacyclopropane] (**6**): ir (CCl_4) 3040, 1245, 900, 835 cm^{-1}; nmr (CCl_4) δ 2.77 (s, 2 >CCH_2O), 2.2–1.1 (m, 10 >CH + >CH_2).

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.01; H, 9.93.

The structure assignment of **6** was confirmed by reduction with lithium aluminum hydride to give 7-methyl-7-hydroxynorbornane (**9**).[3]

Fraction 2 was recrystallized from chloroform to give 95 mg of a white solid: mp 211–212°; ir (KBr) 3420, 3330 (OH stretch, bonded), 1307, 1302 (OH, bending), 1059 (CO), 1005 (S=O), 1110, 1080, 1035 cm^{-1}; nmr (*cf.* Figure 1B) ($CDCl_3$) δ 3.5 (s, concentration dependent, 2 OH), 3.26 (s, 2 >CCHHSO-), 3.22 (s, 2 >CCHHSO-), 2.2–1.1 (m, 20 >CH + >CH_2).

Anal. Calcd for $C_{16}H_{26}O_3S$: C, 64.39; H, 8.78; S, 10.74. Found: C, 64.42; H, 8.75; S, 10.95.

We have assigned the structure **8**, bis[7-(7-hydroxynorbornyl)-carbinyl] sulfoxide, to this compound on the basis of these spectral and analytical data.

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[14] Melting points are uncorrected. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. The ir spectra were determined on a Perkin-Elmer grating spectrophotometer, Model 337, except for the high-dilution spectra which were run on a Perkin-Elmer Model 521 using 1-cm quartz cells. The nmr spectra were determined on a Varian A-60 spectrophotometer. The glpc analyses are corrected for differences in thermal conductivity of the components and were run on an F & M Model 500 gas chromatograph using a 10 ft × 0.25 in. column packed with 20% of a 2:1 mixture of Quadrol and SAIB[2] on 60–80 mesh, nonacid-washed Chromosorb P.

When **8** was recrystallized from acetone–water, it precipitated as a monohydrate: ir (KBr) $\sim$3370 (very broad), 3450 (sh), 3280 (sh) (OH, bonded), 1322, 1305 (OH bending), 1032 (CO?), 975 (S=O), 1087, 1129 cm^{-1}; the nmr, except for a more intense OH resonance, is identical with that of the anhydrous product.

Anal. Calcd for $C_{15}H_{26}O_3S \cdot H_2O$: C, 60.73; H, 8.92; S, 10.13. Found: C, 60.64; H, 8.96; S, 10.11.

Anhydrous **8** could be regenerated by heating of the monohydrate at 70° (1 mm) overnight or by recrystallizing it from chloroform.

The composition of this fraction was found to be dependent upon the reaction time as well as the ratio of starting ketone to ylide. When the reaction was allowed to proceed for several hours or when the K/Y ratio was low, fraction 2 consisted almost entirely of **8** or its monohydrate. However, when short reaction times and high K/Y ratios were employed only traces of **8** could be detected by ir. Instead large amounts of a new material (**10**) were isolated: ir (KBr) 3400 (broad, OH stretching, bonded), 1498, 1475, 1400, 1380, 1310, 1200, 1181, 1165, 1141, 1130, 1109, 1082, 1045, 1025 cm^{-1}. This product is almost totally insoluble in cold water, aqueous acid or base, acetone, chloroform, or benzene. It undergoes extensive decomposition when allowed to stand at room temperature or when heated with benzene or chloroform (*vide infra*). An analytical sample[15] was prepared by washing the crude product with chloroform and drying it at room temperature (1 mm) for 1 hr.

Anal. Calcd for $C_{24}H_{38}O_4S$: C, 68.21; H, 9.06; S, 7.59. Found: C, 66.37; H, 9.09; S, 8.13.

Fraction 3 was washed with saturated sodium chloride, dried (Na_2SO_4), and evaporated under reduced pressure to give 0.270 g of a semisolid residue. Fractional recrystallization from chloroform–hexane gave two crystalline materials. The more-soluble product (34 mg, mp 111–113°) was identical with authentic **7**, *vide supra*, while the less soluble product (38 mg, mp 210–212°) was identical with **8**, isolated from fraction 2.

B. Dependence of Product Composition on Reaction Conditions.—Solutions containing 0.505 g (4.6 mmol) of 7-ketonorbornane (**3**) in 5 ml of DMSO were added rapidly with stirring to samples of differing amounts of dimethyloxosulfonium methylide in 5 ml of dimethyl sulfoxide. The mixtures were stirred at room temperature for 1–24 hr, each was poured into $\sim$25 ml of ice–water, and the products separated into three fractions as described in part A.

Fraction 1 was analyzed by glpc on the Quadrol/SAIB column at 115°, the solvent was distilled at atmospheric pressure, and the residue was sublimed at 70° (20 mm). The yields of the epoxide 6 and recovered ketone 3 were estimated from the glpc analyses and from the weight of the sublimate. The results are summarized in Table I.

Fraction 2 was dried under vacuum at room temperature and the crude product was analyzed by ir.

Fraction 3 was dried at 100° (1 mm), weighed, dissolved in a measured volume of deuteriochloroform, and analyzed by nmr. The sulfoxides **7** and **8** constituted the major part of this fraction. Each sample also showed a sharp singlet of varying intensity at δ 2.65 which was presumably due to traces of DMSO. The nmr spectra of the crude mixtures suggested the presence of one or more other components. Runs 4 and 6 each showed a resonance at δ 4.9 which was absent in the spectra of the authentic **7** and **8**. In each sample the relative area of the δ 1.0–2.5 region was somewhat larger than that calculated for **7** and **8**. We estimate that the unidentified components constitute 10–30% of the total weight of fraction 3. The amounts of **7** and **8** in each sample can be estimated by comparing the peak areas at δ 3.13 and 3.25 (*i.e.*, the corresponding $>CCH_2SO-$ signals) with those of standard solutions of known concentration. The results are summarized in Table I. In the case of **8**, the values given represent the total product isolated from fractions 2 and 3.

The Reaction of the Metastable Intermediate (10) with 7-Ketonorbornene (1).—To a solution of 33 mg (0.31 mmol) of 7-ketonorbornene (**1**) in 2 ml of DMSO was added 66 mg (0.15 mmol) of **10** (from run 6; *cf.* Table I) and the mixture was stirred at room temperature. After $\sim$2 days all of the solid had dissolved. Stirring was continued for an additional 4 days. The solution was poured into $\sim$10 ml of cold water and extracted successively with five 3-ml portions of pentane and five 3-ml portions of chloroform. The pentane extract was concentrated to $\sim$1 ml and analyzed by glpc on the Quadrol/SAIB column at 115°. Unreacted **1** constituted about half of the volatile components. The chromatogram showed three additional peaks with relative retention times (areas) of 1.0 (25%), 1.4 (15%), and 1.7 (60%). The products were collected from the Quadrol/SAIB column and identified from their ir spectra as **5**, **6**, and **3**, respectively.

The chloroform extract was washed with saturated sodium chloride, dried (Na_2SO_4), and evaporated under reduced pressure to give 27 mg of crystalline residue. An nmr analysis showed this fraction to consist of a mixture of **7** and **8** (mole ratio, 1.0:1.5).

The Decomposition of the Intermediate 10. A. In Benzene.—A mixture of 100 mg of **10** and 2 ml of benzene was heated under reflux for 3 hr, cooled, poured into 4 ml of pentane, and filtered to give 33 mg of crystalline product. An nmr analysis indicated the presence of **7** and **8** in a mole ratio of 1.7:1.0. The filtrate was analyzed by glpc on the Quadrol/SAIB column, concentrated under atmospheric pressure, and distilled in a short-path still [70° (20 mm)] to give 32 mg of a liquid composed of **6** (47%) and **3** (53%). The nmr spectrum of the residue showed a small amount of **7** (estimated $\sim$4 mg) and a trace of DMSO.

B. In DMSO.—A suspension of 35 mg of **10** in 2 ml of DMSO was stirred at room temperature for 6 days. The mixture was worked up in the usual manner and analyzed by glpc and nmr. The volatile pentane-soluble products consisted of **6** (65%) and **3** (35%). The nonvolatile chloroform-soluble products were composed of **7** and **8** (mole ratio 1.3:1.0) and of unidentified product(s) (30%).

Registry No.—Dimethyloxosulfonium methylide, 14407-16-0; **3**, 10218-02-7; **6**, 159-42-2; **7**, 18592-72-8; **8**, 18592-73-9.

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(15) In addition to **10** the sample probably contains some **8** and may be contaminated with a trace of DMSO.