Anal. Calcd for $C_{13}H_{11}ClN_2O_4$: C, 52.99; H, 3.76; N, 9.51. Found: C, 53.45; H, 3.92; N, 9.47.

Addition of sodium hydroxide to an aqueous solution of the product afforded a fluorescent colorless crystalline compound, mp 134-135°, which by ir spectra and mixture melting point was shown to be identical with an authentic sample[8] of 2-phenylimidazopyridine.

Registry No.—**7** (R = Bu) bromide, 19770-05-9; **9** perchlorate, 13794-84-8; **10** (R = Bu) perchlorate, 19770-06-0; **10** (R = Ph) perchlorate, 19770-07-1; **10** (R = p-$NO_2C_6H_4$) perchlorate, 19789-58-3; **10** (R = p-HOC_6H_4) perchlorate, 19770-08-2; **10** (R = $EtOOCC_6H_4$) perchlorate, 19770-09-3; **10** (R = α-$C_{10}H_7$) perchlorate, 19770-10-6; **13** bromide, 19770-11-7; **13** perchlorate, 19770-12-8; **14** bromide, 19770-13-9; **14** perchlorate, 19770-14-0; **15** perchlorate, 19770-15-1; **16,** 19770-16-2; **17,** 19770-17-3; **18,** 19770-18-4; **19** perchlorate, 19770-19-5; **21** bromide, 19770-20-8; **21** perchlorate, 19770-21-9; **22** perchlorate, 19770-22-0; **23,** 19770-23-1.

The Synthesis of Oxiranes from Aqueous Solutions of Simple Alkyl, Allyl, and Benzylsulfonium Salts[1a]

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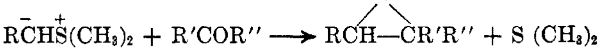
The reaction of simple sulfonium salts with warm aqueous NaOH and carbonyl compounds yields various oxiranes (epoxides). Previously, oxirane syntheses from such sulfonium salts has been achieved only in nonaqueous solutions of much stronger bases. The present work shows that often sufficient sulfonium ylide is formed in aqueous bases to permit trapping reactions. Trimethyl- or triethylsulfonium chlorides gave oxiranes with benzaldehyde (*ca.* 70%). No oxiranes were formed with formaldehyde nor acetaldehyde, since Cannizzaro or aldol condensation reactions apparently intervened. Allyldimethylsulfonium chloride reacted well with benzaldehyde (*ca.* 70% oxirane), poorly with formaldehyde (8%), and not at all with acetaldehyde. A side reaction, leading to propylene oxide, also occurred. Benzyldimethylfonium chloride gave oxiranes with both benzaldehyde and formaldehyde (85 and 87%) and, under conditions of minimal exposure to NaOH, with acetaldehyde also (48%).

Previous workers have described the formation of ylides from alkyl- or benzylsulfonium ions in *nonaqueous* solutions of very strong bases, *e.g.*, methylsulfinyl carbanion in dimethyl sulfoxide,[2] and the reaction of the unstable ylides with aldehydes or ketones to yield oxiranes.[2-5] However, the prospects appeared to be questionable for using *aqueous* solutions in this synthetic reaction of simple[6] sulfonium salts. Thus, the reaction in water of unsubstituted benzyldimethylsulfonium ion and hydroxide ion was known to give only a high yield of benzyl alcohol by an apparent SN2 mechanism.[7] This result indicated that even with the extra ylide stabilization conveyed by the phenyl group, the aqueous ylide concentration was very small, too small at least to yield any carbene and resulting olefin.[8]

The present investigation originated from the following idea. Although in aqueous NaOH, simple sulfonium ylides could be present only in concentrations so small that no olefin-producing carbene intermediate would be produced, *the ylide concentration still might be sufficient for "trapping" reactions to occur with reactive carbonyl compounds.* Preliminary experimental results

$$RCH_2\overset{+}{S}(CH_3)_2\ O\overset{-}{H} \rightleftarrows R\overset{-}{C}H\overset{+}{S}(CH_3)_2 + H_2O$$



$$R\overset{-}{C}H\overset{+}{S}(CH_3)_2 + R'COR'' \longrightarrow RCH\overset{O}{\frown}CR'R'' + S\ (CH_3)_2$$

indeed demonstrated that such trapping reactions are possible, and that synthetically useful yields of oxiranes might be achieved. Studies therefore were made to explore the scope and limitations of the reactions.

The experimental conditions generally were similar. Excess aqueous NaOH (50% solids) was added to a warm, stirred mixture of aqueous sulfonium salt, carbonyl compound, and (usually) an immiscible solvent. After reaction times which ranged from a few minutes to several hours at 70-80°, the immiscible solvent (or distillate) was analyzed for oxirane content by use of a pyridine-pyridine-hydrochloride mixture,[9] and product epoxide was then further isolated and/or characterized.

Reaction of Trialkylsulfonium Salts.—Even trialkylsulfonium salts were sufficiently acidic to react in

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(1) (a) This work was reported at the 22nd Annual Southwest Regional Meeting of the American Chemical Society, Albuquerque, N. M., Nov 1966. (b) Chemistry Department, New Mexico Institute of Mining and Technology, Socorro, N. M. 87801.

(2) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1353 (1965).

(3) E. J. Corey and W. O. Oppolzer, *ibid.*, **86**, 1899 (1964). One may note that this oxirane synthesis bears obvious analogy to the classical Darzen glycidic ester synthesis.

(4) A. W. Johnson, V. J. Hruby, and J. L. Williams, *ibid.*, **86**, 918 (1964).

(5) (a) V. Franzen and H. E. Fruessen, *Chem. Ber*, **96**, 1881 (1963). (b) A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966, pp 328-337, gives a review of the reaction. This author (p 2) also suggests the term "ylid," rather than "ylide."

(6) In this article, simple sulfonium salts are considered to be those containing only alkyl, allyl, or benzyl groups which have no substituents or at least have no strongly electron-withdrawing substituents.

(7) C. G. Swain and E. R. Thornton, *J. Amer. Chem. Soc.*, **83**, 4033 (1961).

(8) Previously known to exist in water were sulfonium ylides in which the carbanionic center is stabilized considerably by conjugation to electron-withdrawing groups in *addition* to the adjacent sulfonium center. (These, then, were nonsimple sulfonium ylides.) Thus, dimethylsulfonium fluorenylide was prepared in aqueous solution by C. K. Ingold and J. A. Jessop, *J. Chem. Soc.*, 713 (1930), and this stabilized ylide could react with certain carbonyl compounds, at least in nonaqueous solution, to yield epoxides, as shown by A. W. Johnson and R. B. LaCount, *J. Amer. Chem., Soc.*, **83**, 417 (1961). Dimethylsulfonium p-nitrobenzylide in aqueous solution was suggested as a reaction intermediate which led to the carbene and corresponding stilbene in the work of Swain and Thornton.[7] This contrasted with their above-cited results from unsubstituted benzylsulfonium ion. The phenyl group would provide far less stabilization of a carbanionic center than would the p-nitrophenyl group, of course.

(9) F. E. Critchfield, "Organic Functional Group Analysis," Pergamon Press, Inc., New York, N. Y., 1963, pp 133-136. This method is only semiquantitative with some disubstituted oxiranes. It will give 10-15% low results often in such cases, as indicated by studies in this laboratory with purified *trans*-stilbene oxide (*trans*-2,3-diphenyloxirane). With styrene oxide, the method gave results that were reproducible to ±5%, and averaged about 5% lower than theory.

aqueous bases with *some* carbonyl compounds. Thus, trimethylsulfonium chloride, sodium hydroxide, and benzaldehyde yielded styrene oxide (68%). Triethylsulfonium bromide, sodium hydroxide, and benzaldehyde readily formed 2-methyl-3-phenyloxirane (*cis* and *trans* mixture, *trans* predominant, 80% yield). This latter experiment showed that even in sulfonium salts containing β-hydrogen atoms, ylide formation and reaction could compete very well with any anticipated complications[3,4] of E2 elimination.

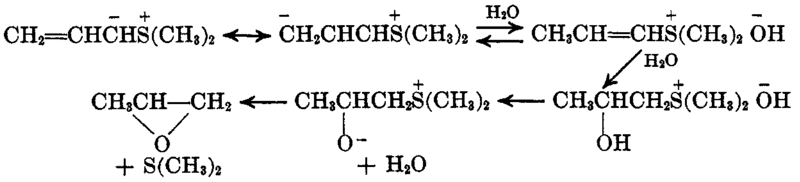
A rough kinetic study was made of the effect of the presence of benzaldehyde on the rate of reaction of trimethylsulfonium or triethylsulfonium ions with NaOH (stirred, aqueous–alcoholic systems, containing benzene extractant). When benzaldehyde was present, the initial rates of NaOH consumption were increased at least fivefold in both cases. (See the Experimental Section for details.) These results indicated that the benzaldehyde was diverting the normal S_N2 or E2 reaction courses of the sulfonium ions by addition reaction with very small concentrations present of rapidly, reversibly formed ylide.

Reaction of aqueous trimethylsulfonium chloride with NaOH and formaldehyde or acetone yielded no detectable oxirane. The rapid Cannizzaro reaction of formaldehyde with hot NaOH probably prevented ethylene oxide formation. Similarly, condensation reactions of acetone may have prevented isobutylene oxide formation.

Reactions of Allylsulfonium Salts.—The allylic ylide from allyldimethylsulfonium ion should have increased stability, relative to ylides from trialkylsulfonium ions, due to some conjugation of the carbanionic center with the adjacent vinyl group. The resulting higher ylide concentration could lead to improved reaction with carbonyl compounds.

Indeed, about 8% yield of butadiene monoepoxide (2-vinyloxirane) was achieved with formaldehyde (15-min reaction). With benzaldehyde, 60% or better yields of phenylbutadiene monoepoxide (2-phenyl-3-vinyloxirane, *cis* and *trans* mixture, predominately *trans*) resulted. However, only trace amounts or none of the desired oxiranes formed in the reaction of aqueous allyldimethylsulfonium chloride, NaOH, and acetaldehyde, heptaldehyde, acrolein, or acetone.

Besides competing Cannizzaro and aldol condensation reactions of the carbonyl compounds, possible side reactions of allylsulfonium salts and bases[10] also limited the possibilities of obtaining the desired epoxide products.



One side reaction, surprisingly, led to the formation of propylene oxide (2-methyloxirane), generally in yields from 10 to 40%. The carbonyl compound was not involved in this side reaction, since allyldimethylsulfonium chloride and sodium hydroxide when allowed to react directly together gave about 50% yield of propylene oxide product. Its origin could be rationalized as follows. Hydroxide ion catalyzed isomerization of the allylsulfonium ion to a propenylsulfonium ion was followed by Michael addition of water, deprotonation of the hydroxypropyl group, and ring closure to propylene oxide and dimethyl sulfide. The isomerization of analogous allyl and propenyl phosphonium ylides is known.[11]

In the reaction of allyldimethylsulfonium ion, hydroxide ion, and benzaldehyde to yield phenylbutadiene monoepoxide, the propylene oxide by-product essentially could be eliminated by conducting the reaction at room temperature, or by using an alcohol cosolvent. (The adduct epoxide is not very labile to base.) See Table I for details.

Reactions of Benzylsulfonium Salts.—Due to conjugation of the carbanionic center with the benzene ring, one expects greater stability in the benzylic ylide derived from benzyldimethylsulfonium ion than would be present in an allylic ylide; one might therefore expect improved reactivity with carbonyl compounds. Indeed, benzylic sulfonium salts proved to be better reaction intermediates than those with allylic conjugation. High yields of styrene oxide resulted by reaction of benzyldimethylsulfonium chloride, formaldehyde, and NaOH. Within a few minutes after this very fast reaction was over, the Cannizzaro reaction consumed all residual formaldehyde.

Benzyldimethylsulfonium chloride also reacted well with benzaldehyde and NaOH to yield stilbene oxide (as expected since favorable results were obtained even with formaldehyde, which undergoes the competitive Cannizarro reaction more readily). In contrast, only self-condensation and polymerization reactions of acetaldehyde or acrolein were evident under the usual reaction conditions. The slow addition of benzene-diluted acetaldehyde or acrolein to preheated mixture of benzyldimethylsulfonium chloride and NaOH ("inverse addition") did give modest yields of the desired epoxide products (1,2-epoxypropylbenzene and 2-phenyl-3-vinyloxirane, respectively). Inverse addition of aqueous glyoxal to the basic sulfonium salt solution yielded no detectable epoxide, however. With acetone or acetophenone, fair yields of the corresponding epoxides were produced (2,2-dimethyl-3-phenyloxirane and 2,3-diphenyl-2-methyloxirane).

Benzylbis(2-hydroxyethyl)sulfonium chloride reacted with benzaldehyde and NaOH to give a modest yield of *trans*-stilbene oxide. This experiment indicated that benzylic ylide formation and reaction successfully competed with proton removal from the alcoholic OH groups followed by neighboring-group displacement reaction at the sulfonium center, which would have yielded ethylene oxide.

An empirical study was made of the synthesis of sty-

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[10] For example, see the communication of J. E. Baldwin, R. E. Hackler, and D. P. Kelley, *J. Amer. Chem. Soc.*, **90**, 4758 (1968), and the work cited therein.

[11] E. E. Schweizer, E. T. Shaffer, C. T. Hughes, and C. S. Berninger, *J. Org. Chem.*, **31**, 2907 (1966).

TABLE I

PHENYLBUTADIENE MONOEPOXIDE PREPARATIONS

Initial sulfonium molarity[a]	Reactant ratios[b]		Solvent[g]	Temp, °C		Reaction time, min	Yield (%) of epoxide products[c]		
	Benz-aldehyde	Hydroxide		Initial	Max		Total	Propylene oxide	Phenylbutadiene monoepoxide
2.8	3.0	1.4	Benzene	40	72	60	70	13	57
3.4	1.0	1.6	Benzene	37	62	15	58	21	37
3.0	1.0	2.5	Benzene	35	65	10	65	18	48
2.8	1.0	3.0	Toluene	55	83	90	15	4	11
3.4	1.0	1.6	Toluene	35	60	15	65	18	48
3.4	1.0	1.6	Toluene	5	25	1000[d]	60	<1	60
1.2[f]	1.0	1.3	Methanol[f]	25	50	120	65	<2	63[e]
1.6[f]	1.0	1.6	Isopropyl alcohol[f]	35	68	150	73	<1	73

[a] Total moles of allyldimethylsulfonium chloride was 0.150. Concentration based on volume of aqueous phase of reaction mixture (after addition of aqueous NaOH). [b] Initial moles per mole of sulfonium salt. The hydroxide used was NaOH in all cases. [c] Total epoxide yield by pyridine hydrochloride analysis[9] of product solution. Propylene oxide yield by gas chromatographic comparison with authenic standards, and by pyridine hydrochloride analysis of all products distilling under 65°. Phenylbutadiene monoepoxide yield by pyridine hydrochloride analysis of 65° distillation residue. [d] Approximate; reaction held under 15° for 60 min, then let stand overnight at room temperature. [e] Value by difference. [f] With these compatibilizing solvents, concentration was based on total volume of the system. [g] Approximately 75 ml of water-immiscible solvents were used. Approximately 70 ml of methanol and 45 ml of isopropyl alcohol was used.

TABLE II

STYRENE OXIDE PREPARATIONS

Initial sulfonium molarity[a]	Reactant ratios[b]		Solvent[f]	Temp, °C		Reaction time, min	Yield (%)[c] of styrene oxide
	Formal-dehyde	Hydroxide		Initial	Max		
1.48*	2.8	1.42	*n*-Hexane	25	30	4000	14
1.48*	2.8	1.42	Benzene	40	67	60[d]	48
1.58	2.8	1.42	Toluene	80	88	5	48
1.28	2.8	4.25	Benzene	27	60	2	61
1.28	2.8	4.25	Toluene	55	84	2	86
1.28	2.8	4.25	Toluene	55	84	10	84
1.25	2.8	4.25	Ethylbenzene	55	87	2	88
1.28	2.8	4.25	Heptane[e]	75	84	2	66
1.51	1.41	4.25	Toluene	55	84	2	70
1.13	1.41	8.0	Toluene	55	84	2	34

[a] Total moles of benzyldimethylsulfonium chloride was 0.330 in starred runs and 0.165 in all others. Concentration based on volume of aqueous phase of reaction mixture, after addition of aqueous CH_2O and aqueous NaOH. [b] Initial moles per mole of sulfonium salt. The hydroxide used was NaOH in all cases. [c] Yield, by pyridine hydrochloride analysis of product solution, based on sulfonium salt. [d] Yield was 41% when this reaction was run 6 min. [e] With toluene under these conditions, the reaction boiled over (recovered yield, 80%) and slower addition of NaOH reduced the yield (65%). [f] Approximately 75 ml of solvent was used.

rene oxide from benzyldimethylsulfonium chloride, formaldehyde, and NaOH (see Table II).

The product yield increased at higher temperatures and higher formaldehyde and NaOH loadings, using solvents like benzene or preferably toluene or ethyl benzene. The following describes a typical good run. With a solution of 1.28 *M* sulfonium chloride, 3.6 *M* formaldehyde, stirred well with about 1 vol of toluene and preheated to 55°, rapid addition of 4.25 mol of 50% NaOH/mol of sulfonium chloride gave immediate exotherm to 84° (reflux). After 2 min, the reaction was terminated with ice and an 86% yield of styrene oxide was present in the toluene. A study of the mechanism of this reaction by means of deuterium labeling has been reported elsewhere.[12]

One might expect the reaction of negatively substituted benzylic sulfonium salts with carbonyl compounds and NaOH should be more facile than the reaction of unsubstituted benzylic sulfonium salts. (Actually, *p*-nitrobenzyl chloride itself is known to undergo a Darzens reaction with various aromatic aldehydes.[13,14]) However, if the sulfonium ylides are too stabilized and/or sterically hindered, their reactivities with carbonyl compounds may drop off again. Thus, sulfonium fluorenylides are known to be limited in the types of carbonyl compounds with which they will form epoxides.[4,15] Also, *p*-nitrobenzylsulfonium salts might give the corresponding stilbene instead of epoxides, since the carbene forms readily.[7]

Conclusions.—The present work demonstrates that a sulfonium substituent is in the same class in ability to make α-methylene groups acidic and thereby "activate" them for carbonyl condensation reactions as are the well-known "activating" groups, such as keto groups. Consequently, in order to perform such condensation reactions with sulfonium salts, one need not always resort to the previously used low-temperature preparations of ylides in extremely basic, nonaqueous systems. Direct reactions in basic aqueous or alcoholic media, with resulting advantages of convenience and economy, often will serve. The scope of synthetically useful reactions of aqueous sulfonium salts, carbonyl compounds, and NaOH to produce oxiranes is quite broad, but is subject to structural factors and reaction conditions. Within limits, increasing acidity of the sulfonium salts, and decreasing base-catalyzed self-reactivity of the carbonyl compounds will favor the formation of

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(12) M. Yoshimine and M. J. Hatch, *J. Amer. Chem. Soc.*, **89**, 5831 (1967).

(13) E. Kleucker, *Chem. Ber.*, **55B**, 1634 (1922).

(14) E. Bergmann, and J. Hervey, *ibid.*, **62B**, 893 (1929).

(15) Johnson and LaCount, ref 8.

the desired epoxy products. Many side reactions are possible, especially with the benzylic and *allylic* sulfonium salts.

Experimental Section[16]

Trimethylsulfonium Chloride.—Crystalline trimethylsulfonium iodide was prepared similarly to the method of Emeleus and Heal[17] by the reaction of methyl iodide and dimethyl sulfide. The sulfonium iodide (430 g), dissolved in water (*ca.* 900 ml), was converted to trimethylsulfonium chloride by passage through a bed (3.2 l.) of chloride-form anion-exchange resin (Dowex 1, 8% cross-linked 50–100 mesh[18]). The elutate fractions were monitored by potentiometric titrations for ionic chloride and iodide ($AgNO_3$), and the iodide-free fractions (83% yield) were concentrated (to *ca.* 5 *M*) *in vacuo* at room temperature, by use of a rotary evaporator.

Triethylsulfonium bromide was prepared in aqueous solution by refluxing a stirred mixture of ethyl sulfide (100 g, 1.11 mol), ethyl bromide (123 g, 1.11 mol), ethanol (120 ml), and water (35 ml) for 20 hr. The final aqueous phase (120 ml), separated and washed with benzene, contained the sulfonium bromide (2.78 mol) in 30% conversion, and HBr (hydrolysis product) in 2.3% conversion, as shown by ionic bromide and acidity titrations ($AgNO_3$ and NaOH, respectively).

Allyldimethylsulfonium chloride was prepared in aqueous solution by stirring at room temperature a mixture of allyl chloride (282 g, 3.8 mol), dimethyl sulfide (255 g, 4.1 mol), and water (300 ml). After 8 days the separated, nitrogen-blown aqueous solution contained 89% yield of the product (4.7 *M*), as shown by analysis for ionic chloride. (Hydrolysis was less than 5%.)

Benzyldimethylsulfonium chloride was prepared in aqueous solution by stirring at reflux (35–40°) a mixture of benzyl chloride (2000 g, 15.8 mol), dimethyl sulfide (1080 g, 17.4 mol), and water (2.4 l.). After 20 hr, the separated, nitrogen-blown solution contained the product (3.4 *M*) in essentially quantitative yield, as shown by analysis for ionic chloride. (Hydrolysis was less than 1%.)

Benzylbis(2-hydroxyethyl)sulfonium chloride was prepared in aqueous solution by heating a stirred mixture of benzyl chloride (690 g, 5.5 mol), bis(2-hydroxyethyl) sulfide (665 g, 5.5 mol), and water (550 ml) at about 70° for 2 hr. The mixture was allowed to stir overnight without heating to give a single-phase, aqueous solution of the sulfonium salt. Ionic chloride analyses indicated 95% conversion to sulfonium salt and 5% hydrolysis.

Styrene Oxide from Trimethylsulfonium Chloride.—The reaction was run (hood) in a three-neck flask, equipped with heating mantle, mechanical stirrer, and reflux condensor. To a stirred mixture of the sulfonium salt (50 ml, aqueous, 0.28 mol), benzaldehyde (28 ml, 0.28 mol), benzene (200 ml), *n*-propyl alcohol (100 ml), and water (12 ml) at 50°, aqueous NaOH (21 ml, 0.39 mol) was added rapidly. There was little or no heat evolution. The mixture was heated at reflux (*ca.* 70°) for 1 hr and cooled, and the separated oil layer was washed with water and dried ($MgSO_4$). Gas chromatographic analysis comparing known styrene oxide (Aldrich Chemical Co.,) indicated styrene oxide (68% yield) was present in the product oil. Vacuum distillation (seven-plate Vigreux column) yielded styrene oxide (22 g, 69–73°, 10 mm) which contained about 7% benzaldehyde, as shown by comparison of the infrared spectra with known standards.

1,2-Epoxypropylbenzene from Triethylsulfonium Bromide.—To a stirred mixture of the sulfonium salt (100 ml, aqueous, 0.28 mol), benzaldehyde (30 ml, 0.30 mol), benzene (200 ml), ethanol (80 ml), and water (15 ml) at 50°, was added rapidly aqueous NaOH (22 ml, 0.42 mol). There was a little heat evolution. The mixture was heated at reflux (*ca.* 70°) for 2 hr and cooled, and the oil phase was separated. Semiquantitative chemical analysis[9] indicated that product oxirane was present (over 70% yield). Distillation (as above) yielded a mixture of *cis*- and *trans*-2-methyl-3-phenyloxirane (26 g, 47–50°, 2 mm) which contained about 10% benzaldehyde, as shown by infrared analysis. Reported for racemic *cis*- and *trans*-2-methyl-3-phenyloxiranes, respectively, are *cis*, bp 83–84° (13 mm); *trans*, bp 88° (13 mm).[19] Benzaldehyde could be extracted from the product oxirane mixture by use of aqueous Girard's reagent, $NH_2NHCOCH_2{}^+N(CH_3)_3\ Cl^-$. Comparison of the infrared spectra with reported spectra[20] identified the oxirane products. The *trans* product appeared to be dominant, based on the spectra.

Reaction of Sulfonium Salts with NaOH in the Absence and Presence of Benzaldehyde.—The following systems were studied: (A) triethylsulfonium bromide (aqueous, 5.0 ml, 17 mmol), NaOH (aqueous, 1.20 ml, 23.5 mmol), water (1.0 ml), ethanol (4.0 ml), benzene (10.0 ml), NaCl (2.5 g); (B) like A, minus NaCl and plus benzaldehyde (1.7 ml, 17 mmol); (C) trimethylsulfonium chloride (aqueous, 2.5 ml, 13.7 mmol), NaOH (aqueous 1.00 ml, 19.7 mmol), water (1.0 ml), *n*-propyl alcohol (5.0 ml), benzene (10.0 ml), NaCl (2.5 g); (D) like C minus NaCl and plus benzaldehyde (1.7 ml, 17 mmol). Each system, minus NaOH, was heated to 50° with stirring. Then the NaOH solution was added and the system was heated at reflux for the appropriate time, quenched in water, and analyzed for residual NaOH by titration with acid. The results follow: (A) in 15, 30, and 60 min, 15, 24, and 30% NaOH was consumed, respectively; (B) in 5, 15, and 30 min, 42, 58, and 65% NaOH was consumed, respectively; (C) in 15, 30, and 60 min, 28, 31, and 34% NaOH was consumed, respectively; (D) in 5, 15, and 30 min, 60, 65, and 80% NaOH was consumed, respectively.

2-Vinyloxirane and By-product from Allyldimethylsulfonium Chloride.—A mixture of the sulfonium salt (75 ml, aqueous, 0.33 mol), CH_2O (75 ml, aqueous 1.00 mol, CH_3OH inhibitor), and benzene (100 ml) was stirred at 45°. Then aqueous NaOH (23 ml, 0.45 mol) was added in three portions during 3 min, and the temperature rose to 68°. The reaction was allowed to proceed without additional heating until the temperature dropped to 40°; then the separated oil phase was washed with water. The washed oil contained 2-vinyloxirane (7% yield) as shown by gas chromatography, using an authentic sample for comparison. In related experiments at higher temperatures, using toluene instead of benzene, the unwashed product oil was distilled (seven-plate Vigreux column). The distillate (37–40°) contained both 2-methoxyoxirane (12% yield) and 2-vinyloxirane (8% yield), as shown by comparison of infrared spectra of distillate cuts with the spectra of known samples.

2-Phenyl-3-vinyloxirane and By-products from Allyldimethylsulfonium Chloride.—To a stirred mixture of the sulfonium salt (63 ml, aqueous, 0.30 mol), benzaldehyde (30 ml, 0.30 mol), and toluene (100 ml) which was heated to 35°, was added aqueous NaOH (25 ml, 0.47 mol) over a period of 1 min. The temperature rose to 63°, and after 15 min at slightly above 55°, the oil layer (143 g) was separated. The reaction was repeated five times on the same scale, and once using threefold quantities; then the oil layers were combined (958 g out of 1140) and distilled (20-plate Podbelniak column). The cold trap cut (27–47.5°, 100 mm) contained considerable propylene oxide (24 g, 21% yield). Benzaldehyde (58–60, 10 mm) was recovered (89 g, 42%). A product, which apparently was 3-butenyl methyl sulfide (61–63.5°, 100 mm, equals[21] approx 122°, 760 mm; lit.[22] for the analogous butyl methyl sulfide, 123°, at 760 mm), was isolated (26 g, 12% yield). The infrared spectrum showed vinyl absorption (6.10 and 10.95 μ) and the nmr spectrum was consistent with this structure. Peaks were obtained at δ 2.03 (singlet, 3 H), 2.1–2.8 (multiplet, 4 H), 5.4–6.2 (multiplet, 1 H), and 4.8–5.2 ppm (multiplet, 2 H). Product of this structure could arise by a known type of ylide rearrangement.[10]

2-Phenyl-3-vinyloxirane (49–50.5°, 0.7 mm, equals[21] $\sim$220°, 760 mm; lit.[23] 99–101°, 16 mm, equals[21] $\sim$218°, 760 mm) was obtained as a mixture of *cis* and *trans* isomers (77 g, 27% yield). Analysis[9] for epoxide groups gave 84% of the theoretical value, but the method used is expected[9] to give low results. The oxirane (69 g) was redistilled (seven-plate Vigreux column), yielding

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[16] When dimethyl sulfide was a reactant or product, a good hood was used. All melting points are uncorrected. Infrared spectra were obtained on a Beckman IR-5 instrument, nmr spectra on a Varian A-60 instrument. Extensive assistance in conducting the experimental work was provided by Mr. Hugh B. Smith and Mr. John A. Dillon of this laboratory. The nmr analyses were provided by the Chemical Physics Laboratory (The Dow Chemical Co.); combustion microanalyses were provided by the Dow Special Services Laboratory. Purity analyses by freezing point curves were provided by the Dow Analytical Laboratory.

[17] H. J. Emeleus and H. G. Heal, *J. Chem. Soc.*, 1126 (1946).

[18] Product of The Dow Chemical Co., Midland, Mich.

[19] F. Fisher, *Chem. Ber.*, **89**, 2438 (1956).

[20] C. M. Froltz and B. Witkop, *J. Amer. Chem. Soc.*, **79**, 203 (1957).

[21] F. J. Zuiderweg, "Laboratory Manual of Batch Distillation," Interscience Publishers, Inc., New York, N. Y., 1957, p 120.

[22] "Handbook of Chemistry and Physics," 46th ed, The Chemical Rubber Publishing Co., Cleveland, Ohio, 1965, p C-552.

[23] D. Abragam and Y. Deux, *Compt. Rend.*, **205**, 285 (1937).

four cuts at 0.5 mm: (1) 46°, 3.8 g; (2) 46–50°, 10.8 g; (3) 50–52°, 25.0 g; (4) 52°, 29 g (residue, 0.5 g). Gas chromatography (9.5 ft × $^3/_{16}$ in., diethylene glycol succinate on acid-washed silanized Chromosorb, on-column injection, 95°) showed two main peaks in all the cuts, at ratios of 48:48, 34:66, 34:65, 24:76, 10:90, respectively. Gas chromatography at 125° apparently produced isomerization. *Anal.* Calcd for $C_{10}H_{10}O$: C, 82.2; H, 6.90. Found for cut 3: C, 82.6; H, 7.1.

Propylene Oxide from Allydimethylsulfonium Chloride and Sodium Hydroxide.—To a mixture of the sulfonium salt (138 ml, 0.69 mol) and NaOH (70 ml, 0.69 mol) stirred and rapidly heated to 60°, benzene ($\sim$250 ml) was added during a period of 20 min. After another 30 min at about 70°, the oil phase was separated, washed twice with equal volumes of water, dried and analyzed[9] for epoxide content: found 48% yield. Distillation (seven-plate Vigreux column) gave product (35–38°, 743 mm) which was shown to be a mixture (about 50:50) of propylene oxide and dimethyl sulfide (25.2 g, oxide yield 35%). The analysis was made by comparison of the infrared spectra with spectra of known mixtures of the two compounds.

Styrene Oxide from Benzyldimethylsulfonium Chloride.—To a well-stirred mixture of the sulfonium salt (59.6 ml, aqueous, 0.165 mol), CH_2O (37.5 ml, aqueous, 0.465 mol, CH_3OH inhibitor), and ethylbenzene (75 ml) at 55°, NaOH solution was added rapidly (36.0 ml, aqueous, 0.70 mol). The temperature rose quickly to 87° (reflux). After 2 min, ice was added to cool the mixture, and the oil phase (92 g) was separated. By analysis[9] it contained 87% yield of styrene oxide, based on starting sulfonium salt. Most of the oil phase (71 g) was distilled (seven-plate Vigreux column). Styrene oxide (71–73°, 10 mm) which was 94% pure, based on epoxide analysis,[9] was obtained (15 g). By freezing-point analysis (fp $-38.14°$) the mole per cent purity was 96.8. Thus the isolated yield was over 90% if the impurities had about the same molecular weight as styrene oxide itself.

Stilbene Oxide from Benzyldimethylsulfonium Chloride.—The sulfonium salt (100 ml, aqueous, 0.33 mol), ethanol (200 ml), and benzaldehyde formed a clear solution on mixing. NaOH (50 ml, 0.05 mol) was added, the mixture was heated to 65°, and more NaOH was added (35 ml, 0.435 mol). The solution clouded immediately and cleared on addition of more ethanol (75 ml). After heating at reflux (70°) for about 1 hr, the mixture was diluted with water (1000 ml) and extracted with CH_2Cl_2 (300 ml). Evaporation of the CH_2Cl_2 layer gave a heavy oil which crystallized. The white solid was slurried in a small amount of methanol, filtered, washed with methanol, and dried, (mp 67–70°, 28 g, 45% yield, lit.[7] 68° for *trans*-stilbene oxide). The infrared spectrum was identical with that of authentic *trans*-stilbene oxide.

A similar reaction of benzylbis(hydroxyethyl)sulfonium chloride, NaOH, and benzaldehyde gave a 19% yield of *trans*-stilbene oxide.

Large-scale preparations, using benzyldimethylsulfonium chloride (1000 ml, 3.4 mol), excess benzaldehyde (686 ml, 6.86 mol), excess NaOH (284 ml, aqueous, 5.6 mol), and toluene (1500 ml) and heating at reflux (*ca.* 80° for 30 min) gave 85% corrected[9] analytical yield of stilbene oxide. Pure *trans* isomer easily was isolated (57% yield) by evaporating (vac) most of the toluene and cooling the concentrate.

1,2-Epoxypropylbenzene from Benzyldimethylsulfonium Chloride.—The sulfonium salt (150 ml, aqueous 0.54 mol) and NaOH (55 ml, 0.54 mol) were stirred and heated to 60°, and a solution of CH_3CHO (32 ml, 0.54 mol, in 150 ml of benzene) was added over a period of 10 min. The temperature rose gradually to about 64° during the addition. Heating the mixture at reflux for another 20 min gave a slightly dark oil phase. The aqueous phase (160 ml) contained 0.136 equiv of base, so 76% of the theoretical amount of NaOH had reacted. The separated oil phase (200 g) contained 0.27 equiv of epoxide[9] (67% yield, based on NaOH reacted). Distillation of the oil phase (seven-plate Vigreux column) yielded 1,2-epoxypropylbenzene (40–44°, 0.5 mm, 26 g, 48% yield based on NaOH reacted). Its infrared spectrum was very similar to the spectrum of 1,2-epoxypropylbenzene, prepared by reaction of triethylsulfonium chloride, benzaldehyde, and NaOH (see above), and indicated that the *trans* product was dominant.

2-Phenyl-3-vinyloxirane from Benzyldimethylsulfonium Chloride.—Acrolein (25 ml, 0.44 mol) in benzene (150 ml) was added over a period of 10 min to a well-stirred mixture of the sulfonium salt (160 ml, aqueous, 0.44 mol) and NaOH (50 ml, aqueous, 0.47 mol), which had been rapidly preheated to 60°. The mixture was heated at reflux (68–70°) for an additional 15 min, then the oil phase was separated (148 g) and analyzed[9] for epoxide content (16% yield). Distillation (seven-plate Vigreux column) of the oil layer gave a fraction (13 g, 50–53°, 0.9–0.8 mm) whose infrared spectrum, on comparison with that of known 34/65 *cis/trans* mixture of 2-phenyl-3-vinyloxirane,[24] showed the fraction was about 50% 2-phenyl-3-vinyloxirane. The quantitative estimation was made from the comparative intensities of the vinyl (10.13 and 10.8 μ) and epoxide ring (8.00 and 11.43 μ) infrared absorption peaks. Chemical analysis[9] of the fraction for epoxide functionality also indicated about 50% 2-phenyl-3-vinyloxirane content.

2,2-Dimethyl-3-phenyloxirane from Benzyldimethylsulfonium Chloride.—The sulfonium salt (100 ml, 0.30 mol), acetone (60 ml, 0.83 mol), and *n*-hexane (150 ml) were mixed and stirred at 24°. Then NaOH (38 ml, aqueous, 0.47 mol) was added. The temperature rose slightly to 27°. The mixture was heated at reflux (50°), and NaOH consumption was found by titration of samples with acid. After 20 min, NaOH consumed was about 0.26 equiv; after 45 and 60 min, about 0.33 equiv. The oil phase was separated (208 ml) and filtered, and the volatile solvent was evaporated.

Chemical analysis[9] of the final oil (26 g) for epoxide content indicated that it contained at least 40% yield. Part (12 g) of the oil was distilled (seven-plate Vigreux column) to give 2,2-dimethyl-3-phenyloxirane (10.5 g, 57% yield, 77°, 10 mm, equals[21] $\sim$200°, 760 mm; lit.[25] 87–90°, 15 mm, equals[21] $\sim$200–204°, 760 mm). *Anal.* Calcd for $C_{10}H_{12}O$: C, 81.0; H, 8.1. Found: C, 80.8; H, 7.9.

2,3-Diphenyl-2-methyloxirane from Benzyldimethylsulfonium Chloride.—To a stirred mixture of the sulfonium salt (100 ml, aqueous, 0.30 mol), acetophenone (120 ml, 1.03 mol), and hexane (150 ml) at room temperature was added NaOH (38 ml, aqueous, 0.46 mol). The temperature rose 2°. The mixture was heated at reflux (50–60°) for about 2 hr. The oil layer then was separated and the solvent was evaporated. Chemical analysis[9] of the residue (141 g) for epoxide content indicated at least 45% yield. The oil was filtered and part (94 g) was distilled at 0.7 mm (seven-plate Vigreux column). Decomposition was evident in the pot material as the product began to distill and only a small amount was collected (3.6 g, 97–115°, 0.7–1.5 mm). The distillate formed a white solid, mp 45–47° (lit.[26] 45–47° for 2,3-diphenyl-2-methyloxirane).

Registry No.—Trimethylsulfonium chloride, 3086-29-1; triethylsulfonium bromide, 3378-18-5; allyldimethylsulfonium chloride, 19766-51-9; benzyldimethylsulfonium chloride, 14182-14-0; benzylbis(2-hydroxyethyl)sulfonium chloride, 19766-53-1.

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(24) Redistilled product, cut 3, from the reaction of allyldimethylsulfonium chloride, benzaldehyde, and NaOH (see above).

(25) J. Levy and A. Tabart, *Bull. Soc. Chim. Fr.*, **49**, 1776 (1931).

(26) F. Kayser, *Ann. Chim.*, **11**, 236 (1936).