

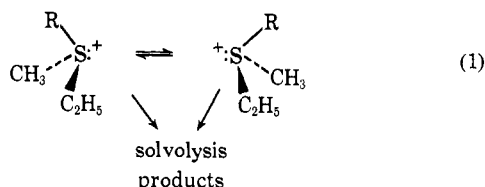
Solvolysis of *tert*-Butylethylmethylsulfonium Salts. The Effect of the Anion on Product Distribution¹

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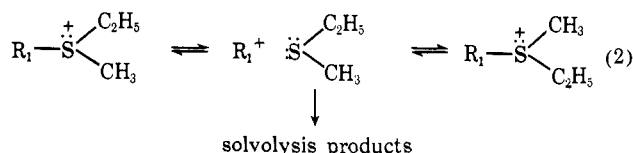
Abstract: The rate constants for solvolysis of *tert*-butylethylmethylsulfonium perchlorate and bromide have been measured in ethanol, acetic acid, and 50% acetic acid-acetic anhydride. The sulfonium bromide reacts *ca.* 20% more rapidly than the perchlorate. The relative amounts of olefin and substitution products from solvolysis of the bromide and perchlorate salts are markedly different. In general, a higher yield of olefin is obtained from the bromide than from the perchlorate salt. Similarly, the fraction of olefin formed on solvolysis of *tert*-amylethylmethylsulfonium and 1-phenyl-2-methyl-2-propylethylmethylsulfonium salts changes markedly when the anion is changed from perchlorate to halide. The addition of lithium chloride to *tert*-butylethylmethylsulfonium perchlorate in solvent ethanol or acetic acid altered the relative amounts of olefin and substitution products. In addition, *tert*-butyl chloride was formed under these conditions. These results clearly indicate that the products formed on solvolysis of sulfonium salts depend on the nature of the counterion. The results are interpreted using an ion-pair mechanism.

The racemization of optically active *tert*-butylethylmethylsulfonium perchlorate and a number of its derivatives has been shown to be faster than solvolysis in a variety of solvents.⁴ The excess of racemization over solvolysis ($k_a - k_t$) was interpreted as racemization via pyramidal inversion of the sulfonium salt (eq 1).



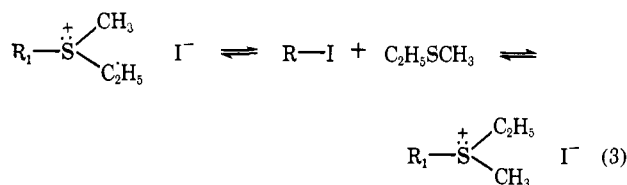
Subsequent studies showed that similar behavior was exhibited by 1-adamantylethylmethylsulfonium perchlorate⁵ and benzyl-, *p*-nitrobenzyl- and phenacylethylmethylsulfonium perchlorates.⁶

The racemization of *p*-methoxybenzylethylmethylsulfonium perchlorate was interpreted by an alternative mechanism⁶ involving carbon-sulfur bond heterolysis to form an ion-neutral molecule pair which could return to give racemic sulfonium salt or react to give solvolysis products as shown in eq 2.



A third pathway which can lead to racemization of sulfonium salts is shown in eq 3. In this process, a reversible nucleophilic displacement on the active sulfonium salt results in the formation of inactive alkyl

halide and sulfide, which generate racemic sulfonium salt by recombination. This reaction sequence was proposed by Kenyon and coworkers⁷ to account for the racemization of phenacylethylmethylsulfonium iodide.



In extending our studies to the racemization of sulfonium halides, we undertook the study of the effects of the counterion on the solvolysis of sulfonium salts. In this paper we report on the solvolysis of *tert*-butyl-, *tert*-amyl-, and 1-phenyl-2-methyl-2-propylethylmethylsulfonium salts and show the drastic changes in product composition brought about by changing the counterion from perchlorate to a halide ion.

Results and Discussion

Kinetics. A summary of the first-order rate constants for solvolysis of *tert*-butylethylmethylsulfonium bromide and perchlorate in solvents ethanol, acetic acid, and 50% acetic acid-acetic anhydride is presented in Table I. At both 25 and 50°, the solvolysis of the sulfonium bromide is *ca.* 20% faster than that of the perchlorate salt. Similar behavior has been noted previously on solvolysis of *tert*-butyldimethylsulfonium salts.^{8,9} For example, Swain, *et al.*,⁸ reported relative rate constants of 1.00:1.17:1.12:1.13 for the solvolysis of *tert*-butyldimethylsulfonium perchlorate, chloride, bromide, and iodide, respectively, in 90% acetone-10% water solution at 50°.

A comparison of the solvolysis of the *tert*-butylethylmethylsulfonium salts and *tert*-butyldimethylsulfonium chloride⁸ at 50° shows that the change of leaving group from dimethyl sulfide to ethyl methyl sulfide increases the rate constant by three- to fivefold in solvents ethanol

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Table I. The Solvolysis of *tert*-Butylethylmethylsulfonium Salts in Various Solvents

Solvent	Salt	[Salt], <i>M</i>	Temp, °C	10 ⁶ <i>k</i> , sec ⁻¹
C ₂ H ₅ OH ^a	Br ⁻	0.01203	25.0	1.09 ± 0.04
C ₂ H ₅ OH ^a	Br ⁻	0.01150	50.0	58.9 ± 0.3
C ₂ H ₅ OH	ClO ₄ ⁻	0.01187	25.0	0.857 ± 0.015
C ₂ H ₅ OH	ClO ₄ ⁻	0.01209	50.0	45.1 ± 0.6
HOAc ^b	Br ⁻	0.01486	25.0	0.831 ± 0.05
HOAc ^b	Br ⁻	0.01486	50.0	43.6 ± 2
HOAc ^b	ClO ₄ ⁻	0.01445	25.0	0.657 ± 0.014
HOAc ^b	ClO ₄ ⁻	0.01462	50.0	36.2 ± 1.0
50% Ac ₂ O ^{b,c}	Br ⁻	0.01477	25.0	0.537 ± 0.023
50% Ac ₂ O ^{b,c}	Br ⁻	0.01471	50.0	25.9 ± 3.5
50% Ac ₂ O ^{b,c}	ClO ₄ ⁻	0.01441	25.0	0.451 ± 0.008
50% Ac ₂ O ^{b,c}	ClO ₄ ⁻	0.01517	50.0	26.3 ± 0.3

^a Contained 0.0508 *M* 2,6-lutidine. ^b Contained 0.0293 *M* NaOAc. ^c 50 vol % acetic acid-acetic anhydride.

dimethyl sulfide to ethyl methyl sulfide has a marked effect upon the kinetics of the solvolysis reaction. Within experimental error, the activation parameters ΔH^\ddagger and ΔS^\ddagger are 30 kcal/mol and 14 eu, respectively, for the reactions of both the bromide and perchlorate salts in all three solvents. All the data are consistent with the formation of a carbonium ion species as an intermediate in the reaction.

Products of Solvolysis. Summaries of the products of solvolysis to *t*-butyl-, *t*-amyl- and 1-phenyl-2-methyl-2-propylethylmethylsulfonium salts are presented in Tables II, III, and IV, respectively. Product analyses were carried out using gc analyses with an appropriate internal standard in each case. Suitable controls were carried out to show that the analyses were accurate and reproducible. In every case the change in anion from

Table II. Product Analyses of *tert*-Butylethylmethylsulfonium Salts at 70.00°

Compound ^a	Solvent	Added salt	[Salt], <i>M</i>	Isobutylene	Products, mol %			
					<i>tert</i> -BuOEt	EtSMe	H ⁺	<i>tert</i> -BuCl
<i>tert</i> -BuEtMeSClO ₄	EtOH ^b			20 ± 2	81 ± 1	100 ± 2	100 ± 2	
<i>tert</i> -BuEtMeSBr	EtOH ^b			40 ± 1	60 ± 1	98 ± 2	100 ± 2	
<i>tert</i> -BuEtMeSClO ₄	EtOH ^b	LiCl	0.01738	33 ± 1	62 ± 1	98 ± 1	98 ± 1	3 ± 1
	EtOH ^b	LiCl	0.1527	51	47	101	96	7
<i>tert</i> -BuCl	EtOH ^b	LiCl	0.1335	54 ± 2	49 ± 1		98 ± 1	
<i>tert</i> -BuEtMeSClO ₄	AcOH ^c			12 ± 1	87 ± 1 ^e	98 ± 4	98 ± 1	
<i>tert</i> -BuEtMeSBr	AcOH ^c			68 ± 3	35 ± 4 ^e	102 ± 2	100 ± 1	
<i>tert</i> -BuEtMeSClO ₄	AcOH ^c	LiCl	0.160	47	42 ^e	100		11
<i>tert</i> -BuEtMeSClO ₄	50% Ac ₂ O ^{e,d}			13 ± 1	84 ± 1 ^e	99 ± 2	97 ± 1	
<i>tert</i> -BuEtMeSBr	50% Ac ₂ O ^{e,d}			68 ± 2	37 ± 2 ^e	100 ± 1	94 ± 1	

^a Sulfonium salts were 0.01–0.02 *M*. ^b Contained 0.05 *M* 2,6-lutidine. ^c Contained 0.03–0.06 *M* NaOAc. ^d 50 vol % acetic acid-acetic anhydride. ^e *tert*-Butyl acetate.

Table III. Product Analyses of *tert*-Amylethylmethylsulfonium Salts at 50.00°

Solvent	Salt	[Salt], <i>M</i>	Products, mol %					
			Et(Me)-C=CH ₂	(Me) ₂ C=C-(Me)H	<i>tert</i> -AmOEt	<i>tert</i> -AmOAc	EtSMe	H ⁺ ^a
EtOH ^b	ClO ₄ ⁻	0.01590	6 ± 1	16 ± 1	77 ± 1		98 ± 1	99 ± 1
EtOH ^b	I ⁻	0.01322	13 ± 1	53 ± 1	28 ± 2		98 ± 1	
HOAc ^c	ClO ₄ ⁻	0.01546	4 ± 1	16 ± 1		83 ± 1	98 ± 2	100 ± 1
50% AcOAc ^{e,d}	ClO ₄ ⁻	0.01546	5 ± 1	17 ± 1		80 ± 5	99 ± 1	99 ± 1

^a Obtained by titration. ^b Contained 0.05 *M* 2,6-lutidine. ^c Contained 0.031 *M* NaOAc. ^d 50 vol % acetic acid-acetic anhydride.

Table IV. Product Analyses of 1-Phenyl-2-methyl-2-propylethylmethylsulfonium Salts at 70.00°

Solvent	Salt	[Salt], <i>M</i>	[Base], <i>M</i>	Products, mol %					
				PhCH ₂ -(Me)-C=CH ₂	Ph(H)(C=C)-Me ₂	PhCH ₂ -(Me)-C(Me)OEt	PhCH ₂ -(Me)-C(Me)-OAc	EtSMe	H ⁺ ^a
EtOH	ClO ₄ ⁻	0.01555	0.05044 ^b	16 ± 1	21 ± 1	63 ± 1		99 ± 1	99 ± 1
EtOH	I ⁻	0.01281	0.0544 ^b	22 ± 1	53 ± 1	24 ± 1		99 ± 2	
EtOH	ClO ₄ ⁻	0.01594 ^d	0.05053 ^{b,d}	21 ± 1	51 ± 1	28 ± 1		99 ± 2	
HOAc	ClO ₄ ⁻	0.01614	0.03052 ^c	13 ± 1	15 ± 1		69 ± 2	100 ± 3	98 ± 1
HOAc	I ⁻	0.01307	0.03052 ^c	28 ± 1	67 ± 1				

^a Obtained by titration. ^b 2,6-Lutidine. ^c NaOAc. ^d Contained 0.1330 *M* lithium chloride.

and acetic acid. This rate increase may reflect an increase in nonbonded interactions in the ground state of *tert*-butylethylmethylsulfonium salts relative to the *tert*-butyldimethylsulfonium salts and the relief of these interactions at the transition state. It is clear from the data that neither the change of counterion from perchlorate to halide nor the change in leaving group from

perchlorate to a halide (chloride, bromide or iodide) results in a substantial change in product distribution. There is always more olefin and less substitution product formed in the presence of halide ion than in its absence.

The distribution between substitution and elimination products was first discussed by Ingold, *et al.*¹⁰ In their

pioneering studies, Ingold, *et al.*, emphasized that in the solvolysis of *tert*-butyl chloride, bromide, iodide, and dimethylsulfonium salts in 80% ethanol gave rise to nearly the same per cent olefin even though the rates of solvolysis varied by *ca.* three powers of ten. This near constancy of per cent olefin was taken as evidence that a common carbonium ion intermediate gave rise to products from all the systems.

Cocivera and Winstein¹¹ reexamined the solvolyses of these systems in solvents acetic acid and anhydrous ethanol. They reported that the per cent elimination depended on the leaving group. Some of their data are reproduced in Table V. The variation in per cent

Table V. Mole Per Cent Olefin from Solvolysis in Several Solvents at 75.0°^a

Compound ^a	H ₂ O ^b	EtOH ^b	AcOH ^c
<i>tert</i> -Butyl chloride	7.6 ± 1.0	44.2 ± 1.0	73.2
<i>tert</i> -Butyl bromide	6.6 ± 1.0	36.0 ± 1.0	69.5
<i>tert</i> -Butyl iodide	6.0 ± 1.0	32.3 ± 1.0	
<i>tert</i> -Butyl SMe ₂ ⁺ ClO ₄ ⁻	6.5 ± 1.0	17.8 ± 1.4	11.7 ± 1.0
<i>tert</i> -BuOH ₂ ⁺	4.7		
<i>tert</i> -Amyl chloride	8.9 ± 0.4		85

^a *Ca.* 0.04 M. ^b Contained 0.07–0.14 M 2,6-lutidine. ^c Contained 0.025–0.103 M NaOAc. ^d Reference 11.

elimination with variation in leaving group was suggested to provide evidence that ion pairs were the precursors of the elimination products. They used *tert*-butyldimethylsulfonium perchlorate as a model for a system which would yield products from a dissociated ion.

A comparison of the results of Cocivera and Winstein and our results (Table II) shows that the per cent olefin formed on solvolysis of *tert*-butyldimethyl- and *tert*-butylethylmethylsulfonium perchlorate are the same within experimental error. The change in leaving group from dimethyl sulfide to methyl ethyl sulfide has a negligible effect upon the product distribution. The large variations in product distribution recorded in Tables II, III, and IV are associated with a change in the negative ion and could be ascribed to several alternative processes which are considered below.

First, the sulfonium halide and perchlorate could react at identical rates to give the same product distribution *via* solvolysis. The increase in the per cent elimination for the halide salts would reflect the incursion of an independent elimination reaction (E2 type). The increase in the rate of solvolysis of *tert*-butylethylmethylsulfonium bromide relative to the perchlorate would be attributed to the independent elimination reaction. We do not have sufficient information from kinetics and product analyses to rule this process out unequivocally in all cases. The data are sufficient for this scheme to be excluded to the solvolysis of *tert*-butylethylmethylsulfonium bromide in solvents acetic acid and 50% acetic acid–acetic anhydride.

For example, in solvent acetic acid the sulfonium perchlorate gives 12% olefin and 87% *tert*-butyl acetate, whereas the sulfonium bromide gives 68% olefin and 35% acetate. If the increase in olefin arose from an independent elimination mechanism, then only 5%

(10) E. D. Hughes and C. K. Ingold, *et al.*, *J. Chem. Soc.*, 1280, 1283 (1937); 2038 (1948).

(11) M. Cocivera and S. Winstein, *J. Amer. Chem. Soc.*, 85, 1702 (1963).

[35/87(12)] of the elimination product could have been formed by solvolysis and only 40% of the reaction would have been solvolysis. This would require that the rate constant for reaction of the sulfonium bromide be greater than the rate constant for solvolysis of the sulfonium perchlorate by a factor of 2.5. This is not observed. In 50% acetic anhydride, the per cent olefin increases from 13 to 68 on changing the anion from perchlorate to bromide, but the rates of solvolysis are the same. The above discussion rules out an independent elimination competing with solvolysis of the sulfonium salts for the case where the sulfonium perchlorate and bromide undergo solvolysis at similar rates. It can, however, be argued that this requirement is too stringent and may not be correct.

An independent elimination reaction would be compatible with our kinetic data provided that the rate constant for solvolysis of the sulfonium bromide was significantly smaller than the rate constant for solvolysis of the sulfonium perchlorate. The difference between the observed rate constant, k_{obsd} , and the solvolysis rate constant, k_{solv} , for the bromide salt would represent the rate constant for the independent elimination reaction, k_{E} . For this scheme to be correct would require that the similarity of k_{obsd} for the sulfonium bromide and the rate constant for solvolysis of the sulfonium perchlorate be accidental. The nearly identical yields of olefin produced on acetolysis of the sulfonium bromide and *tert*-butyl bromide, recorded in Tables II and V, respectively, would also have to be accidental. (A 5° temperature difference should not greatly affect the per cent olefin produced in the reaction.)

Furthermore, it is noteworthy that in solvent ethanol the per cent elimination from the sulfonium bromide and *tert*-butyl bromide is the same within experimental error. Similarly, the per cent elimination from *tert*-butylethylmethylsulfonium perchlorate in the presence of 0.15 M lithium chloride (53%) is nearly identical with that from *tert*-butyl chloride in the presence of 0.13 M lithium chloride (54%). If elimination by halide ion results from a reaction independent of solvolysis, then the identity of products from these latter reactions would have to be ascribed to fortuitous accident. It is clear that a remarkable series of accidental coincidences in observed rate constants and percentage yields of olefins would be required for the scheme involving an independent elimination reaction to be valid. On this basis we tend to disfavor such a scheme.

An alternative explanation for the product distributions is that a common intermediate gives rise to solvolysis products from both the sulfonium halide and the *tert*-butyl halide. One candidate for the common intermediate would be the alkyl halide. Thus, if *tert*-butylethylmethylsulfonium bromide reacts to give *tert*-butyl bromide which is then rapidly solvolyzed, this could conceivably account for the observed results. *tert*-Butyl bromide undergoes solvolysis faster than *tert*-butylethylmethylsulfonium perchlorate in solvents ethanol and acetic acid. In contrast, the solvolysis of *tert*-butylethylmethylsulfonium perchlorate is nearly ten times faster than the solvolysis of *tert*-butyl chloride in solvents acetic acid and ethanol. If *tert*-butyl chloride was formed it should be a detectable intermediate.

At 70° in solvents ethanol and acetic acid, the formation of *tert*-butyl chloride was detected on solvolysis of

tert-butylethylmethylsulfonium perchlorate in the presence of lithium chloride. The amount of *tert*-butyl chloride produced rises to a maximum and then decreases as the *tert*-butyl chloride undergoes solvolysis. Summaries of the amounts of olefin, substitution product, and *tert*-butyl chloride which are formed at various times are presented in Tables VI and VII for the reactions in ethanol and acetic acid, respectively.

Table VI. Product Analyses of *tert*-Butylethylmethylsulfonium Perchlorate (0.01585 *M*) with Added Lithium Chloride (0.1527 *M*) and 2,6-Lutidine (0.05123 *M*) in Anhydrous Ethanol at 70.00°

Time, min	Iso-butylene	Products, mol %			H ⁺ ^a
		<i>tert</i> -BuCl	<i>tert</i> -BuOEt	EtSMe	
4	5	1	6	15	14
12	20	7	21	44	43
20	35	6	35	75	68
36	42	10	40	93	84
64	45	11	43	97	93
184	51	7	47	101	96
1380	53	1	49	100	97

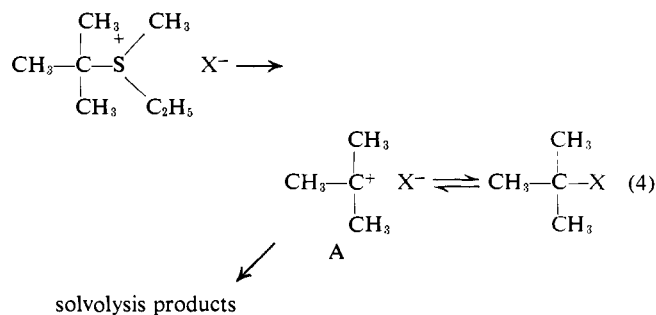
^a Obtained by titration.

Table VII. Product Analyses of *tert*-Butylmethylsulfonium Perchlorate (0.01581 *M*) with Added Lithium Acetate (0.6372 *M*) and Lithium Chloride (0.1602 *M*) in Anhydrous Acetic Acid at 70.00°

Time, min	Iso-butylene	Products, mol %		
		<i>tert</i> -BuCl	<i>tert</i> -BuOAc	EtSMe
4	4	6		18
8	8	10	7	29
13	22	13	12	49
20	25	20	15	61
28	27	20	19	73
40	34	25	31	92
56	36	27	32	97
250	45	13	42	102
430	47	11	42	100

In both solvents only a portion of the sulfonium salt reacts to produce *tert*-butyl chloride. The portion of the sulfonium salt which reacts to give products directly, and does not first form *tert*-butyl chloride, gives rise to the same high yields of olefin as are produced in the solvolysis of *tert*-butyl chloride. This can be seen most clearly from Tables VI and VII by noting that the ratio of (% olefin: % olefin + % substitution product) remains nearly constant throughout the reaction. If *tert*-butyl chloride were the common intermediate which accounted for the increase in olefin yield in the presence of chloride ion, then the sulfonium salt would have to be nearly quantitatively converted to *tert*-butyl chloride. This behavior is not observed, and therefore one can rule out the mechanism in which the sulfonium salt reacts to give *tert*-butyl halide exclusively which subsequently undergoes solvolysis to yield the observed products.

An alternative explanation of the results is that the solvolyses of *tert*-butyl sulfonium halides and the corresponding *tert*-butyl halides proceed through a common ionic intermediate. This intermediate would be a *tert*-butyl cation-halide ion pair. The solvolysis of the sulfonium salts would then be represented by eq 4.



This scheme would account for the identical product distributions and would also account for the formation of *tert*-butyl chloride from the sulfonium salt in the presence of chloride ion. The ion pair A has been shown as identical in structure from the sulfonium salt and the *tert*-butyl halide. A sulfide molecule has not been incorporated in this scheme. This is clearly an oversimplification, as it is probable that the ion pair formed from the sulfonium salt has a sulfide molecule intimately associated with it. Modifications of eq 4 in which different ion pairs are first formed from the sulfonium salt and the alkyl halide can be envisaged. In cases where ion-neutral molecule pair formation and return of the type shown in eq 2 are detected, another intermediate incorporating the sulfide molecule is clearly required.

We have drawn only the intermediate A for simplicity. The important feature of this scheme is that the sulfonium halide yields an ion pair which gives a product distribution which is identical, or nearly identical, with that observed on solvolysis of the *tert*-butyl halide. Refinement of this scheme must await further studies of these systems. The scheme shown in eq 4, or some variant of it, is the simplest process which will account for all our observations, and we prefer it as our best working hypothesis.

The formation of *tert*-butyl chloride during the solvolysis of the sulfonium halide is represented as equivalent to the detection of return from the ion pair intermediate(s) formed on solvolysis of *tert*-butyl chloride. It is not possible to observe ion-pair return directly on solvolysis of *tert*-alkyl halides. Thus the sulfonium salts may prove to be excellent models for the study of the nature and behavior of the intermediates involved in the solvolysis of *tert*-alkyl halides.

It is clear from our results that Cocivera and Winstein¹¹ very wisely selected the sulfonium perchlorates for their study. If an ion pair is formed from a sulfonium perchlorate, it should rapidly decompose to olefin and solvolysis products. The nonnucleophilic and nonbasic perchlorate ion should not greatly influence product formation, and the products may be similar to those from the free ion. The observation of Ingold, *et al.*,¹⁰ that nearly identical product distributions were obtained from sulfonium salts and *tert*-butyl halides could be accounted for in two ways. The solvent utilized by Ingold, *et al.*,¹⁰ was 80% ethanol. Ion-pair formation may be somewhat less important in this solvent than in ethanol and acetic acid. Hence, product distributions would be more nearly identical. More importantly, Ingold, *et al.*, used *tert*-butyldimethylsulfonium chloride in their studies and hence the product distribution should have been nearly the same as that observed for *tert*-butyl chloride.

Table VIII. Columns and Conditions of Operation for Gas Chromatographic Analyses

Compound	Solvent	Column ^d (length, m)	Temp, °C	Products (retention time, min)
I ^a	EtOH	F (2)	27	Isobutane (0.8), <i>tert</i> -BuCl (3.6), <i>tert</i> -BuOEt (5.4), EtSMe (9), CH ₂ Cl ₂ internal standard (16)
I ^a	HOAc	R (5)	89	Isobutylene (1.3), <i>tert</i> -BuCl (2.6), EtSMe (4.2), <i>tert</i> -BuOAc (6.8), toluene internal standard (13)
II ^b	EtOH	F (2)	27	2-Me-1-butene (1.4), 2-Me-2-butene (1.8), <i>tert</i> -AmOEt (13), CH ₂ Cl ₂ internal standard (16)
II ^b	HOAc	R (5)	89	2-Me-1-butene (1.8), 2-Me-2-butene (2.1), <i>tert</i> -AmOAc (14), EtSMe (4.2), benzene internal standard (6.8)
III ^c	EtOH	C (2)	152	3-Ph-2-Me-propene (5.9), 1-Ph-2-Me-propene (7.6), 1-Ph-2-Me-PrOEt (16), naphthalene internal standard (13)
III ^c	HOAc	P (2)	122	2-Ph-2-Me-propene (2.9), 1-Ph-2-Me-propene (3.5), 1-Ph-2-Me-2-PrOAc (16), naphthalene internal standard (20)

^a *tert*-Butylethylmethylsulfonium. ^b *tert*-Amylethylmethylsulfonium. ^c 1-Phenyl-2-methyl-2-propylethylmethylsulfonium. ^d Perkin-Elmer columns.

As regards the study of the kinetics of solvolysis of sulfonium halides, our results show that it is not always possible to evaluate the rate of decomposition of a sulfonium salt by measuring the rate of acid production. As shown in Tables VI and VII, the mole per cent sulfide reached 100% faster than the mole per cent acid produced reached the same value. This reflects the reaction in which *tert*-butyl chloride and ethyl methyl sulfide are formed but acid is not produced. Hence, titrimetric rate studies such as those by Swain⁸ and our studies on the solvolysis of the sulfonium bromide need not be true gauges of the rate of disappearance of the sulfonium salt.

Experimental Section

***tert*-Butyl Ethyl Sulfide.** A 400-g quantity of 75 wt % sulfuric acid was cooled to 0° using an ice-water bath. *tert*-Butyl alcohol (60 g, 0.8 mol) and ethyl mercaptan (25 g, 0.4 mol) were successively added dropwise with stirring into the sulfuric acid. After the addition was complete, the cooling bath was removed and stirring was continued for 2 hr. Crushed ice (ca. 1000 g) was added to the solution and the mixture was extracted three times with 200-ml portions of ethyl ether. The combined ethereal extracts were washed with water, a 10% sodium hydroxide solution, and then three times with water. The ether solution was dried over anhydrous potassium carbonate and fractionally distilled through a Vigreux column: yield 42 g (88%); bp 116.5–117.8°; η^{25D} 1.4405 (lit.¹² bp 120.4°, η^{25D} 1.4390).

***tert*-Butylethylmethylsulfonium Iodide.** Nitromethane (300 ml) was added to an excess of *tert*-butyl ethyl sulfide (172 g, 1.5 mol) in iodomethane (200 g, 1.4 mol). The mixture was allowed to stand in the dark at room temperature for 2 hr and then was kept in the freezer compartment of the refrigerator for 1 day. The resulting crystals were filtered and washed with ether. The sulfonium iodide was recrystallized from methanol-ether, yield 230 g (62%), mp 135° dec. *Anal.* Calcd for C₇H₁₇IS: C, 32.31; H, 6.59. Found: C, 32.44; H, 6.36.

***dl*-*tert*-Butylethylmethylsulfonium Perchlorate.** A 10.4-g (0.04 mol) quantity of *tert*-butylethylmethylsulfonium iodide dissolved in 25 ml of 90% methanol-10% water was passed through a column containing Dowex 1 X 8 anion exchange resin in its hydroxide form. Elution with 90% methanol-10% water was continued until the sulfonium hydroxide was removed from the column. The eluate

was tested after each 50-ml cut to certify that iodide ions were absent. The sulfonium hydroxide was neutralized with 5% perchloric acid and the solvent was removed using a rotary evaporator.

Caution: Care was taken to ensure that the pH was never less than 7 when the solvent was removed. The solid product was crystallized from methanol-ether solution to yield 6.6 g (71%) of *tert*-butylethylmethylsulfonium perchlorate, mp 148° dec. *Anal.* Calcd for C₇H₁₇ClO₄S: C, 36.12; H, 7.36; S, 13.78. Found: C, 36.37, 35.88; H, 7.20, 7.21; S, 13.67, 13.97.

***dl*-*tert*-Butylethylmethylsulfonium Bromide.** This salt was prepared from the corresponding sulfonium iodide in a manner analogous to the preparation of *tert*-butylethylmethylsulfonium perchlorate. The compound had mp 121° dec after crystallization from nitromethane-ether. *Anal.* Calcd for C₇H₁₇BrS: C, 39.44; H, 8.04. Found: C, 39.37; H, 7.84.

***tert*-Amyl Ethyl Sulfide.** This compound was prepared from *tert*-amyl alcohol by the procedure described for the preparation of *tert*-butyl ethyl sulfide. The compound had bp 144–145° and η^{25D} 1.4498. *Anal.* Calcd for C₇H₁₆S: C, 63.56; H, 12.19. Found: C, 63.85, 63.61; H, 12.06, 12.08.

***dl*-*tert*-Amylethylmethylsulfonium Iodide.** *tert*-Amylethylmethylsulfonium iodide was prepared and purified in the manner described for the preparation of *tert*-butylethylmethylsulfonium iodide. The compound had mp 101° dec. *Anal.* Calcd for C₈H₁₉SI: C, 35.04; H, 6.98. Found: C, 35.40, 35.15; H, 6.95, 6.87.

***dl*-*tert*-Amylethylmethylsulfonium Perchlorate.** This compound was prepared from the sulfonium iodide by the procedure described for the preparation of *tert*-butylethylmethylsulfonium perchlorate. The compound had mp 135° dec. *Anal.* Calcd for C₈H₁₉ClO₄S: C, 38.94; H, 7.76. Found: C, 38.60; H, 7.87.

1-Phenyl-2-methyl-2-propyl Ethyl Sulfide. This compound was prepared from 1-phenyl-2-methyl-2-propanol (K & K Laboratories "phenyl-*tert*-butanol") by the procedure described for the preparation of *tert*-butyl ethyl sulfide. The compound had bp 134° (16 mm), η^{25D} 1.5321. *Anal.* Calcd for C₁₂H₁₉S: C, 74.16; H, 9.34. Found: C, 74.5; H, 9.73.

***dl*-1-Phenyl-2-methyl-2-propylethylmethylsulfonium Iodide.** This compound was prepared from 1-phenyl-2-methyl-2-propyl ethyl sulfide by the procedure described for the preparation of *tert*-butylethylmethylsulfonium iodide. This compound had mp 114° dec. *Anal.* Calcd for C₁₃H₂₁IS: C, 46.43; H, 6.29. Found: C, 46.44; H, 6.23.

***dl*-1-Phenyl-2-methyl-2-propylethylmethylsulfonium Perchlorate.** This compound, mp 104° dec, was prepared from 1-phenyl-2-methyl-2-propylethylmethylsulfonium iodide by the method described for the preparation of *tert*-butylethylmethylsulfonium perchlorate. *Anal.* Calcd for C₁₃H₂₁ClO₄S: C, 50.56; H, 6.86. Found: C, 50.49; H, 6.66.

(12) D. T. McAllan, *et al.*, *J. Amer. Chem. Soc.*, 73, 3627 (1951).

Product Analyses. Product analyses were carried out using a Perkin-Elmer vapor fractometer. The areas of the peaks were measured using a Honeywell Disc Integrator. For the product analyses of the *tert*-butyl- and *tert*-amylethylmethylsulfonium salts, accurately known quantities of the sulfonium salt, internal standard, and base were dissolved in the appropriate solvent and the solutions made up to the mark with solvent in a volumetric flask. Aliquots of the solution were transferred to ampoules and sealed. The sealed ampoules were placed in an appropriate constant-temperature bath for a time corresponding to 10–20 half-lives for the reaction. The ampoules were then removed from the bath and cooled to 10°. Upon opening the ampoules, a 50- μ l aliquot of the solution was immediately injected into the gas chromatography apparatus. The amount of each material relative to the internal standard was then determined, and the absolute yield of each product was calculated.

A similar procedure was used for the analysis of the products of solvolysis of 1-phenyl-2-methyl-2-propylethylmethylsulfonium salts with the following modification. After removal of the ampoules from the constant-temperature bath, a 5-ml aliquot of the solution was taken and dissolved in 25 ml of ether. The ether layer was washed, to remove the ethanol or acetic acid, and dried over potassium carbonate, and the ether solution was concentrated to a volume of 1 ml. A 50- μ l aliquot of the solution was then delivered into the gc apparatus and analysis was carried out in the usual manner.

A summary of the chromatography columns, internal standards, and retention times for analysis of the various products is given in Table VIII.

Kinetic Measurements. The sulfonium salt was accurately weighed in a tared volumetric flask. Enough solvent to dissolve the salt, together with as many aliquots of standard stock solutions of base or salt as required, was added to the flask. The solution was then made up to the mark by addition of solvent. The sealed-ampoule technique was used. Each ampoule contained approximately 5.3 ml of solution. The ampoules were placed in a constant-temperature bath at 25.00 ± 0.02 or $50.00 \pm 0.02^\circ$. At appropriate time intervals, the ampoules were removed from the bath. For reactions studied at 50° the ampoules were quenched in an ice-water bath and then equilibrated to 25.0°. A 5-ml aliquot of the solution and titrated with standard base or acid. For reactions at 25°, the ampoules were removed from the constant-temperature bath and immediately opened without quenching. A 5-ml aliquot of the solution was then titrated. The time recorded was that at the beginning of the titration. For reactions in solvent ethanol, the aliquots of the solution were transferred to a 50-ml volumetric flask containing 25 ml of boiled distilled water. Each sample was titrated with standard sodium methoxide in methanol using phenolphthalein as indicator. For reactions in acetic acid and 50% acetic acid-acetic anhydride, the solutions contained an excess of sodium acetate. Each aliquot was titrated for excess base with a standard solution of perchloric acid in acetic acid using *p*-naphtholbenzein as indicator. The "zero point" for each reaction was taken at least 4 min after the ampoules were placed in the constant-temperature bath. "Infinity" measurements were taken after 10 and 20 half-lives for the reactions.

The integrated first-order rate constants were calculated using the experimental infinity values, usually $100 \pm 3\%$ of the theoretical value. The rates were followed to *ca.* 85% completion.

Nuclear Magnetic Resonance Spectra and Characterization of Some Quinone Methides¹

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Abstract: A method is described for preparing nmr samples of even rather unstable quinone methides, by oxidation of the corresponding phenol in carbon tetrachloride solution with silver oxide. The nonequivalence of the ring protons in the nmr spectra of quinone methides with unsymmetrical substitution on the terminal methylene is attributed to van der Waals deshieldings. 4-Allylidene-2,6-dimethyl-2,5-cyclohexadien-1-one was isolated as an unstable crystalline compound and fully characterized. The stabilizing influence of the vinyl substituent is reflected in the low rate of addition of neutral methanol. This quinone methide is reduced by LiAlH_4 to a 63:37 mixture of 4-allyl-2,6-dimethylphenol and 4-propenyl-2,6-dimethylphenol.

Ingold and Brownstein³ report that the stilbene quinones Ia and Ib have nmr spectra in which both the ring protons and the alkyl protons are nonequivalent. Similar nonequivalence has been reported for indophenols⁴ and for quinone methides of type II ($R_1 = \textit{tert}$ -butyl; $R_2 = \text{H}$; $R_3 = \text{CH}_3, \text{OCH}_3, \text{CN}, \text{etc.}$),⁵ and has been attributed to molecular asymmetry.³ However, no detailed explanation of the spectral nonequivalence has been offered, doubtless because some of the compounds whose spectra should be studied are quinone methides too unstable to isolate.

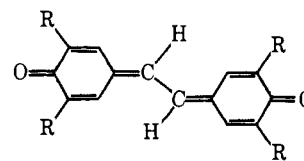
(1) A preliminary account of this work was given to the Fourth Australian Spectroscopy Conference of the Australian Academy of Science, Canberra, Australia, Aug 1963. The work was supported by the Petroleum Research Fund of the American Chemical Society.

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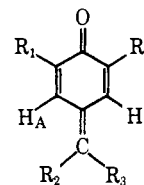
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(4) G. M. Coppinger and J. L. Jungnickel, *J. Chem. Phys.*, **38**, 2589 (1963).

(5) A. Rieker and H. Kessler, *Tetrahedron*, **24**, 5133 (1968).



Ia, R = *tert*-butyl
Ib, R = *tert*-amyl



IIa, $R_1 = \text{CH}_3$; $R_2 = R_3 = \text{H}$
IIb, $R_1 = \text{CH}_3$; $R_2 = \text{H}$; $R_3 = \text{CH}_3$
IIc, $R_1 = \text{CH}_3$; $R_2 = \text{H}$; $R_3 = \text{CH}=\text{CH}_2$
IId, $R_1 = \text{C}(\text{CH}_3)_3$; $R_2 = R_3 = \text{H}$
IIe, $R_1 = \text{C}(\text{CH}_3)_3$; $R_2 = \text{H}$; $R_3 = \text{CH}_3$
IIf, $R_1 = \text{C}(\text{CH}_3)_3$; $R_2 = R_3 = \text{CH}_3$