[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILL.]

Transannular Sulfoxide–Ketone Reactions and Oxygen Transfer[1]

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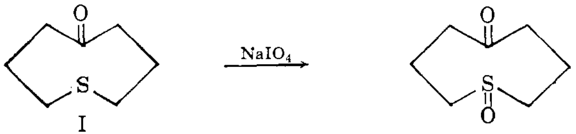
This investigation has established the occurrence of transannular interactions and reactions of the sulfoxide and ketone groups in medium rings. The representative compound, 1-thiacyclooöctan-5-one-1-oxide (II), used in this study was obtained in excellent yield by oxidation of 1-thiacyclooöctan-5-one (I) with aqueous sodium metaperiodate, a general method. The monocyclic 1-thiacyclooöctan-5-one-1-oxide was converted to a bicyclic perchlorate salt by transannular reaction involving protonation of the carbonyl oxygen. From infrared, proton magnetic resonance, kinetic and oxygen-18 exchange data, the perchlorate salt, its methoxy and acetoxy derivatives were assigned the 5-hydroxy-, 5-methoxy- and 5-acetoxy-9-oxa-1-thioniabicyclo[3.3.1]nonane structures (Va, VIa, VIIa), with an oxygen bridge between the sulfur and the carbonyl carbon. Hydrolysis of 5-acetoxy-9-oxa-1-thioniabicyclo[3.3.0]nonane perchlorate (VIIa) was shown to proceed by nucleophilic solvent attack on sulfur. The sequence 1-thiacyclooöctan-5-one-1-oxide to 5-acetoxy-9-oxa-1-thioniabicyclo[3.3.1]nonane perchlorate and hydrolysis back to the sulfoxide–ketone was shown to effect the transannular transfer of an oxygen atom.

In this Laboratory the study of transannular effects of diametrically opposed donor–acceptor groups in mesocycles has now been extended to include the combination of sulfoxide and ketone functions in an eight-membered model system (II).[3] Initial difficulties in arresting the oxidation of the known 1-thiacyclooöctan-5-one (I)[4,6] at the sulfoxide stage (II) were resolved when we turned to sodium metaperiodate as the oxidant.[7] The thiaketone and a slight excess of aqueous sodium metaperiodate, when stirred overnight at ice-bath temperature, gave the extremely hygroscopic 1-thiacyclooctan-5-one-1-oxide in 91% yield.



I

II

Physical Properties.—The infrared spectra of 1-thiacyclooöctan-5-one-1-oxide (II) showed typical carbonyl and sulfoxide absorptions, both giving the expected shifts to lower frequency with increasing polarity of the solvent. These data, accompanied by those of model compounds, are assembled in Table I.

TABLE I

INFRARED ABSORPTION MAXIMA (CM.$^{-1}$)

	Cyclo-octanone	1-Thiacyclooöctan-5-one-1-oxide		Hepta-methylene sulfoxide[8]
Solvent	C=O	C=O	S=O	S=O
C_6H_{12}	1709	1714	1060	1044
CCl_4	1701	1709	1052	1038
CH_3CN	1695	1705	..	..
$CHCl_3$	1689	1704	1023	1011
D_2O	..	1688	..	..

The electric dipole moments of 1-thiacyclooöctan-5-one-1-oxide and the corresponding 1,1-dioxide were obtained in benzene solution. These values, along with others recorded earlier,[6] permit, by simple trigonometric relations, the calculation of the average dihedral angles formed by the C–CO–C and C–X–C planes in our series of mesocyclic ketones (Table III). The assumed C=O and C–X–C moments are taken from the model compounds described in Table II. The dipole moment of the oxygen compound (III, X = O) requires a near-parallel orientation of the C–CO–C and C–O–C dipoles,[6] which in turn may be satisfied by a preponderance of a folded conformation. The average

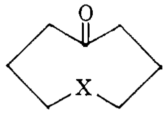
TABLE II

DIPOLE MOMENTS OF MODEL COMPOUNDS

Compound (in benzene)	μ, Debye
Cyclooöctanone	2.93[9]
Diethyl ether	1.22[10]
Diethyl sulfide	1.58[11]
Diethyl sulfoxide	3.85[11]
Diethyl sulfone	4.43[11]

TABLE III

ELECTRIC DIPOLE MOMENT DATA



III

Compound (in benzene)	X	μ, Debye	Av. dihedral angle[a]
1-Oxacyclooöctan-5-one	O	4.09[6]	21°
1-Thiacyclooöctan-5-one (I)	S	3.81[6]	68°
1-Thiacyclooöctan-5-one-1-oxide (II)	SO	3.37	81° (161°)[b]
1-Thiacyclooöctan-5-one-1,1-dioxide	SO_2	3.70	126°

[a] Calculated assuming no transannular induced dipole and the absence of interaction. [b] The dihedral angles of 81° and 161° correspond to the S=O bond at 142.5° and 99.5°, respectively, from the plane of the carbonyl group (see Fig. 2).

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[1] Partial support by research grants (NSF-G6040 and NSF-G14121) from the National Science Foundation is gratefully acknowledged.

[2] Lubrizol Foundation Fellow, 1960–1961.

[3] This work has been reported in part: Abstracts of Papers, 139th Meeting of the American Chemical Society, St. Louis, Mo., March 21–30, 1961, p. 30-O.

[4] N. J. Leonard, T. L. Brown and T. W. Milligan, *J. Am. Chem. Soc.*, **81**, 504 (1959).

[5] C. G. Overberger and A. Lusi, *ibid.*, **81**, 506 (1959).

[6] N. J. Leonard, T. W. Milligan and T. L. Brown, *ibid.*, **82**, 4075 (1960); **83**, 5047 (1961).

[7] N. J. Leonard and C. R. Johnson, *J. Org. Chem.*, **27**, 282 (1962), and references therein.

[8] A. E. Yethon, University of Illinois, private communication.

[9] T. Bürer and Hs. H. Günthard, *Helv. Chim. Acta*, **39**, 356 (1956).

[10] J. W. Smith, "Electric Dipole Moments," Butterworths Publications, Ltd., London, 1955.

[11] C. W. N. Cumper and S. Walker, *Trans. Faraday Soc.*, **52**, 193 (1956).

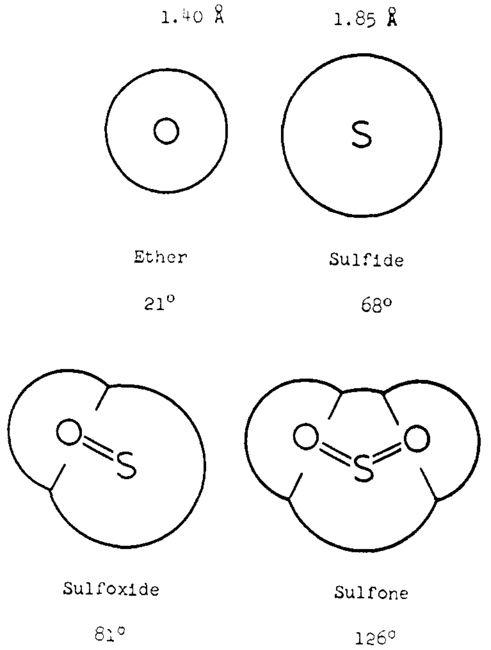
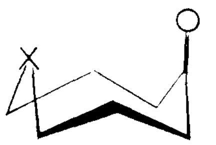


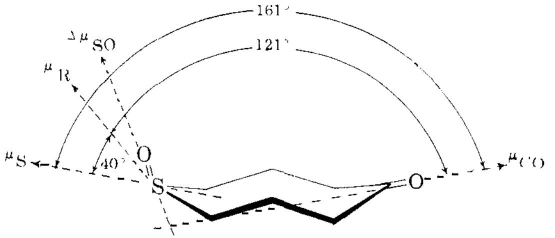
Fig. 1.—C/CO/C–C/X/C dihedral angles (in III); models based on van der Waals radii.

Crown, IIIa

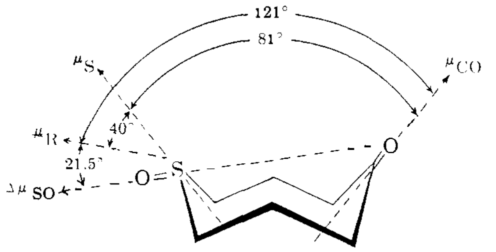


Folded, IIIb

dihedral angle θ of 21° suggests a folded form intermediate between a regular crown (IIIa) and an extreme with $\theta = 0°$ (IIIb), that is, a crown in which the opposed hydrogen interactions are balanced by spreading *between the C-3 and C-7 methylenes* and allowing the O-1 and the C-5 atoms to come into closer proximity.[6,12] The dipole moment of the sulfide ketone I indicates a larger dihedral angle $\theta = 68°$, for a time-average folded conformation, assuming no S–C_{CO} interaction in the ground state.[13] The calculation of the dihedral angle for the sulfoxide ketone II from the observed dipole moment must take into account the fact that the resultant vector of the sulfoxide group does not lie in the C–S–C plane. The value of the angle is based on the assumption of Cumper and Walker[11] that the angle between S=O and the C–S–C plane in a sulfoxide is 61.5°, and on the values of μ_S = 1.61 D. (as in ethyl sulfide) and $\Delta\mu_{SO}$ = 2.82 D. for the change in dipole in the S=O direction in going from the sulfide to the sulfoxide. The dipole moment (3.37 D.) of the eight-membered sulfoxide ketone indicates an angle of 121° between carbonyl (μ_{CO}) and sulfoxide (μ_R, 40° out of the C–S–C plane) dipole vectors. This corresponds to a dihedral angle formed by the C–CO–C and C–S–C planes of either 81° or 161°, since the oxygen may lie above or below the C–S–C plane. A study of models reveals that a dihedral angle of 161° (IIa) results in extremely unfavorable hydrogen–hydrogen non-bonded interactions, so that the dihedral angle of 81° (IIb) better defines a time-average conformation of the sulfoxide ketone, in benzene solution, intermediate between crown and folded. The dipole moment of the sulfone ketone III (X = SO_2) indicates a dihedral angle of 126°, which can be accommodated by a time-average conformation in which the opposing non-bonded interactions result in spreading the crown *between S-1 and C-5*. The interesting structural feature depicted by the dipole moment data is the increase in C/CO/C–C/X/C dihedral angle with a corresponding increase of the steric requirement of group X in the series of compounds III. This is shown clearly by comparison of the van der Waals radii in Fig. 1. The concept of distortion from the regular crown conformation by spreading between C-3 and C-7 or between X-1 and C-5 in compounds of type III, depending upon a balancing of the non-bonded interactions, is potentially useful in application to other eight-membered ring compounds.[12]



IIa



IIb

Although 1-thiacycloöctan-5-one-1-oxide (II) showed no abnormality in infrared spectrum or dipole moment, the medium ring sulfoxide ketone has an unusual ultraviolet spectrum. A maximum appears within the region 226.5 to 235 mμ, depending upon solvent, with an extinction of *ca.* log 2.8 (Table IV). A "blue shift" of this maximum is observed with increasing **Z**, a spectroscopic index of solvent polarity.[14] The parent 1-thiacycloöctan-5-one (I) also exhibits an anomalous maximum within the region 226 to 242 mμ with extinction of *ca.* log

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(12) (a) N. L. Allinger and S.-E. Hu, *J. Am. Chem. Soc.*, **83**, 1664 (1961); (b) N. L. Allinger, *ibid.*, **81**, 5727 (1959). (c) The terms "skewed crown" and "distorted crown" have also been employed (see also G. Chiurdoglu, Th. Doehaerd and B. Tursch, *Chemistry & Industry*, 1453 (1959)).

(13) The shifts in the infrared carbonyl frequency and carbonyl splitting previously observed[6] are now regarded as not necessarily indicative of S–C_{CO} interaction and may be due rather to Fermi resonance and/or combination bands in the infrared.[3]

(14) E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253, 3261, 3267 (1958).

TABLE IV

ULTRAVIOLET ABSORPTION MAXIMA

		1-Thiacycloöctan-5-one-1-oxide		1-Thiacycloöctan-5-one[6]	
Solvent	**Z**	λ_{max}, mμ	log ϵ^a	λ_{max}, mμ	log ϵ
C_6H_{12}	60.1	235	2.78	226	3.39
CH_3CN	71.3	231	2.76	229	3.43
C_2H_5OH	79.6	227	2.83	238	3.41
H_2O	94.6	226.5	2.83	242	3.45

[a] Additional uncertainty due to the extreme hygroscopic nature of the sulfoxide.

TABLE V

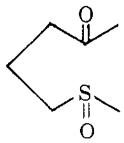
ELECTRONIC ABSORPTION MAXIMA IN CYCLOHEXANE

Compound	λ_{max}, mμ	log ϵ	λ_{max}, mμ	log ϵ	λ_{max}, mμ	log ϵ
1-Thiacycloöctan-5-one-1-oxide (II)	199[a]	3.38	235[a,b]	2.78	~290[b]	1.3
1-Thiacycloöctan-5-one (I)	192[c]	3.52	227[b,c]	3.46	288[b,d]	1.25
Methyl 4-ketopentyl sulfoxide (IV)	207,[a] ~215	3.46	...	..	275[b]	1.3
Methyl 4-ketopentyl sulfide	198,[c] ~210	3.4	...	..	278[b]	1.3
Cycloöctanone	<185[b]	>2.9	...	..	288[b]	1.18
Dimethyl sulfoxide	203[a]	3.4	...	..	...	..

[a] Bausch and Lomb Spectronic 505 spectrophotometer. [b] Cary model 14 spectrophotometer. [c] Beckman DK 2 spectrophotometer. We wish to record our appreciation to Professor C. A. Grob, University of Basel, for providing these spectra from our samples. The technique for short wave length has been described.[17] [d] This maximum exhibits fine structure.

3.4; however, a "red shift" is found with increasing **Z**.

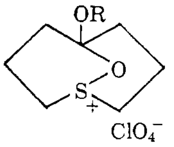
Such a reversal in solvent dependency can only be accounted for by a change in the mode of the electronic transition. The transition for the thiaketone I has been visualized as an effective electron transfer from the divalent sulfur into the nearby carbonyl system.[6] The spectrum observed for 1-thiacycloöctan-5-one-1-oxide (II), by contrast, appears to have retained the character of the sulfoxide chromophore, which is known to give blue shifts with increasing solvent polarity.[15,16] Neither a maximum nor a shoulder appears in the same region in the spectra of dimethyl sulfoxide or methyl 4-ketopentyl sulfoxide (IV), the open-chain model compound (Table V). Accordingly, the absorption maximum for 1-thiacycloöctan-5-one-1-oxide at 226.5 to 235 mμ, depending upon the solvent, apparently results from some electronic interaction between the sulfoxide grouping and the "neighboring" carbonyl across the ring.



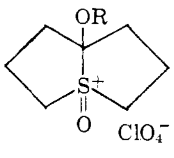
IV

Chemical Properties.—Dropwise addition of 70% perchloric acid to 1-thiacycloöctan-5-one-1-oxide in ether afforded a perchlorate salt in 93% yield. The infrared spectrum (CH_3CN) of the salt was free of carbonyl absorption but possessed a strong O–H stretching band at 3320 cm.$^{-1}$ (*cf.* VIII, ν_{OH} 3300 cm.$^{-1}$). In parallel with the previously obtained bicyclic salts of the aza- and thiacycloöctanones, this was a clear demonstration that salt formation had proceeded by *transannular reaction involving protonation of the carbonyl oxygen.* The ambident character of the sulfoxide grouping introduces a novel and subtle structural question to these studies of transannular reactions—the bicyclic salt may be formed by either transannular oxygen (type A) or sulfur alkylation (type B). The resolution of this problem is now described.

In contrast to 5-hydroxy-1-thioniabicyclo[3.3.0]-octane perchlorate (VIII)[6,18] simple recrystallization of V from methanol or ethanol did not afford the bridgehead alkoxy perchlorates. Nevertheless, easy access to the methoxy derivative VI was gained by treatment of V in acetone with 2,2-dimethoxypropane. Acetylation of V with acetic anhydride gave the 5-acetoxy compound VII.

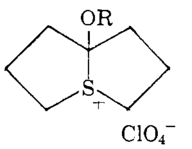


A



B

V, R = H
VI, R = CH_3
VII, R = $COCH_3$



VIII, R = H
IX, R = CH_3
X, R = $COCH_3$

Entirely in agreement with the motif of investigations of transannular effects in medium rings, neither the open chain analog IV nor the common-ring 1-thiacyclohexan-4-one-1-oxide formed salts with perchloric acid under the experimental conditions used for the mesocyclic ketones.

Dimethyl sulfoxide is known to form two series of alkyl derivatives. The products of kinetic control—the O-alkyl derivatives, illustrated by dimethyl-methoxysulfonium perchlorate (XI, Y = ClO_4)—are obtained by isolation of the reaction product of an alkyl arenesulfonate with dimethyl sulfoxide at the proper stage[19] or by alkylation of dimethyl sulfoxide with methyl iodide and silver

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(15) H. P. Koch, *J. Chem. Soc.*, 2829 (1950).

(16) A. Mangini, *Gazz. chim. ital.*, **88**, 1063 (1958).

(17) K. Stich, B. Rotzler and T. Reichstein, *Helv. Chim. Acta*, **42**, 1480 (1959).

(18) Previously[6] this compound has been named 5-hydroxybicyclo-[3.3.0]octane-1-thianium perchlorate. The change is made to conform to IUPAC 1957 Rules: *J. Am. Chem. Soc.*, **82**, 5572 (1960).

(19) S. G. Smith and S. Winstein, *Tetrahedron*, **3**, 317 (1958). The oxo-sulfonium nomenclature of Smith and Winstein, as opposed to "sulfoxonium," correctly emphasizes the sulfonium, rather than the oxonium, character of salts of type XII (*cf.* refs. 21, 22).

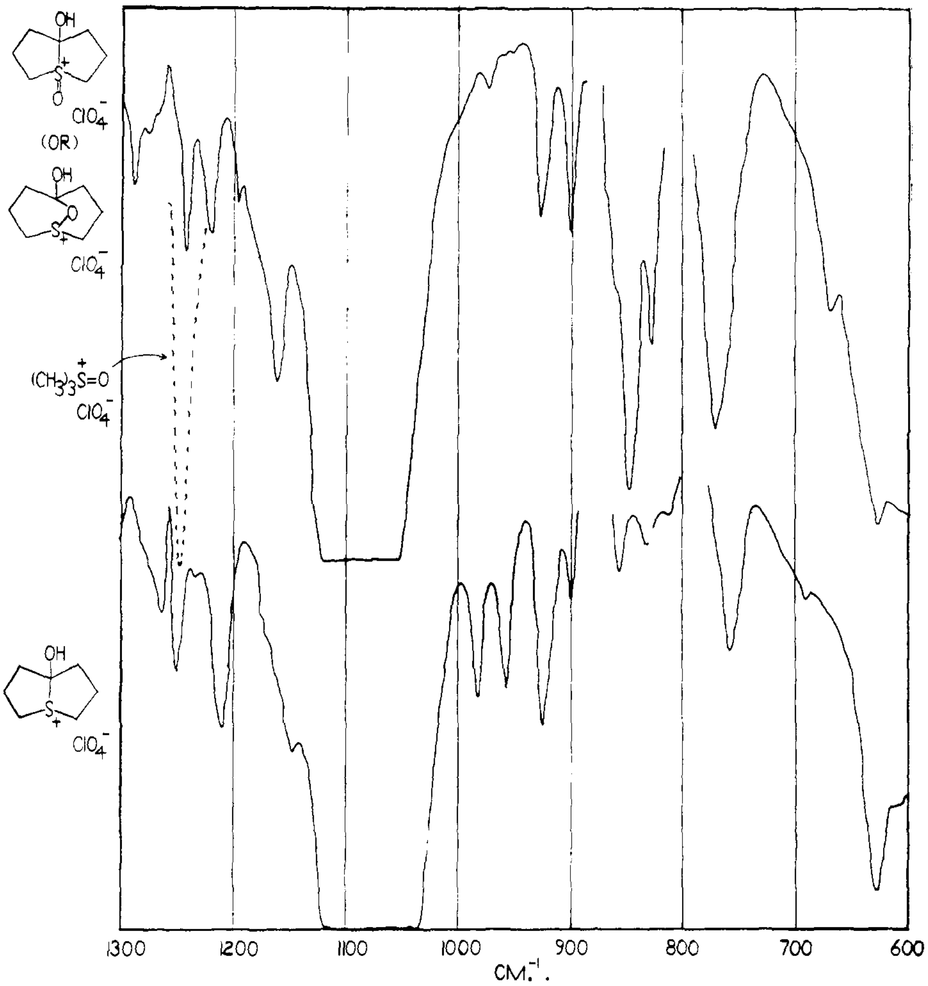
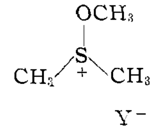
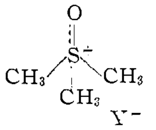


Fig. 2.

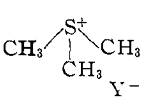
nitrate,[19] fluoroborate[20] or perchlorate. The thermodynamically stable isomeric adduct of type XII (Y = I, trimethyl-oxosulfonium iodide) may be obtained from dimethyl sulfoxide and methyl iodide.[19,21,22] Anion exchange between the iodide and silver salts is readily accomplished.[19,21]


$$\overset{OCH_3}{\underset{+}{CH_3\diagup S \diagdown CH_3}}\quad Y^-$$

XI


$$\overset{O}{\underset{CH_3}{CH_3\diagup S^{+} \diagdown CH_3}}\quad Y^-$$

XII


$$\overset{S^{+}}{\underset{CH_3}{CH_3\diagup\ \diagdown CH_3}}\quad Y^-$$

XIII

The infrared spectra of the S-alkyl sulfoxide adducts would be expected to exhibit a strong $\geqslant S^{+}=O$ absorption. Kuhn and Trischmann[21] have assigned the strong 1227 cm.$^{-1}$ band (Nujol) observed in trimethyl-oxosulfonium iodide (XII, X = I) to the S=O stretching vibration. Trimethyl-oxosulfonium perchlorate, in acetonitrile solution, has this strong band at 1245 cm.$^{-1}$. The only other maximum of trimethyl-oxosulfonium iodide found in the general region of S=O stretch is at 1027 cm.$^{-1}$; however, a band appears at this same position in trimethylsulfonium iodide. Additional evidence for the $^{+}S=O$ stretching assignment is found in the infrared spectrum of the perdeuteriotrimethyl-oxosulfonium iodide.[23] All frequencies below 1300 cm.$^{-1}$ are lowered by more than 20 cm.$^{-1}$ except the band under discussion, which moves from 1227 to 1235 cm.$^{-1}$.

The decrease in electron density at the sulfur atom in trimethyl-oxosulfonium salts would be expected to raise the frequency of the sulfur–oxygen stretching vibration over that of dimethyl sulfoxide (*ca.* 1050 cm.$^{-1}$) by increased contribution of $\geqslant S^{+}=O$ in relation to $\geqslant S^{++}-O^{-}$.[24-26] In the perchlorate V and in its derivatives VI and VII no bands appear in the region near 1245 cm.$^{-1}$ in acetonitrile that are not present in the corresponding sulfonium compounds (VIII, IX, X), suggesting structures of type A (Fig. 2).

A comparison of the proton magnetic resonance spectra of the sulfoxide-ketone perchlorate and

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(20) H. Meerwein, V. Hederich and K. Wunderlich, *Arch. Pharm.*, **291**, 541 (1958).

(21) R. Kuhn and H. Trischmann, *Ann.*, **611**, 117 (1958); *Angew. Chem.*, **69**, 570 (1957).

(22) R. T. Major and H.-J. Hess, *J. Org. Chem.*, **23**, 1563 (1958).

(23) F. A. Cotton, J. H. Fassnacht, W. D. Horrocks, Jr., and N. A. Nelson, *J. Chem. Soc.*, 4138 (1959).

(24) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, 1958, and references cited therein.

(25) A. Simon, H. Kriegsmann and H. Dutz, *Chem. Ber.*, **89**, 2390 (1956).

(26) P. B. D. de la Mare, W. Klyne, D. J. Millen, J. G. Pritchard and D. Watson, *J. Chem. Soc.*, 1813 (1956).

TABLE VI

PROTON MAGNETIC RESONANCE DATA FOR SULFONIUM PERCHLORATES

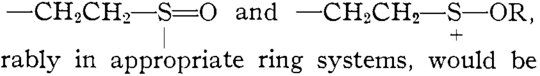
Compound, perchlorate	τ α-Protons	τ β,γ-Protons	τ Other
Trimethylsulfonium[a] (XIII)	6.97s[c]	....	
Dimethyl-methoxysulfonium[a] (XI)	6.58s	....	$-OCH_3$, 5.75s
Trimethyl-oxosulfonium[a] (XII)	6.12s	....	
5-Hydroxy-1-thioniabicyclo[3.3.0]octane[b] (VIII)	6.44m	7.48m	
5-Methoxy-1-thioniabicyclo[3.3.0]octane[b] (IX)	....	....	$-OCH_3$, 6.30s
5-Acetoxy-1-thioniabicyclo[3.3.0]octane[a] (X)	6.23m	7.32m	$-CCH_3$, 7.67s
5-Hydroxy-9-oxa-1-thioniabicyclo[3.3.1]nonane[b] (VA)	6.30m	7.69m	
5-Methoxy-9-oxa-1-thioniabicyclo[3.3.1]nonane[b] (VIA)	....	....	$-OCH_3$, 6.50s
5-Acetoxy-9-oxa-1-thioniabicyclo[3.3.1]nonane[a] (VIIA)	6.25m	7.48m	$-CCH_3$, 7.73s

[a] Trifluoroacetic acid solution. [b] Perdeuterioacetone solution. [c] s = singlet, m = multiplet, value given is the center of the multiplet.

derivatives (V, VI, VII) utilizing both simple model systems (I) and the perchlorate and derivatives of 1-thiacycloöctan-5-one (VIII, IX, X) augments the conclusion that the structures in question are of type A.

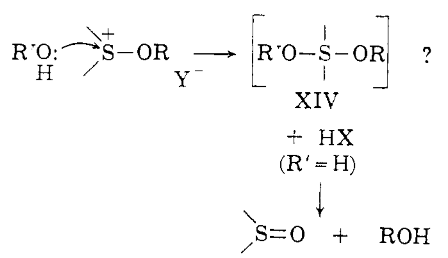
An examination of the n.m.r. signals of the protons alpha to the positive sulfur of the compounds enumerated in Table VI is instructive. The difference in τ-values observed for the α-protons of trimethylsulfonium perchlorate (XIII, $Y = ClO_4$) and the α-protons of 5-acetoxy-1-thioniabicyclo[3.3.0]octane perchlorate (X) is 0.74. Approximately the same relationship would be expected to hold with trimethyl-oxosulfonium perchlorate (XII, $Y = ClO_4$) and the bicyclic analog, 5-acetoxy-1-thioniabicyclo[3.3.0]octane-1-oxide perchlorate (VIIB). This assumption then leads to the prediction of a value of $6.12 - 0.74$ or 5.38 for the α-protons in a formulation like VIIB. In like manner, using the value of 6.58 for the S-methyl protons of dimethyl-methoxysulfonium perchlorate, and correcting by +0.15 for the transition from a five- to a six-membered ring,[27] one estimates 5.99 for the α-protons in expression VIIA. With similar treatment of data, the estimations of 6.20 and 5.58 are obtained for the α-protons in VA and VB, respectively. The observed values of the acetoxy compound (6.25) and the hydroxy compound (6.30) are indicative of the bicyclononane systems VIIA and VA, respectively.

The upfield shift of the signal of the β,γ-protons in the sulfoxide-perchlorates (VA, VIIA) in comparison with the thiaketone perchlorates (VIII, X) is consistent with a transition from a five- to a six-membered ring system. The existence of the type A structure is also supported by the resonance of the O-methyl protons of VI at 6.50 as compared with 6.30 in IX (*cf.* $(CH_3O)_2C(CH_3)_2$, $\tau = 6.93$). Upon examination of the models the conclusion is reached that the O-methyl proton resonance in the expression 5-methoxy-1-thioniabicyclo[3.3.0]octane-1-oxide perchlorate (VIB) would be at least at as low a field as that of 5-methoxy-1-thioniabicyclo-[3.3.0]octane perchlorate (IX), especially in view of the recent conclusion of Pritchard and Lauterbur[28] that the contribution made by magnetic anisotropy to the chemical shift of protons above the S=O bond is toward lower field.

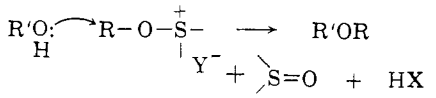
Additional model compounds for n.m.r. spectroscopy, especially examples containing the groupings  $-CH_2CH_2-\overset{+|}{\underset{|}{S}}=O$ and $-CH_2CH_2-\overset{|}{\underset{+}{S}}-OR$, preferably in appropriate ring systems, would be advantageous. Such compounds were not accessible by the synthetic routes chosen, possibly because of competing elimination reactions.

Smith and Winstein[19] have recently found the O-alkyl adducts of dimethyl sulfoxide to be rapidly hydrolyzed in aqueous media, whereas the S-alkyl adducts, like sulfonium salts, were inert. The solvolysis of these O-alkyl derivatives could proceed either by nucleophilic attack on sulfur or by carbon–oxygen cleavage, depicted by schemes a and b. Smith[29] did not find benzyl methyl ether produced by the solvolysis of dimethyl-benzyloxysulfonium tosylate in absolute methanol but, rather, benzyl alcohol was isolated after addition of water. The production of acid without the accompanying formation of an ether follows scheme a; moreover, the possible intervention of a neutral intermediate (perhaps XIV) is suggested. Such a compound (XIV), which might be capable of being isolated, may be named a "sulfoxal." In ketal hydrolysis Kreevoy, Morgan and Taft[30] have found the rates to indicate that the transition state has considerable carbonium ion geometry. One would predict, then, in the breakdown of a hypothetical

Scheme a



Scheme b



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[27] For example, we find the multiplets attributable to the ring α-protons of 1-methyl-1-thioniacyclopentane and 1-methyl-1-thioniacyclohexane perchlorate centered at 6.37 and 6.52.

[28] J. G. Pritchard and P. C. Lauterbur, *J. Am. Chem. Soc.*, **83**, 2105 (1961).

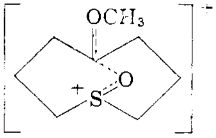
[29] S. G. Smith, Ph.D. Thesis, University of California, Los Angeles, Calif., 1959.

[30] M. M. Kreevoy, C. R. Morgan and R. W. Taft, Jr., *J. Am. Chem. Soc.*, **82**, 3064 (1960).

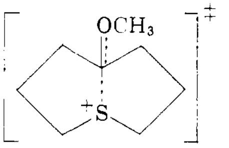
intermediate such as XIV (R = alkyl), that the transition state would have substantial sulfonium ion character.

In order to gain additional evidence for nucleophilic solvent attack on sulfur, dimethyl-methoxysulfonium perchlorate (XI, Y = ClO_4) was solvolyzed in oxygen-18 enriched water (1.67 atom % excess oxygen-18). That path a was predominant was shown by the oxygen-18 enrichment (1.48 atom % excess) of the dimethyl sulfoxide isolated from the solvolysis, in consideration with the observation that dimethyl sulfoxide did not exchange oxygen under acid (perchloric) conditions.[31]

On the basis of these observations it appeared that chemical evidence for expression A, heretofore argued from physical data, might be at hand through a comparison of solvolytic rates and oxygen-18 exchange reactions of the bicyclic systems with those of simple model compounds. The bridge-head acetates VII and X were chosen for the initial experiments, since if structure VIIA were correct the solvolysis of the bicyclic salt, in analogy to the model compound dimethyl-methoxysulfonium perchlorate, might proceed by solvent attack on sulfur. The solvolysis of the corresponding methoxy compounds (VI and X) more likely would occur *via* ionization (XV and XVI) facilitated by stabilization of the incipient carbonium ion by the methoxyl group.



XV



XVI

The first indication of the great difference in reactivity between 5-acetoxy-1-thioniabicyclo[3.3.0]octane perchlorate (X) and 5-acetoxy-9-oxa-1-thioniabicyclo[3.3.1]nonane perchlorate (VIIA) was provided by following the extent of their solvolyses in water from the appearance of the ultraviolet maxima of the parent ketones. While the full extinction expected of the sulfoxide ketone was observed thirty seconds after mixing VIIA with water, the solvolysis of 1-acetoxy-1-thioniabicyclo[3.3.0]octane perchlorate in water was less than 25% complete after 180 hours at room temperature. In consideration of the known stability of both trimethylsulfonium and trimethyl-oxosulfonium perchlorates in water, there can be little doubt, therefore, that a change in structure more deep-seated than going from system X to VIIB would be required to produce such a difference in the rates of solvolysis. Kinetic data for both bicyclic and model systems were available by titration of the acid developed during solvolysis. The results catalogued in Table VII were obtained through use of an automatic recording titrimeter, set to hold constant pH 5, with sodium methoxide as the titrant. Absolute and 95% methanol were used as solvents. The key points of these data are the similarity of the rates of solvolysis of the bicyclic salt VIIA and dimethyl-methoxysulfonium perchlorate and the inert nature of the isomeric trimethyl-oxosulfonium perchlorate. The increase in rate of the bridgehead methoxy compounds over the corresponding acetoxy compounds in both the sulfide and sulfoxide series is taken to reflect the predicted change of mechanism to solvolysis by ionization rather than by solvent participation (XV, XVI).

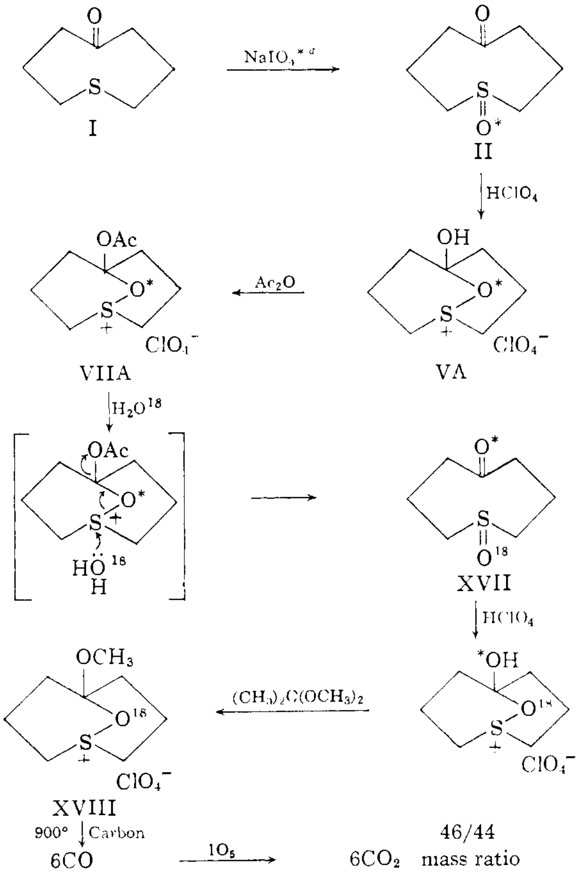
TABLE VII

SUMMARY OF SOLVOLYTIC RATE CONSTANTS FOR SULFONIUM PERCHLORATES[a]

Compound, perchlorate	Temp., °C.	$10^3 k_1$, sec.$^{-1}$ (pH 5) Methanol	95% methanol
Trimethylsulfonium (XIII)	25	N.R.[b]	N.R.
Trimethyl-oxosulfonium (XII)	25	N.R.	N.R.
Dimethyl-methoxysulfonium (XI)	2	7.3	..
	4	..	41
5-Acetoxy-9-oxa-1-thionia-bicyclo[3.3.1]nonane (VIIA)	2	3.0	..
	4	..	12
5-Acetoxy-1-thioniabicyclo-[3.3.0]octane (X)	25	..	<0.01
5-Methoxy-9-oxa-1-thionia-bicyclo[3.3.1]nonane (VIA)	4	>100	..
5-Methoxy-1-thioniabicyclo-[3.3.0]octane (IX)	4	~15	..

[a] For complete data see Table IX in Experimental section.
[b] N.R. means no reaction.

Scheme c



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[a] The asterisk does not signify isotopic label, but serves only to indicate the oxygen derived originally from periodate.

[31] S. Oae, T. Kitao and Y. Kitaoka, *Chemistry & Industry*, 291 (1961), likewise, found that phenyl sulfoxide in concentrated sulfuric acid solution did not incorporate the label when the solution was diluted with oxygen-18 enriched water.

TABLE VIII

SUMMARY OF OXYGEN-18 LABELING DATA

Compound	Source	R^a	Excess^b O-18 (atom %)
Dimethyl sulfoxide	CH_3SOCH_3, $HClO_4$, H_2O^{18}	0.00407	0.00
Dimethyl sulfoxide	$(CH_3)_2\overset{+}{S}OCH_3\ ClO_4^-$, H_2O^{18}	.01910	1.48
Trimethyl-oxosulfonium iodide	$(CH_3)_3\overset{+}{S}O\ I^-$, recovd. from H_2O^{18}	.00501	0.09
5-Methoxy-9-oxa-1-thioniabicyclo[3.3.1]nonane perchlorate	Refer to scheme c	.00662	1.51^c
5-Methoxy-9-oxa-1-thioniabicyclo[3.3.1]nonane perchlorate	$VA \xrightarrow{H_2O^{18}} II \longrightarrow VA \longrightarrow VIA$	.00408	0.00
Enriched water	Weizmann Institute	.02118	1.67

[a] Mass ratio 46/44, normalized. [b] In excess of natural abundance, 0.204 atom %. [c] Label in position 9 only.

Acetate VIIA was solvolyzed to the sulfoxide ketone in oxygen-18 enriched water. After extraction into chloroform, the free ketone XVII was converted to the perchlorate, which, in turn, was transformed to 5-methoxy-9-oxa-1-thioniabicyclo-[3.3.1]nonane perchlorate (XVIII) by reaction with 2,2-dimethoxypropane (scheme c). Step by step analysis of the sequence reveals that in the sulfoxide-ketone XVII produced by the solvolysis, the *only* oxygen present which remained throughout the scheme was the sulfoxide oxygen. (The perchlorate anion of the product XVIII was not exposed to enriched water, and the carbonyl oxygen of the ketone XVIII was replaced in the conversion to the methoxy compound.) Pyrolysis of XVIII over hot carbon to carbon monoxide, oxidation of the carbon monoxide to carbon dioxide by the Unterzaucher method, followed by mass spectrographic determination of the 46/44 mass ratio showed XVIII to contain 0.252 atom per cent. excess oxygen-18. Since by the method of synthesis all of the excess isotope must be present in the bridged oxygen, this must contain (6 × 0.252) or 1.51 atom per cent. excess oxygen-18, in good agreement with the water (1.67 atom %).

That such an exchange could occur only with structure VIIA follows from the data provided in Table VIII. Exchange occurred with dimethylmethoxysulfonium perchlorate (the model for system A) but not with dimethyl sulfoxide, even under acid conditions; by contrast, the model compound for structures of type B, trimethyl-oxosulfonium iodide, in oxygen-18 enriched water solution incorporated relatively small amounts (*ca.* 0.1 atom %) of label, even at steam-bath temperatures. To prove that incorporation of oxygen-18 took place *during* but not *after* the solvolysis of the bicyclic acetate VIIA, 5-hydroxy-9-oxa-1-thioniabicyclo-[3.3.1]nonane perchlorate (VA) was treated in a manner identical with that described above for the corresponding acetate. No excess isotope was found in the product.

In addition to providing evidence for the existence of the bridged-oxygen structure in the salts of the sulfoxide ketone and aiding in the understanding of the mechanism of solvolysis of alkoxysulfonium salts, these oxygen exchange experiments revealed another interesting feature—the reaction sequence 1-thiacyclooöctan-5-one-1-oxide (II) to 5-acetoxy-9-oxa-1-thioniabicyclo[3.3.1]nonane perchlorate (VIIA) and back to the sulfoxide ketone effects *the transannular transfer of an oxygen atom, i.e.*, the sulfoxide oxygen becomes the carbonyl oxygen, as formulated in detail in scheme c.

Acknowledgment.—It is a pleasure to acknowledge the helpful discussions and generous assistance of our colleagues Dr. Stanley G. Smith and Dr. Theodore L. Brown.

Experimental[32]

1-Thiacyclooöctan-5-one-1-oxide (II).[7]—1-Thiacyclooöctan-5-one[4-6,33] (1.44 g., 10 mmoles), m.p. 53–54°, was added to an aqueous solution of sodium metaperiodate (220 ml., 0.05 *M*, 11 mmoles) at 0°. Crude product (1.45 g., 91%) was obtained by continuous extraction with chloroform, drying the extract over anhydrous magnesium sulfate, and evaporation of the solvent at reduced pressure. The 1-thiacyclooöctan-5-one-1-oxide was purified by regeneration from the perchlorate (see below).

5-Hydroxy-9-oxa-1-thioniabicyclo[3.3.1]nonane Perchlorate (VA).—Perchloric acid (70%) was added dropwise to an ether solution containing 500 mg. (3.12 mmoles) of 1-thiacyclooöctan-5-one-1-oxide until precipitation was complete. The salt (740 mg., 93%) was thoroughly washed with ether and recrystallized as colorless needles from acetone–ether; m.p. 106.5° dec. Its infrared spectrum (15%, CH_3CN) was free of absorption in the 6 μ region but had a strong band at 3320 cm.$^{-1}$ (O–H).

Anal. Calcd. for $C_7H_{13}ClO_6S$: C, 32.25; H, 5.03; O, 36.83; neut. equiv., 260.7. Found: C, 32.17, H, 4.94; O, 37.00; neut. equiv., 262.

The sulfoxide-perchlorate VA failed to exchange $-OH$ for $-OCH_3$ or $-OC_2H_5$ when recrystallized from methanol or ethanol. Under these conditions exchange occurs with 5-hydroxy-1-thioniabicyclo[3.3.0]octane perchlorate (VIII).[6]

Regeneration of 1-Thiacyclooöctan-5-one-1-oxide from its Perchlorate by Base.—The perchlorate (809 mg., 3.11 mmoles) was dissolved in 10 ml. of water and titrated to phenolphthalein end-point with sodium hydroxide (0.100 *N*, 30.80 ml.). The basic solution was extracted continuously for 20 hr. with chloroform. The chloroform solution was dried and concentrated at reduced pressure, leaving 475 mg. (97%) of analytically pure 1-thiacyclooöctan-5-one-1-oxide, m.p. 91–92°. This sulfoxide is extremely hygroscopic, rapidly becoming a sirup on exposure to the atmosphere. The infrared spectrum (2.5% in CCl_4) had selected maxima at 1709 (C=O) and 1052 cm.$^{-1}$ (S=O).

Anal. Calcd. for $C_7H_{12}O_2S$: C, 52.48; H, 7.55. Found: C, 52.46; H, 7.86.

5-Acetoxy-9-oxa-1-thioniabicyclo[3.3.1]nonane Perchlorate (VIIA).—One hundred milligrams (0.385 mmole) of the perchlorate salt VA was dissolved slowly in 1 ml. of acetic anhydride. The solution was allowed to stand at room temperature for 30 min., then diluted with 10 ml. of ether. The

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[32] Melting points are corrected; boiling points are uncorrected. The authors are indebted to Mr. Josef Nemeth and his associates for the microanalyses, to Mr. Oliver Norton, Mr. Dick Johnson and their associates for the n.m.r. and the infrared spectra and to Mr. Josef Nemeth and Mrs. Nancy Neilson for assistance with the oxygen-18 analyses.

[33] The authors are indebted to their colleagues Mr. W. L. Rippie, Dr. Takeo Sato and Mr. K. R. Fountain for timely gifts of 1-thiacyclooctan-5-one during the course of this investigation.

TABLE IX

KINETIC DATA FOR THE SOLVOLYSES OF SULFONIUM PERCHLORATES AT *p*H 5

Compound, perchlorate	Solvent	Temp., °C.	Time, sec.	Microequiv. acid produced	$k_1 \times 10^3$, sec.$^{-1}$	Av. $k_1 \times 10^3$, sec.$^{-1}$
Dimethyl-methoxysulfonium	CH_3OH	2	0.0	8.40		
			15.6	11.2	7.23	
			33.0	13.9	7.25	
			95	21.3	7.28	7.28 ± 0.04
			123	23.7	7.34	
			∞	34.3		
Dimethyl-methoxysulfonium	95% CH_3OH	4	0.0	5.40		
			5.4	8.90	36	
			10.8	12.5	41	
			20.8	16.1	37	
			24	18.9	46	41 ± 4
			63	21.7	46	
			∞	25.6		
5-Acetoxy-9-oxa-1-thioniabicyclo-[3.3.1]nonane	CH_3OH	2	0.0	0.80		
			24	1.70	3.06	
			48	2.54	3.02	
			112	4.40	2.98	
			239	7.30	3.02	3.02 ± 0.02
			302	8.50	3.03	
			∞	13.4		
5-Acetoxy-9-oxa-1-thioniabicyclo-[3.3.1]nonane	95% CH_3OH	4	0.0	2.50		
			32	6.40	12.8	
			62	8.60	12.2	12.0 ± 0.5
			99	10.3	11.6	
			135	11.5	11.6	
			∞	13.9		
5-Methoxy-1-thioniabicyclo[3.3.0]-octane	CH_3OH	4	0.0	3.80		
			10.2	7.20	14.8	
			16.2	8.30	15.0	15.2 ± 0.4
			24.6	10.4	14.8	
			46.2	13.3	15.8	
			∞	15.4		
5-Methoxy-9-oxa-1-thioniabicyclo-[3.3.1]nonane	CH_3OH	4	40	..	..	>100
5-Acetoxy-1-thioniabicyclo[3.3.0]-octane	95% CH_3OH	25	0	0.00		
			3600	.00	..	<0.01
			4280	.90		
Trimethylsulfonium	95% CH_3OH	25		No reacn.		
Trimethyl-oxosulfonium	95% CH_3OH	25		No reacn.		

crystals (102 mg., 87%) were collected, washed thoroughly with ether, then recrystallized as fine colorless needles from acetic anhydride–ether; m.p. 107–109° dec. (tube inserted in bath at 90°; m.p. depends on rate of heating); $\nu_{\max}^{CH_3CN(2.5\%)}$ 1777 cm.$^{-1}$ (acetate), devoid of absorption above 3 μ. The compound was found to be unstable on standing (3 days).

Anal. Calcd. for $C_9H_{15}ClO_7S$: C, 35.73; H, 5.00; neut. equiv., 151.8. Found: C, 35.54; H, 5.13; neut. equiv., 153.1.

5-Methoxy-9-oxa-1-thioniabicyclo[3.3.1]nonane Perchlorate (VIA).—To 180 mg. of 5-hydroxy-9-oxa-1-thioniabicyclo[3.3.1]nonane perchlorate dissolved in 3 ml. of acetone 2 ml. of 2,2-dimethoxypropane was added. After a few minutes crystals began to appear. The mixture was allowed to stand for 4 hours at room temperature and then was diluted with ether to complete the precipitation of the product. The infrared spectrum (Nujol) of the crude salt, 186 mg. (97%), m.p. 150–152° dec., was free of C=O and O—H absorption. The 5-methoxy-9-oxa-1-thioniabicyclo[3.3.1]-nonane perchlorate was recrystallized once from methanol–ether affording lustrous colorless needles, m.p. 151–152° dec.

Anal. Calcd. for $C_8H_{15}ClO_6S$: C, 34.98; H, 5.46; neut. equiv., 275.5. Found: C, 34.94; H, 5.40; neut. equiv., 275.5.

5-Methoxy-1-thioniabicyclo[3.3.0]octane Perchlorate (IX).—To 3 ml. of acetone solution containing 180 mg. of 5-hydroxy-1-thioniabicyclo[3.3.0]octane perchlorate (VIII) 2 ml. of 2,2-dimethoxypropane was added. Crystals began to appear after a few minutes. After 4 hours at room temperature ether was added to complete the precipitation. No C=O or O—H absorption was present in the infrared spectrum (CH_3CN) of the crude product, 185 mg. (96%), m.p. 154–155° dec. A single recrystallization from methanol afforded analytically pure material, m.p. 154–155° dec. (reported earlier[6] 147.5–149.5° dec.).

Anal. Calcd. for $C_8H_{15}ClO_5S$: C, 37.14; H, 5.84; neut. equiv., 259.5. Found: C, 37.39; H, 5.97; neut. equiv., 260.0.

The same compound has been obtained previously by simple recrystallization of the perchlorate VIII from methanol.[6]

1-Thiacycloöctan-5-one-1,1-dioxide (III, **X** = SO_2).—In an attempt to prepare the sulfoxide by treatment of 1-thiacycloöctan-5-one in methylene chloride at −50° with ozone only the sulfone was obtained, lustrous needles from ethanol; m.p. 134–134.5° (reported[6] 124–127°). The infrared spectrum was identical with that previously reported.[6]

Anal. Calcd. for $C_7H_{12}O_3S$: C, 47.70; H, 6.87. Found: C, 47.87; H, 7.17.

Methyl 4-Ketopentyl Sulfoxide (IV).[7]—To a solution (0.5 *M*) of sodium metaperiodate (19.8 g., 92 mmoles) in 185 ml. of water was added 11.1 g. (84 mmoles) of 5-methylmercapto-2-pentanone (methyl 4-ketopentyl sulfide).[6] The mixture was stirred overnight in an ice-bath, the precipitated sodium iodate was removed by filtration, and the solution was extracted with 5 volumes of chloroform. The chloroform solution was dried over anhydrous magnesium sulfate and concentrated at reduced pressure leaving 12.1 g. (98%) of crude product. A single vacuum distillation afforded 8.1 g. (65%) of analytically pure methyl 4-ketopentyl sulfoxide, b.p. 99–101° (0.12 mm.), n^{25}D 1.4873, m.p. 22.5–23.5°; selected infrared maxima (2.5% in chloroform): 1718 (C=O) and 1058 cm.$^{-1}$ (S=O).

Anal. Calcd. for $C_6H_{12}O_2S$: C, 48.66; H, 8.17. Found: C, 48.86; H, 8.25.

Under the identical conditions required for the formation of the perchlorate salt of 1-thiacycloöctan-5-one-1-oxide no reaction was observed for this open-chain compound.

The 1-thiacyclohexan-4-one-1-oxide[7] also failed to yield a perchlorate salt under the conditions for the formation of 5-hydroxy-9-oxa-1-thioniabicyclo[3.3.1]nonane perchlorate.

Trimethyl-oxosulfonium Perchlorate (XII, Y = ClO_4) was prepared in good yield by exchange between trimethyl-oxosulfonium iodide[19,21,22] and silver perchlorate in aqueous solution; m.p. 271–275° dec. *Caution! In a subsequent m.p. check the sample violently exploded at 262°, demolishing the Hershberg apparatus.* The infrared spectra were identical with those of an authentic sample kindly furnished by Dr. S. G. Smith,[29] ν_{max}^{Nujol} 1227(s), 1100 (perchlorate), 945 and 753 cm.$^{-1}$, $\nu_{max}^{CH_3CN}$ 1245(s) cm.$^{-1}$. The n.m.r. spectrum in trifluoroacetic acid showed only a singlet at 6.12.

Dimethyl-methoxysulfonium Perchlorate (XI, Y = ClO_4).—The procedure is an adaptation of that used for the analogous tetrafluoroborate salt.[20] *Caution! A sample of this material spontaneously exploded under storage in a desiccator.* Dimethyl sulfoxide (1.88 g., 24 mmoles) was added to a stirred suspension of anhydrous silver perchlorate (5.0 g., 24 mmoles) in 50 ml. of ethylene chloride, then excess methyl iodide (10 ml.) was added. Precipitation of salts began immediately and the solution became quite warm. After standing for 15 hours, the precipitated salts were filtered with suction. The desired perchlorate was eluted from the silver iodide with acetonitrile. The dimethyl-methoxysulfonium perchlorate precipitated from acetonitrile by addition of carbon tetrachloride, was recrystallized from acetonitrile–ether; yield 2.3 g. (48%); $\nu_{max}^{CH_3CN(10\%)}$ 1100 (broad perchlorate), 955 and 760 cm.$^{-1}$ (absence of 1245 cm.$^{-1}$ band of $\overset{+}{S}$=O). The n.m.r. spectrum in trifluoroacetic acid [τ = 5.75 (OCH_3) and 6.58 (2 $\overset{+}{S}CH_3$)] indicated the oxygen-alkylated structure. Due to the thermo- and impact-sensitive nature of this compound the microanalysis and m.p. were not obtained.

Anal. Calcd. for $C_3H_9ClO_5S$: neut. equiv., 201.5. Found: neut. equiv., 200.3.

Attempted Alkylation of Other Sulfoxides.—Efforts to alkylate *n*-butyl sulfoxide and tetramethylene sulfoxide by refluxing methyl iodide or sealed tube reaction with methyl bromide afforded the corresponding sulfonium salts as the only crystalline products. No crystalline product was obtained from the reaction of acetoxymethyl methyl sulfoxide and methyl iodide.

An attempted preparation of ethyldimethyl-oxosulfonium iodide from ethyl iodide and dimethyl sulfoxide yielded only trimethyl-oxosulfonium iodide.

Analysis for Oxygen-18.—The procedure and apparatus used for the analyses were those of Doering and Dorfman[34] as modified by Denney and Greenbaum.[35] The calculations were made using the equations of Miller and Anderson.[36]

The nitrogen carrier gas used in the analyses was passed through metallic copper heated to 600° by an A. H. Thomas preheater furnace to remove traces of oxygen. During the combustions, the flow rate was maintained at 13 ml. per minute. The samples were vaporized by a small flame into a combustion chamber, containing a platinum sleeve in the entrance area and carbon–platinum packing, heated to 890–

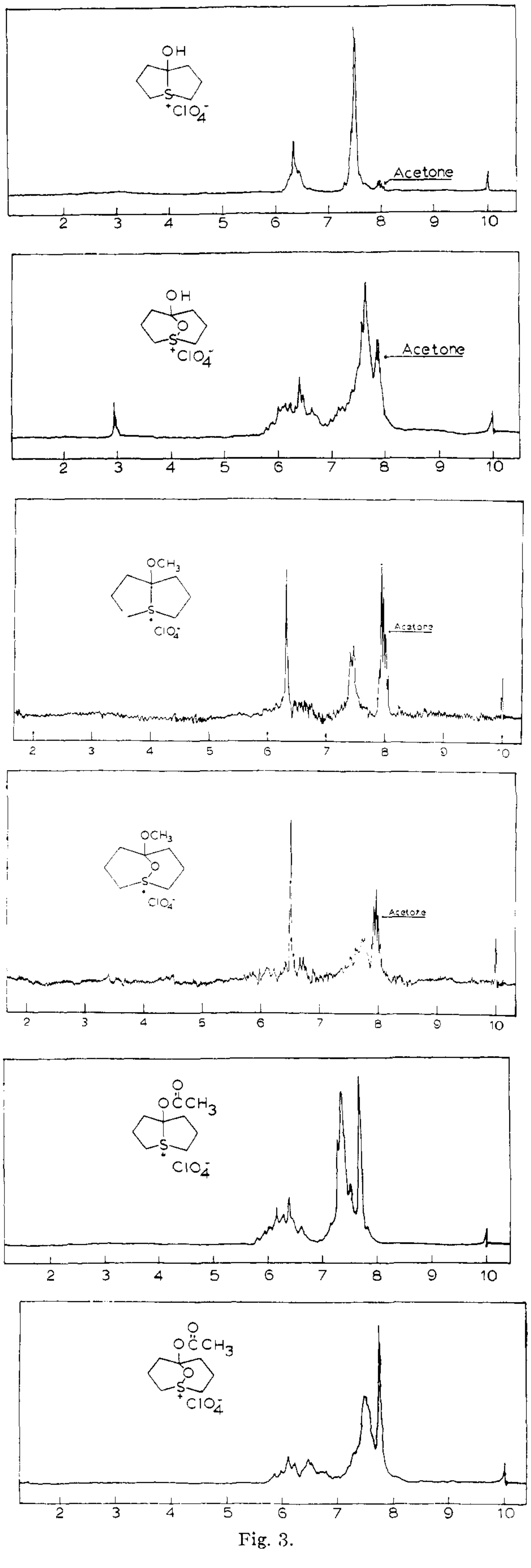

Fig. 3.

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(34) W. von E. Doering and E. Dorfman, *J. Am. Chem. Soc.*, **75**, 5595 (1953).

(35) D. B. Denney and M. A. Greenbaum, *ibid.*, **79**, 979 (1957).

(36) W. G. Miller and L. Anderson, *Anal. Chem.*, **31**, 1668 (1959).

900° by a Linberg micro combustion furnace, no. 5674F, with automatic control. The effluent carbon monoxide was oxidized to carbon dioxide in a tube containing iodine pentoxide at 115°. After passing through a packing of sodium thiosulfate and magnesium perchlorate, the samples were collected in U-tubes cooled in liquid nitrogen and evacuated with cooling at 1–2 mm. to remove nitrogen.

The isotope ratios were obtained on a Consolidated–Nier isotope-ratio mass spectrometer. Each day's runs were standardized by analysis of tank carbon dioxide and the results normalized using 0.204 atom per cent. as the normal abundance of oxygen-18.

Compounds containing hydrogen/carbon ratios greater than 1.5 tend to give high gravimetric oxygen analysis, which results in somewhat lower than the expected value for oxygen-18 in enriched samples.[37] The platinum sleeve in the entrance area of the combustion furnace evidently improves the analytical results by limiting any reaction with the quartz tubing which results in water and silicon monoxide.

Solvolysis of Dimethyl-methoxysulfonium Perchlorate in H_2O^{18}.—A solution of 4.0 g. of dimethyl-methoxysulfonium perchlorate in 10 ml. of enriched water (1.67 atom % excess oxygen-18) was allowed to stand at room temperature for several minutes. Anhydrous sodium carbonate was added to *p*H 5. The solution was extracted several times with chloroform, the combined extracts were dried over anhydrous magnesium sulfate and concentrated on the rotary evaporator. The residue was distilled at reduced pressure in a Hickman tube. The product, n^{26}D 1.4747 (reagent dimethyl sulfoxide, n^{26}D 1.4745), infrared spectrum (smear) identical in all respects with that of reagent dimethyl sulfoxide, contained 1.48 atom % excess oxygen-18.

Treatment of Dimethyl Sulfoxide with Acidic H_2O^{18}.—One ml. of dimethyl sulfoxide, n^{26}D 1.4745, was dissolved in a mixture of 2 ml. of H_2O^{18} (1.67 atom % excess oxygen-18) and 0.25 ml. of 70% perchloric acid. After several minutes anhydrous sodium carbonate was added to *p*H 5. The dimethyl sulfoxide, n^{26}D 1.4744 (0.00 atom % excess oxygen-18), after extraction and distillation, had infrared spectrum (smear) identical with that of the starting material.

Treatment of Trimethyl-oxosulfonium Iodide with H_2O^{18}.—A sample of trimethyl-oxosulfonium iodide was dissolved in a minimum volume of H_2O^{18} (1.67 atom % excess oxygen-18) at room temperature. After standing for several minutes, the mixture was frozen and the water was removed by lyophilization. The recovered trimethyl-oxosulfonium iodide showed 0.09 atom % excess oxygen-18.

A sample of trimethyl-oxosulfonium iodide, recrystallized from the enriched water by warming on the steam-bath, showed 0.10 atom % excess oxygen-18 incorporation.

Solvolysis of 5-Acetoxy-9-oxa-1-thioniabicyclo[3.3.1]nonane Perchlorate in H_2O^{18}.—A solution of 40 mg. of 5-acetoxy-9-oxa-1-thioniabicyclo[3.3.1]nonane perchlorate in 0.25 ml. of H_2O^{18} (1.67 atom % excess oxygen-18) was allowed to stand for several minutes at room temperature. The solution, neutralized to *p*H 5 with anhydrous sodium carbonate, was extracted three times with 10 ml. of chloroform. The combined extracts were dried over anhydrous magnesium sulfate and the solvent was removed at reduced pressure. The residue was taken up in 10 ml. of ether and 70% perchloric acid added until precipitation of the salt was complete. The perchlorate was converted to 5-methoxy-9-oxa-1-thioniabicyclo[3.3.1]nonane perchlorate by the method outlined previously. The recrystallized product, yield 15 mg. (0.252 atom % excess oxygen-18, or 1.51 atom % excess oxygen-18 in the 9-position), had infrared spectrum (CH_3-CN) and m.p. identical with those of the non-isotopic sample.

Dissociation of 5-Hydroxy-9-oxa-1-thioniabicyclo[3.3.1]-nonane Perchlorate in H_2O^{18}.—A solution of 40 mg. of 5-hydroxy-9-oxa-1-thioniabicyclo[3.3.1]nonane perchlorate in 0.25 ml. of H_2O^{18} was treated in a manner identical with that described above for the acetate VIIA. The final product, 5-methoxy-9-oxa-1-thioniabicyclo[3.3.1]nonane perchlorate, 20 mg., infrared spectrum and m.p. identical with those recorded above, contained 0.00 atom % excess oxygen-18.

Kinetic Procedure.—The solvolyses were followed by titration of the acid developed with 0.0198 *N* sodium methoxide in methanol using a Polarad Electronic Corp. model AT-2A automatic recording titrator set to hold constant *p*H 5. The temperatures reported are accurate only to ±0.5°. The solvent, adjusted to *p*H 5, was allowed to come to proper temperature in the titration vessel with the electrodes in position and with magnetic stirring. The solid sample then was added. In each case solution was effected immediately. The rate of the early stages of the reaction exceeded the response of the instrument, and a "zero time" was taken only after the automatic titrator was adding base at intervals. The orders of magnitude of the observed rates (Table IX) provided the necessary comparative figures for the conclusions we have drawn.

Physical Measurements. Infrared Spectra.—Measurements were made with either a Perkin–Elmer model 21 or a Beckman IR-7 spectrometer using matched sodium chloride cells or, in the case of deuterium oxide solutions, calcium fluoride cells with pure solvent in the case of deuterium oxide solutions, calcium fluoride cells with pure solvent in the reference beam. Solvents were reagent grade commercially available samples; acetonitrile and trichloroacetonitrile were distilled from phosphorus pentoxide. The instruments were calibrated with the vibrational bands of water vapor and/or polystyrene.

Ultraviolet Spectra.—The electronic absorption spectra were obtained on a Bausch and Lomb Spectronic 505 on a Cary model 14 recording spectrophotometer, and maxima are considered accurate to ±1 mμ. Cyclohexane was freed from benzene by stirring with powdered silica gel. Absolute ethanol was reagent grade, used without further purification. Acetonitrile was distilled from phosphorus pentoxide.

Nuclear Magnetic Resonance Spectra.—The n.m.r. spectra were obtained on a Varian Associates instrument model 4300B with a 60 Mc. probe, or on a model A-60. Tetramethylsilane was used as an internal standard (τ = 10.0).[38] The n.m.r. spectra of the pairs VIII and VA (in perdeuterioacetone), IX and VIA (in perdeuterioacetone), and X and VIIA (in trifluoroacetic acid) are given in Fig. 3 (see also Table VI).

Dipole Moments.—The electric moments of 1-thiacyclooctan-5-one-1-oxide and 1-thiacycloöctan-5-one-1,1-dioxide were measured in benzene solution. The dielectric constants and densities of several solutions, ranging in concentration from 0.004 to 0.0013 in weight fraction for the sulfoxide and from 0.003 to 0.0009 for the sulfone, were measured at 25°. The constants ϵ, α, ν_1, β of the Halverstadt–Kumler equation are shown in Table X for each compound along with the derived value of the molar polarization of solute at infinite dilution, P_2. The sum of the electronic and atomic polarizations was taken to be equal to the molecular refraction *MR*D calculated from empirical constants. The observed values of the electric moments are shown in Table X; the probable error in each is about ±0.1 D.

TABLE X

EMPIRICAL CONSTANTS AND DIPOLE MOMENTS IN BENZENE SOLUTION AT 25°

1-Thia-cycloöctan-5-one-	ϵ	α	ν_1	β	P_2	*MR*D	μobs.
1-Oxide	2.2741	7.8	1.11439	−0.33	272.3	41.3	3.37
1,1-Dioxide	2.2741	8.6	1.11439	−0.43	321.4	41.1	3.70

Acetoxymethyl methyl sulfide was synthesized from dimethyl sulfoxide and acetic anhydride by the method of Horner and Kaiser.[39] The yield of colorless liquid, b.p. 46–49° (12 mm.), (reported[39] 48.5° (12 mm.)), n^{25}D 1.4320, $\nu_{C=O}^{CH_3CN(2.5\%)}$ 1744 cm.$^{-1}$, was 65%. The brosylate salt was prepared by warming acetoxymethyl methyl sulfide (3.0 g.) with methyl brosylate (3.0 g.) on the steam-bath for 15 min. Addition of ether to the reaction mixture precipitated the crude salt. Crystallization from absolute ethanol–ethyl ether gave pure platelets of **dimethyl acetoxymethylsulfonium *p*-bromobenzenesulfonate**, m.p. 131–133°, $\nu_{C=O}^{CH_3CN(5\%)}$ 1778 cm.$^{-1}$.

Anal. Calcd. for $C_{11}H_{15}BrO_5S_2$: C, 35.60; H, 4.07. Found: C, 35.58; H, 4.13.

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[38] G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

[39] L. Horner and P. Kaiser, *Ann.*, **626**, 19 (1959); **631**, 198 (1960).