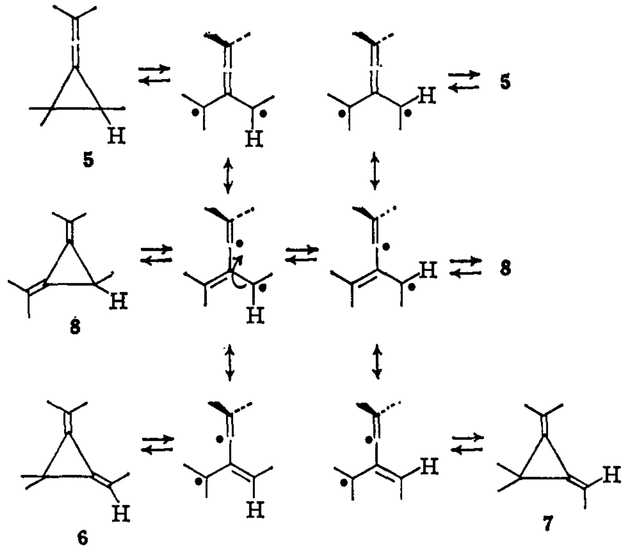
latter system are thought to proceed by way of planar, delocalized trimethylenemethane intermediates.[3] Very recently experimental evidence concerning the existence and nature of this interesting species has been presented.[9] A similar intermediate can be invoked to describe the rearrangements observed above. This differs from trimethylenemethane in that one of the peripheral carbons is sp hybridized. According to simple molecular orbital theory[10] the planar form of this intermediate should also enjoy substantial stabilization. Chart I depicts a rational scheme accounting for the data concerning the pyrolysis of 5 in terms of such an intermediate, denoted here in valence bond terminology. There are two isomeric, trimethylenemethane-type intermediates possible, and it is likely that interconversion by rotation about the designated radial carbon–carbon bond is relatively facile at pyrolysis temperatures. Each of the products can, in theory, be reconverted to the pair of trimethylenemethane intermediates by reversal of its formative process and thus be repartitioned among the three original products. Compounds **6** and **7** undergo this redistribution easily but more drastic conditions are required for **8**. This suggests that bond cleavage to a *nonplanar* diradical precedes formation of the delocalized species. Accordingly **8**, with a single stabilizing methyl on the incipient saturated radical center, requires a greater activation energy to generate the trimethylenemethane intermediates than **6** or **7**, which can form tertiary radicals at this site.

Chart I



The pyrolytic conversion of alkenylidenecyclopropanes appears to be a general synthetic method for preparing dimethylenecyclopropanes, subject only to stability limitations of the compounds involved. The adaptability of the simple reaction procedure to vacuum-line work should allow its use in preparing even thermally labile and oxygen-sensitive materials. We are currently engaged in exploring further aspects of these pyrolysis reactions and examining the chemistry of dimethylenecyclopropanes.

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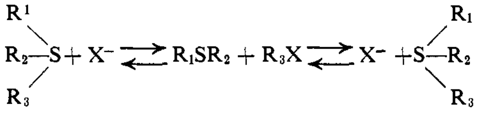
[9] P. Dowd, *J. Am. Chem. Soc.*, **88**, 2587 (1966); R. J. Crawford and D. M. Cameron, *ibid.*, **88**, 2589 (1966).

[10] A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, pp 43–44.

The Racemization of *t*-Butylethylmethylsulfonium Perchlorate[1]

Sir:

Optically active tertiary sulfonium salts have been known for many years.[2–4] The racemization of *l*-phenacylethylmethylsulfonium salts was studied by Balfe, *et al* [4] They concluded that racemization involved a nucleophilic displacement on carbon by halide ion to produce inactive alkyl halide and sulfide followed by formation of the racemic sulfonium salt.



$$\overset{R^1}{R_2{-}\underset{R_3}{S^+}} + X^- \rightleftarrows R_1SR_2 + R_3X \rightleftarrows X^- + \overset{R_1}{\underset{R_3}{{}^+S}}{-}R_2$$

We have studied the racemization of *t*-butylethylmethylsulfonium perchlorate[5] (I) and wish to present evidence that racemization of this system involves a different mechanism.

The optically active salt, I, mp 148.6° dec, $[\alpha]^{25}\mathrm{D}\ -34.6°$ (*c* 1.5, methanol), was obtained by resolution of the corresponding (−)-dibenzoylhydrogentartrate followed by replacement of the dibenzoylhydrogentartrate anion by perchlorate. Compound I racemizes faster than it solvolyzes in a variety of solvents. At 50° the racemization is *ca.* 15 times faster than solvolysis. Some typical rate constants are presented in Table I.

Table I. The Solvolysis of *t*-Butylethylmethylsulfonium Perchlorate in Various Solvents at 50.0°

Isomer	[I], *M*	Solvent	μ	$10^6k_{t'}$,[a] sec^{-1}	$10^6k_{\alpha'}$,[b] sec^{-1}
dl	0.01184	EtOH	0.015	44.9 ± 1.2	
(−)	0.01187	EtOH	0.015	45.1 ± 0.6	471 ± 15
dl	0.01462	HOAc	0.042[c]	36.2 ± 1.0	
(−)	0.01429	HOAc	0.042[c]		413 ± 17
dl	0.02990	H_2O	0.030	16.6	
(−)	0.02999	H_2O	0.030		283 ± 18
dl	0.02370	$(CH_3)_2CO$	0.030[d]	55.9 ± 1.1	
(−)	0.02373	$(CH_3)_2CO$	0.030[d]		460 ± 13

[a] Titrimetric rate constant. [b] Polarimetric rate constant. [c] NaOAc (0.0293 *M*) added. [d] 2,6-Lutidine (0.0510 *M*) added.

The racemization of I cannot involve a reversible nucleophilic displacement on carbon since the only anion present in the solutions is the nonnucleophilic perchlorate ion. Nucleophilic displacement by the solvent or its lyate ion would not be reversible.

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[1] Presented in part before the Division of Organic Chemistry at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

[2] W. J. Pope and S. J. Peachey, *J. Chem. Soc.*, **77**, 1072 (1900).

[3] S. Smiles, *ibid.*, **77**, 1074 (1900).

[4] M. P. Balfe, J. Kenyon, and H. Phillips, *ibid.*, 2554 (1930).

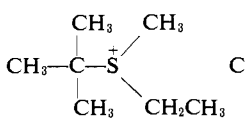
[5] All new compounds gave satisfactory analyses.

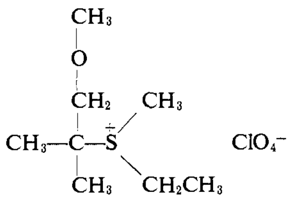
There are two mechanisms which would account for the racemization. These are (i) heterolytic carbon–sulfur bond cleavage to yield a *t*-butyl cation–ethyl methyl sulfide ion neutral molecule pair which could return to racemic sulfonium salt or react with the solvent to yield products, and (ii) inversion about the central sulfur atom analogous to the inversion of an ammonia molecule.

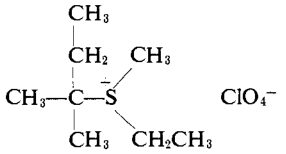
The first mechanism would represent an example of the detection of ion–neutral molecule pair return during solvolysis by racemization of the leaving group analogous to the detection of ion-pair return in solvolysis of neutral molecules by racemization of an optically active leaving group. Such a process has been at least formally demonstrated to occur in the diastereoisomer interconversion observed[6] on solvolysis of α-phenylethyl 2,6-dimethylbenzenesulfinate.

A distinction between the two mechanisms can be made on the basis of the effect of substituents upon the reaction. If the first mechanism obtains, then replacement of a hydrogen on one of the methyls of the *t*-butyl group by an electron-withdrawing substituent should, to a first approximation, slow down the heterolysis rate and hence reduce the rates of racemization and solvolysis by similar amounts. An electron-donating substituent should accelerate both the racemization and solvolysis reactions by both electronic and steric effects. If mechanism ii describes the racemization process, then any substituent introduced into the *t*-butyl group should speed up racemization by a steric effect or leave the racemization process essentially unchanged in rate.

(1-Methoxy-2-methyl-2-propyl)ethylmethylsulfonium perchlorate (II), mp 102°, $[\alpha]^{25}\text{D}$ $-13.5°$ (c 0.64, ethanol), and *t*-amylethylmethylsulfonium perchlorate (III), mp 137° dec, $[\alpha]^{25}\text{D}$ $-25.1°$ (c 0.43, methanol), were prepared.


I

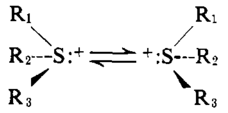

II


III

The relative rates of ethanolysis at 50° of compounds I:II:III are 1:0.06:6.3. These relative rates show the decrease and increase in rate expected for a heterolytic cleavage in which an electron-withdrawing and electron-donating group, respectively, are introduced as a substituent on the *t*-butyl group.

In contrast the relative rates of racemization in ethanol at 50° of compounds I:II:III are 1:1.7:3.8. The replacement of a hydrogen of the *t*-butyl group by a substituent accelerates racemization whether the substituent is electron donating or electron withdrawing. This effect cannot be electronic in origin and instead must be associated with an increase in the nonbonded interactions in the ground state relative to the transition state for racemization on introduction of the substituent. Kincaid and Henriques previously suggested[7] that as the groups attached to the central sulfur of sulfonium salts became larger such nonbonded interactions would increase the inversion rate.

The results indicate that the racemization process is best described as involving an inversion as shown below. One cannot rule out the possibility that some of the racemization of I is proceeding by mechanism i, but the major pathway for racemization must be independent of heterolysis. If this interpretation is correct it represents the first examples of the racemization of sulfonium salts by inversion.



The thermal racemization of sulfoxides is well known.[8] Mislow and co-workers[8] have suggested that many of these systems undergo racemization by a pyramidal inversion mechanism. The difference in racemization rates between the sulfonium salts here reported and the sulfoxides must arise from a combination of steric and electronic effects.

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(6) D. Darwish and R. A. McLaren, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1964, Abstracts, p 45S.

(7) J. F. Kincaid and F. C. Henriques, Jr., *J. Am. Chem. Soc.*, **62**, 1474 (1940).

(8) D. R. Rayner, E. G. Miller, P. Bickart, A. J. Gordon, and K. Mislow, *ibid.*, **88**, 3138 (1966), and references cited therein.

(9) National Research Council of Canada Scholarship holder, 1963–1966.

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Reaction of Copper(I) Chloride with Carbon Tetrachloride in Dimethyl Sulfoxide

Sir:

In previous work from our laboratory,[1] there was reported the rapid formation of copper(I) chloride by the action of copper(I) ion (in the form of the perchlorate) on carbon tetrachloride in 2-butanol containing small but significant amounts of water. In order to gain a better insight into the nature of the reaction of copper(I) ion with carbon tetrachloride, the system copper(I) chloride–carbon tetrachloride–dimethyl sulfoxide was chosen for study. This system permitted the realization of a more nearly anhydrous condition than existed previously since the source of the copper(I) could be prepared pure and anhydrous. Dimethyl sulfoxide was chosen as the medium for reaction because of its ability to dissolve copper(I) chloride. Surprisingly, when carbon tetrachloride was injected into a solution of copper(I) chloride in dimethyl sulfoxide, an almost instantaneous and copious evolution of carbon dioxide was observed. In addition some carbon monoxide was also formed. It soon became evident that copper(I) was oxidized to the dipositive

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(1) I. V. Nelson, R. T. Iwamoto, and J. Kleinberg, *J. Am. Chem. Soc.*, **86**, 364 (1964).