ΔH-ΔS relation was interpreted in terms of the steric effects in the silver ion complexes. From the above comparison, it may be concluded that in the protonation process of alkenyl ethers the steric contribution, if any, of alkyl groups is far less important than that observed in the silver ion complexation.

The Mechanism of the Reaction of Aqueous Benzyldimethylsulfonium Chloride and Formaldehyde with Sodium Hydroxide

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Abstract: The mechanism of the reaction of aqueous benzyldimethylsulfonium chloride, formaldehyde, and sodium hydroxide is (1) a rapid and reversible formation of dimethylsulfonium benzylide, (2) a rate-determining nucleophilic attack of the ylide on formaldehyde to form a betaine intermediate, and (3) a rapid intramolecular displacement of methyl sulfide by the oxyanion to yield styrene oxide. The tentatively identified by-products of the reaction appear to be derived from the OH⁻ displacement reaction on the sulfonium ion, the rearrangement of ylides, and the attack of methyl sulfide and methanol on styrene oxide.

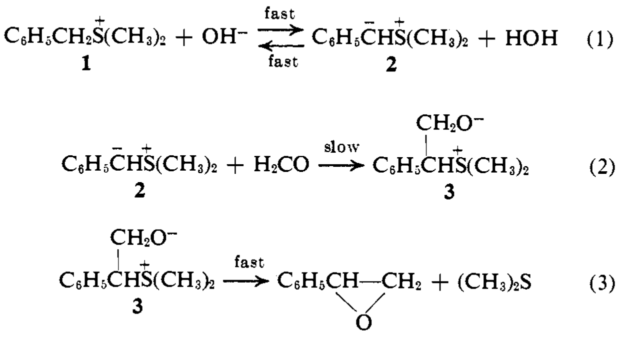
The general utility of the reaction of sulfonium ylides with aldehydes and ketones to yield the corresponding oxiranes has been reported recently.[1-3] The reactions ranged from a stabilized isolable dimethylsulfonium fluorenylide with activated benzaldehydes[4] to the thermally unstable dimethylsulfonium methylide with several ketones and aldehydes.[2] It should be noted that all the reactions were carried out in nonaqueous solvents at low temperatures (25 to −70°).

Hatch[5] has reported a method for selectively trapping the reactive ylide with various aldehydes and ketones in an aqueous alkaline system and removing the oxiranes as formed by an immiscible organic extractant. The reaction of benzyldimethylsulfonium chloride (**1**) with formaldehyde in aqueous sodium hydroxide gave styrene oxide in an 84% yield. The present paper describes a study of the mechanism of this reaction.

The nucleophilic attack of the ylide carbanion on the carbonyl carbon has been generally suggested for the reaction of sulfonium ylides with aldehydes and ketones in nonaqueous systems.[2-4] Sivaramakrishnan and Radhakrishnamurti[6] have proposed recently a carbene mechanism for the reaction of trimethylsulfonium iodide, benzaldehyde, and potassium *t*-butoxide in 90% DMSO.

The proposed mechanism illustrated in Chart I accounts for the products of the reaction (in an aqueous system). This is the mechanism the authors of this paper suggest.

Chart I



$$\underset{\mathbf{1}}{C_6H_5CH_2\overset{+}{S}(CH_3)_2} + OH^- \underset{\text{fast}}{\overset{\text{fast}}{\rightleftarrows}} \underset{\mathbf{2}}{C_6H_5\overset{-}{C}H\overset{+}{S}(CH_3)_2} + HOH \qquad (1)$$

$$\underset{\mathbf{2}}{C_6H_5\overset{-}{C}H\overset{+}{S}(CH_3)_2} + H_2CO \xrightarrow{\text{slow}} \underset{\mathbf{3}}{C_6H_5\overset{CH_2O^-}{\overset{|}{C}}H\overset{+}{S}(CH_3)_2} \qquad (2)$$

$$\underset{\mathbf{3}}{C_6H_5\overset{CH_2O^-}{\overset{|}{C}}H\overset{+}{S}(CH_3)_2} \xrightarrow{\text{fast}} C_6H_5CH{-}CH_2\ (\text{O bridge}) + (CH_3)_2S \qquad (3)$$

The initial step is a rapid and reversible formation of the ylide **2**. The second step is a slow nucleophilic attack of the ylide **2** on the formaldehyde to yield a betaine intermediate **3**. The third step is a fast decomposition of the betaine intermediate **3** *via* an intramolecular displacement of methyl sulfide by the oxyanion to yield styrene oxide.

To elucidate the nature of the first step in the proposed mechanism, the reaction was run short of completion in 38.3% D_2O to yield 18% styrene oxide. The proton nmr analysis of the styrene oxide product indicated approximately 36% deuteration in the α position which was essentially statistical distribution of the deuterium. The proton nmr analysis of the isolated benzyldimethylsulfonium perchlorate indicated approximately 35% deuteration in the benzylic protons and approximately 32% deuteration in the methyl protons. The extent of deuteration of benzylic protons of the benzyldimethylsulfonium perchlorate and of the α position of styrene oxide can be considered essentially the same within the accuracy of the nmr analyses. These results indicate that first step in the proposed mechanism is a rapid and reversible formation of dimethylsulfonium benzylide (**2**).

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(1) A. W. Johnson, V. J. Hruby, and J. L. Williams, *J. Am. Chem. Soc.*, **86**, 918 (1964).

(2) E. J. Corey and M. Chaykovsky, *ibid.*, **87**, 1353 (1965).

(3) V. Franzen and H. E. Driessen, *Tetrahedron Letters*, 661 (1962).

(4) A. W. Johnson and R. B. LaCount, *J. Am. Chem. Soc.*, **83**, 417 (1961).

(5) M. J. Hatch presented this work at the 22nd Annual Southwest Regional Meeting of the American Chemical Society, Albuquerque, N. M., Nov 1966.

(6) R. Sivaramakrishnan and P. S. Radhakrishnamurti, *Current Sci.* (India), **34**, 404 (1965).

Bieber[7] and Vesely[8] have shown that under conditions of this study dilute aqueous formaldehyde solutions exist mostly as the hydrated formaldehyde in a rapidly reversible equilibrium with the unhydrated formaldehyde.

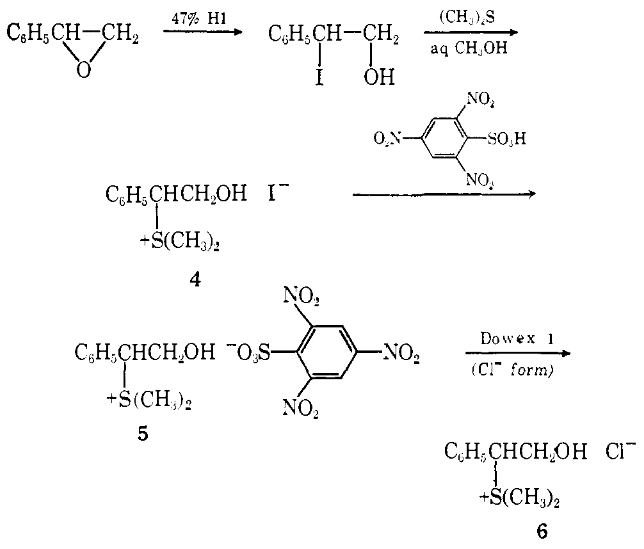
$$H_2C(OH)_2 \rightleftharpoons H_2CO + H_2O$$

In the proposed mechanism it has been assumed that the unhydrated formaldehyde reacts with the ylide **2** to yield the betaine intermediate **3**.

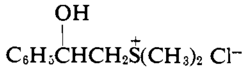
To clarify the nature of the second and third steps of the proposed mechanism, the betaine intermediate **3** was prepared *in situ* and the rates of styrene oxide formation from the betaine intermediate **3** and from the initial reactants were compared qualitatively and competitively. If the ylide attack on the formaldehyde (eq 2) were rate determining, then the ring closure of the betaine intermediate **3** (eq 3) would yield styrene oxide much faster than the rate that prevails in the reaction of the initial reactants. If the ring closure were rate determining and the ylide attack fast, the betaine intermediate **3** would yield styrene oxide at the same rate that prevails during the normal reaction.

The conjugate acid of the betaine intermediate **3**, α-(hydroxymethyl)benzyldimethylsulfonium chloride (**6**), was prepared as illustrated in Chart II. In NaOH solution it should reversibly form an equilibrium concentration of the intermediate betaine **3** with extreme rapidity by proton abstraction from the alcoholic OH group.

Chart II



The crystalline 2,4,6-trinitrobenzenesulfonate **5** was fully characterized by elemental, proton nmr, and infrared analyses before the sulfonate was exchanged for chloride. The reaction of α-(hydroxymethyl)benzyldimethylsulfonium chloride (**6**) with sodium deuterioxide in 99% D_2O yielded styrene oxide with 75% deuteration in the α position and no observable deuteration in the β position. These results confirmed the structure of the sulfonium chloride **6** over the isomer, (2-hydroxy-2-phenyl)ethyldimethylsulfonium chloride (**7**), which would have given styrene oxide with deuteration in the β position.



$C_6H_5CH(OH)CH_2\overset{+}{S}(CH_3)_2\ Cl^-$

7

The reaction of benzyldimethylsulfonium chloride (**1**), formaldehyde, and sodium hydroxide in dilute solution at 54–55° for 2.0 min gave a yield of 0.4% (0.078 mmole) of styrene oxide. In a similar experiment analysis showed that 92% of the initial formaldehyde remained at the termination of the reaction. The reaction of α-(hydroxymethyl)benzyldimethylsulfonium chloride (**6**) and sodium hydroxide under similar conditions gave a yield of 96.5% (1.10 mmoles) of styrene oxide. The α-(hydroxymethyl)benzyldimethylsulfonium ion (**6**), the betaine precursor, therefore yielded styrene oxide at over 100 times the rate from reaction of benzyldimethylsulfonium ion and formaldehyde. A competitive reaction of sulfonium chloride **1**, formaldehyde, sulfonium chloride **6**, and sodium hydroxide also was run under similar conditions. There resulted a yield of 1.12 mmoles of styrene oxide. This yield was only 0.02 mmole more than obtained from the earlier reaction of the sulfonium chloride **6** itself. Thus, again, the reaction suggested that styrene oxide was formed at a much faster rate from sulfonium chloride **6** and sodium hydroxide than it was formed by the reaction of the sulfonium chloride **1**, formaldehyde, and sodium hydroxide. This infers that the ylide attack on the formaldehyde is rate determining and suggests that the reaction proceeds through the betaine intermediate **3**.

The possibility of a slow and reversible betaine **3** formation[1] (eq 2) has been considered. The competitive reaction of 3-chlorobenzaldehyde containing 32% 2,6-dichlorobenzaldehyde and formaldehyde for dimethylsulfonium benzylide (**2**) yielded a reaction mixture with a product ratio of 1-(3-chlorophenyl)-2-phenyloxirane plus 1-(2,6-dichlorophenyl)-2-phenyloxirane to styrene oxide of 35:1. The reaction of α-(hydroxymethyl)benzyldimethylsulfonium chloride (**6**) and sodium hydroxide in the presence of threefold excess of 3-chlorobenzaldehyde (32% 2,6-dichlorobenzaldehyde) was examined. If the formation of the betaine **3** were reversible, dimethylsulfonium benzylide (**2**) would trap the more reactive 3-chlorobenzaldehyde (32% 2,6-dichlorobenzaldehyde) to yield 1-(3-chlorophenyl)-2-phenyloxirane plus 1-(2,6-dichlorophenyl)-2-phenyloxirane.

Analyses of the reaction products by vpc, mass spectrometry, and chemical oxirane determination indicated 94.5% yield of styrene oxide with no detectable quantity of 1-(3-chlorophenyl)-2-phenyloxirane or 1-(2,6-dichlorophenyl)-2-phenyloxirane. The lower limit of vpc detection was less than 0.004 mole %. The results of these experiments suggest that the betaine **3** formation is irreversible.

The comparison of the extent of deuteration of styrene oxide obtained from the reaction sequence of the proposed mechanism (eq 1, 2, and 3) and of the styrene oxide obtained from the reaction sequence of α-(hydroxymethyl)benzyldimethylsulfonium chloride (**6**) with sodium deuterioxide (eq 4 and 5) should give an indication of the relative rate of deuterium exchange as compared to the subsequent reactions in each sequence.

The reaction of benzyldimethylsulfonium chloride (**1**), formaldehyde, and sodium deuterioxide in 99% D_2O gave a 62% yield of styrene oxide. Proton nmr anal-

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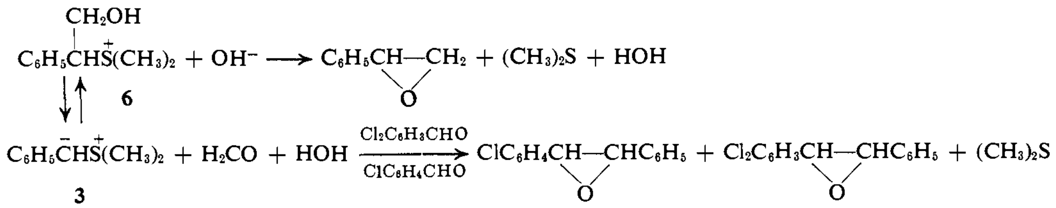
[7] R. Bieber and G. Trümpler, *Helv. Chim. Acta*, **30**, 1860 (1947).

[8] K. Vesely and R. Brdicka, *Collection Czech. Chem. Commun.*, **12**, 313 (1947).

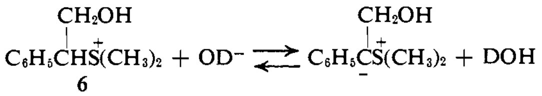


$$C_6H_5\overset{CH_2OH}{\overset{|}{C}}H\overset{+}{S}(CH_3)_2 + OH^- \longrightarrow C_6H_5\underset{O}{CH{-}CH_2} + (CH_3)_2S + HOH \quad \mathbf{6}$$

$$\Updownarrow$$

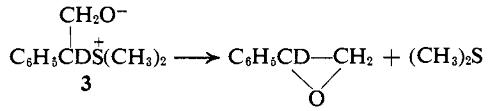
$$C_6H_5\overset{-}{C}H\overset{+}{S}(CH_3)_2 + H_2CO + HOH \xrightarrow[ClC_6H_4CHO]{Cl_2C_6H_3CHO} ClC_6H_4\underset{O}{CH{-}CHC_6H_5} + Cl_2C_6H_3\underset{O}{CH{-}CHC_6H_5} + (CH_3)_2S \quad \mathbf{3}$$

ysis indicated 88% deuteration in the α position, which was essentially statistical distribution of the deuterium, and 5-6% deuteration in the β position. The reaction of α-(hydroxymethyl)benzyldimethylsulfonium chloride (**6**) with sodium deuterioxide in 99% D_2O gave a 99%



$$C_6H_5\overset{CH_2OH}{\overset{|}{C}}H\overset{+}{S}(CH_3)_2 + OD^- \rightleftarrows C_6H_5\overset{CH_2OH}{\overset{|}{\underset{-}{C}}}\overset{+}{S}(CH_3)_2 + DOH \quad (4)$$

6

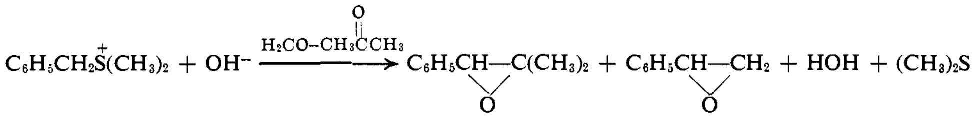


$$C_6H_5\overset{CH_2O^-}{\overset{|}{C}}D\overset{+}{S}(CH_3)_2 \longrightarrow C_6H_5\underset{O}{CD{-}CH_2} + (CH_3)_2S \quad (5)$$

3

yield of styrene oxide. Proton nmr analysis indicated approximately 75% deuteration in the α position with no observable β deuteration. Thus, these experiments show that the rate of deuterium exchange of the sulfonium chloride **1** (eq 1) with respect to the formation of the betaine intermediate **3** (eq 2) is faster than the rate of deuterium exchange of sulfonium chloride **6** (eq 4) with respect to deprotonation and the decomposition of the betaine intermediate **3** (eq 5). These results are reasonable and support the proposed mechanism.

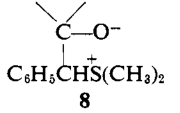
Further evidence for the rate-determining step was obtained from the competitive reaction of acetone and formaldehyde for the sulfonium ylide **2** to yield the corresponding β,β'-dimethylstyrene oxide and styrene oxide.



$$C_6H_5CH_2\overset{+}{S}(CH_3)_2 + OH^- \xrightarrow{H_2CO\text{-}CH_3\overset{O}{\overset{\|}{C}}CH_3} C_6H_5\underset{O}{CH{-}C(CH_3)_2} + C_6H_5\underset{O}{CH{-}CH_2} + HOH + (CH_3)_2S$$

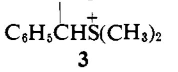
Oxirane formation from the reaction of ethylene chlorohydrin and sodium hydroxide is markedly facilitated by alkyl substitution as shown by the comparison of the rate constants:[9] for $HOCH_2CH_2Cl$, $k/k_{\mathrm{HOCH_2CH_2Cl}} = 1.0$; for $HOCH(CH_3)CH_2Cl$, $k/k_{\mathrm{HOCH_2CH_2Cl}} = 21$; for $HOC(CH_3)_2CH_2Cl$, $k/k_{\mathrm{HOCH_2CH_2Cl}} = 250$.

By analogy, one expects a similar increase in the rate of oxirane formation from the betaine intermediate **8** (from acetone) compared to that of the betaine intermediate **3** (from formaldehyde).



$$C_6H_5\overset{(CH_3)_2C{-}O^-}{\overset{|}{C}}H\overset{+}{S}(CH_3)_2$$

8



$$C_6H_5\overset{CH_2O^-}{\overset{|}{C}}H\overset{+}{S}(CH_3)_2$$

3

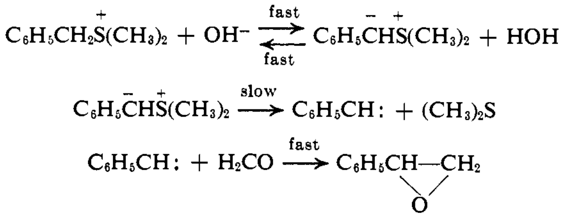
If one assumes that the rate of the attack of the ylide **2** on formaldehyde is greater than, or equal to, the rate of the attack of ylide **2** on acetone, a large ratio of β,β'-dimethylstyrene oxide to styrene oxide in a competitive reaction would indicate that the betaine intermediate formation was fast relative to the decomposition of the betaine intermediate and that the third step in the proposed mechanism was rate determining.

In the competitive reaction, a large excess of benzyldimethylsulfonium chloride (**1**) was utilized in an attempt to minimize the expected reaction of acetone and formaldehyde to form methylolacetone derivatives. Analyses of aliquot portions of the reaction mixtures (see Table III in the Experimental Section) indicated that the initial rate of formation of styrene oxide was much greater than is shown by the ratio of styrene oxide to β,β'-dimethylstyrene oxide, 8.7, at 0.5 min. Within 0.5 min the major portion of the formaldehyde was rapidly consumed, presumably by the methylolation of acetone, and possibly by the Cannizzaro reaction of the formaldehyde. The acetone continued to react with the ylide **2** until the sodium hydroxide was essentially consumed. Therefore, it is unlikely that the decomposition of the betaine intermediate **3** is the slow step (eq 3).

Another possible mechanism (see Chart III) which involves the decomposition of the sulfonium ylide to phenylcarbene and subsequent reaction of the phenylcarbene with formaldehyde to yield styrene oxide has been rejected based on experimental data and considerations as follows.

Swain and Thornton[10] have shown that p-nitrobenzyldimethylsulfonium p-toluenesulfonate reacted with aqueous sodium hydroxide to form p,p'-dinitrostilbene in high yield. No p-nitrobenzyl alcohol was detected. The reaction was first order in hydroxide ion and first order in sulfonium ion. Deuterium exchanged into the ylide, and the over-all sulfur isotope effect suggested the reaction scheme[10,11] shown in Chart IV. The slow

Chart III



$$C_6H_5CH_2\overset{+}{S}(CH_3)_2 + OH^- \underset{fast}{\overset{fast}{\rightleftarrows}} C_6H_5\overset{-}{C}H\overset{+}{S}(CH_3)_2 + HOH$$

$$C_6H_5\overset{-}{C}H\overset{+}{S}(CH_3)_2 \xrightarrow{slow} C_6H_5CH\!: + (CH_3)_2S$$

$$C_6H_5CH\!: + H_2CO \xrightarrow{fast} C_6H_5\underset{O}{CH{-}CH_2}$$

step was presumably the formation of p-nitrophenylcarbene.

Under similar conditions Swain and Thornton[12] have shown that aqueous sodium hydroxide reacted with p-methyl-, m-chloro-, and benzyldimethylsulfonium p-toluenesulfonate to form the corresponding benzyl alcohols in high yields. The reaction was first order in hydroxide ion and first order in sulfonium ion. An enhanced rate for the p-methyl over the benzyldimethylsulfonium ion

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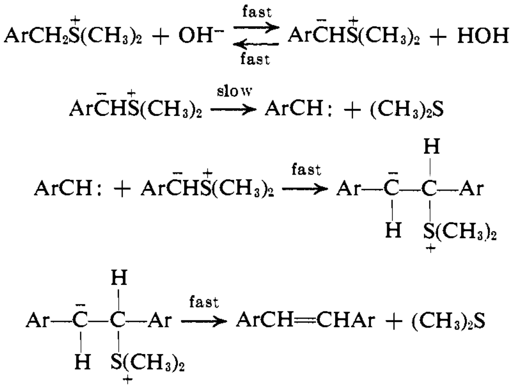
[9] H. Nilsson and L. Smith, *Z. Physik. Chem.*, **166A**, 136 (1933).

[10] C. G. Swain and E. R. Thornton, *J. Am. Chem. Soc.*, **83**, 4033 (1961).

[11] I. Rothberg and E. R. Thornton, *ibid.*, **86**, 3296 (1964).

[12] C. G. Swain and E. R. Thornton, *J. Org. Chem.*, **26**, 4808 (1961).

Chart IV

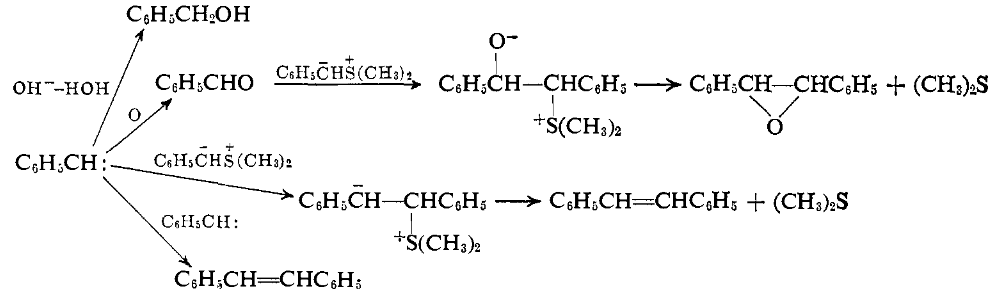


(Ar = $C_6H_4NO_2$)

which one should expect for the formation of phenylcarbenes was not observed. The sulfur isotope effect suggested an SN2 displacement reaction. As expected in a noncarbene reaction sequence, no stilbene was detected.

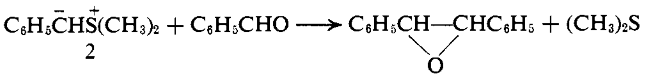
In this study, conditions similar to those of Swain and Thornton[12] were employed to synthesize styrene oxide. The reaction residue was analyzed by vpc, mass spectrometry, and infrared spectroscopy for possible reaction products of phenylcarbene (see Chart V).

Chart V



Trace amounts of benzyl alcohol were detected in the starting sulfonium chloride solution **1** and in the reaction mixture. If benzyl alcohol were produced during the reaction, it is likely that the alcohol was formed from a displacement reaction on the sulfonium chloride **1**.

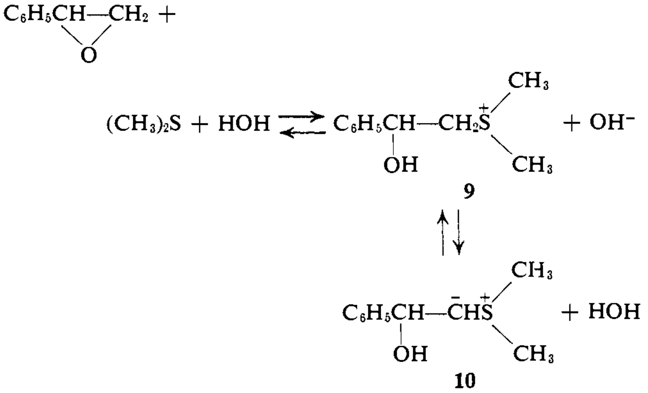
Trace amounts of stilbene oxide were detected in the reaction residue. However, a trace of benzaldehyde was also detected in the starting sulfonium chloride solution **1**. The stilbene oxide was most likely produced by the reaction of the ylide **2** with benzaldehyde.[5]



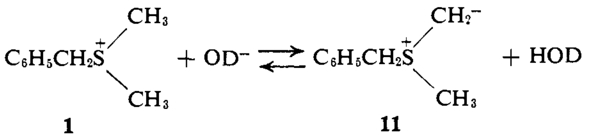
If the major reaction sequence included a phenylcarbene intermediate, one would expect at least trace amounts of stilbenes. No *cis*- or *trans*-stilbene was detected, even by careful vpc studies of the residue. The lower limit of detection was less than 0.0006 mole %.

Based on the consideration of Swain and Thornton's studies[10-12] and experimental data of this study, a carbene mechanism has been rejected in favor of the proposed mechanism.

A possible reversible reaction of styrene oxide and methyl sulfide was suggested in the form of β deuteration of styrene oxide. When styrene oxide was synthesized in 99% D_2O, it contained an unexpected 5–6% deuteration in the β position and 88% deuteration in the α position. The β deuteration could arise from the reversible reaction involving the products, styrene oxide and methyl sulfide, or from the deuteration of formaldehyde during the reaction. It is unlikely that the formaldehyde is deuterated under the conditions prevailing in this study since formaldehyde is not deuterated under similar Cannizzaro reaction conditions.[13] However, styrene oxide, methyl sulfide, and water did yield a reaction mixture basic to phenolphthalein, suggesting ring opening. It is possible that the methyl sulfide attacked the styrene oxide to open the epoxide ring. In the presence of base, the newly formed sulfonium ion **9** would equilibrate with the ylide **10** permitting deuterium exchange. The reaction then would reverse, deuterating styrene oxide in the β position.



The side reactions of benzyldimethylsulfonium chloride, formaldehyde, and sodium deuterioxide in 99% D_2O to yield deuterated styrene oxide also are of interest. Mass spectrometric analysis of the methyl sulfide obtained as a major product indicated 82.4% deuteration of the methyl groups. The deuterium analysis by nmr supported the mass spectrometric analysis. It was shown that methyl sulfide was not deuterated under the conditions of the styrene oxide synthesis. The deuteration of the methyl groups therefore resulted from the reversible formation of benzylmethylsulfonium methylide (**11**).



Since the benzylic protons should be more acidic than the methyl protons, the high amount of exchange

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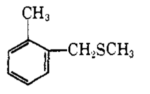
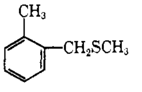
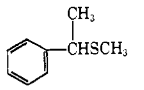
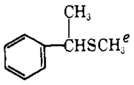
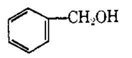
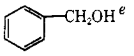
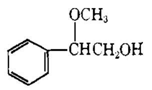
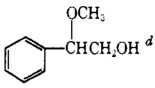
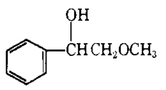
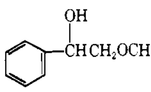
(13) H. Fredenhagen and K. F. Bonhoeffer, *Z. Physik. Chem.*, **181A**, 379 (1938).

Table I. Mass Spectrometric Analyses of Styrene Oxide Distillation Fraction (bp 59–60° (5 mm))

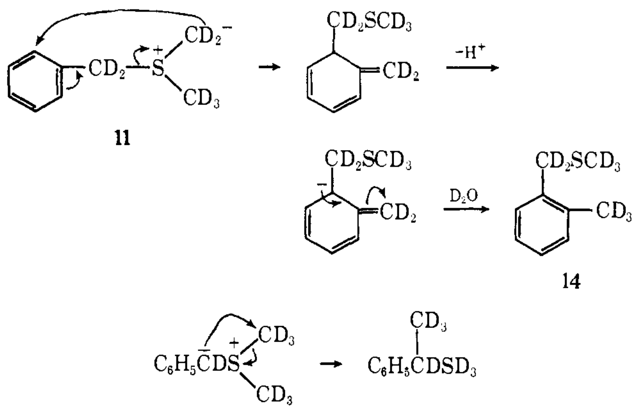
Reaction in H_2O		Reaction in 99% D_2O	
Parent peak, *m/e*	Probable structure	Parent peak, *m/e*	Probable structure
138	$C_6H_5CH_2SCH_3$ (trace)	143 142 141	Deuterated $C_6H_5CH_2SCH_3$ (trace)
	Not $C_6H_5\underset{OH}{CH}-\underset{OH}{CH_2}$		Not $C_6H_5\underset{OH}{CH}-\underset{OH}{CH_2}$

The rearrangements of sulfonium salts are known to occur and the Sommelet rearrangement[14] of the benzyldimethylsulfonium methylide (**11**) accounts for the *o*-methylbenzyl methyl sulfide (**14**). The detection of the maximum of eight deuterium atoms in the product suggests the sulfide **14**. However, there is a possibility that the vpc fraction also contains α-methylbenzyl methyl sulfide (**15**) with a maximum of seven deuterium atoms obtained by a Steven's rearrangement[15] of ylide **2**. The study of the mass spectrometric cracking pattern could not distinguish between the two possibilities, pure sulfide **14** or a mixture of sulfide **14** and sulfide **15**.

Table II. Mass Spectrometric Analyses of Vpc Cuts of the Distillation Residue[a]

Reaction in H_2O		Reaction in 99% D_2O		
Parent peak, *m/e*	Probable structure	Parent peak, *m/e*	Probable structure[b]	Mole %[b]
152[f]				4.4
		160[e] 159[f] 158[f] 157[f]		
108		110 109 108		>1.3[c]
		*d*		2
152		153		2.5

[a] Vpc analyses; 4 ft × 0.25 in. glass column, 15% E4000 on Teflon, 125°; He, 100 cc/min. [b] Approximate mole per cent of combined styrene oxide fraction and residue. [c] Low because some of the benzyl alcohol was extracted by the aqueous layer. [d] Parent peak not detected. [e] Deuterated. [f] Either of two structures is possible.



11

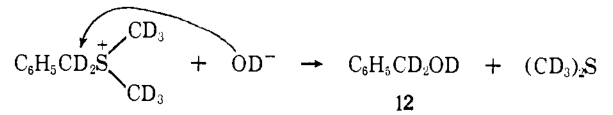
14

2 15

obtained in the methyl sulfide again supports the conclusion that benzylide formation is very fast and reversible compared with the ylide reaction with formaldehyde.

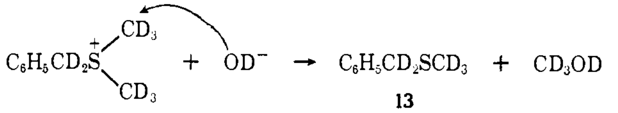
The products of some side reactions have been detected by mass spectrometric analyses of the styrene oxide distillation fractions and of the vpc cuts of the distillation residues. The probable structures and amounts are listed in Tables I and II.

The partially deuterated benzyl alcohol **12** and the deuterated benzyl methyl sulfide **13** are probably products of the displacement of the deuterioxide ion on the benzyl carbon and the methyl carbon of the deuterated benzyldimethylsulfonium ion.



$$C_6H_5CD_2\overset{+}{S}{<}^{CD_3}_{CD_3} + OD^- \longrightarrow C_6H_5CD_2OD + (CD_3)_2S$$

12



$$C_6H_5CD_2\overset{+}{S}{<}^{CD_3}_{CD_3} + OD^- \longrightarrow C_6H_5CD_2SCD_3 + CD_3OD$$

13

The possibility that the sulfide **13** is the product of the reaction of the sulfonium ylide **11** with formaldehyde is unlikely since no ethylene oxide or ethylene glycol has been detected. Hatch[5] reported that the reaction of trimethylsulfonium chloride, aqueous sodium hydroxide, and formaldehyde did not yield any detectable ethylene oxide which supports the above results.

Three possible reactions involving the final product, styrene oxide, were observed. The first reaction may be the methanolysis of the styrene oxide (due to the methanol present as a stabilizer for the formaldehyde used, or formed by the Cannizzaro reaction of the formaldehyde) to yield 2-methoxy-2-phenylethanol (**16**) and 2-methoxy-1-phenylethanol (**17**). The second reaction is the possible attack of methyl sulfide on styrene oxide. The reversibility of this reaction has been pro-

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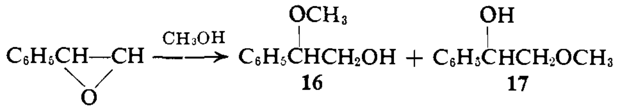
(14) C. R. Hauser, S. W. Kantor, and W. R. Brasen, *J. Am. Chem. Soc.*, 75, 2660 (1953).

(15) T. Thompson and T. S. Steven, *J. Chem. Soc.*, 69 (1932).



posed earlier in the form of β deuteration of the styrene oxide. The third reaction is the expected hydrolysis of styrene oxide. Trace amounts of styrene glycol were detected in the aqueous layer of the reaction mixture.

Experimental Section[16]

Reaction of Aqueous Benzyldimethylsulfonium Chloride (1), Formaldehyde, and Sodium Hydroxide in 38.3% D_2O. To a 500-ml, three-necked flask equipped with a reflux condenser, stirrer, thermometer, and a dropping funnel were added 31.8 ml (0.111 mole) of 3.50 *M* benzyldimethylsulfonium chloride (1), 30 ml of toluene, and 19.5 ml (0.258 mole) of 36.6% formaldehyde. To the stirred reaction mixture, preheated to 50°, was added 2.0 g (0.05 mole) of sodium hydroxide in 18 ml of 99.8% D_2O. The temperature rose to 51°, and the mixture was heated to 75°. The temperature dropped to 65° over a period of 30 min. The aqueous layer was separated and immediately neutralized with concentrated hydrochloric acid. To the aqueous solution was added 50 ml of saturated sodium perchlorate solution to yield a turbid mixture. Cooling the mixture in the refrigerator overnight yielded 19.1 g (0.0855 mole or 68.2% recovery) of white crystals, which were filtered and dried (mp 103.5–104.5°). The benzyldimethylsulfonium perchlorate was crystallized from 2B absolute ethanol to yield 16.2 g of white glistening plates, mp 104–105°. The toluene layer was washed three times with water and dried over anhydrous $MgSO_4$. The total volume of toluene was 26.5 ml. Oxirane determination by the pyridine-HCl method[17] indicated that the solution contained 8.9 mmoles of styrene oxide (yield of 18%, based on 50 mmoles of sodium hydroxide). The toluene layer was distilled at 104–112° (50 mm) using DC 200 fluid (2 cstokes) as a chaser to yield 1.6 g of styrene oxide. The proton nmr analysis of the styrene oxide in CCl_4 indicated approximately 36% α-deuteration. The proton nmr analysis of benzyldimethylsulfonium perchlorate in DMSO-d_6 indicated approximately 35% deuteration of the benzylic protons and approximately 32% deuteration of the methyl protons based on the aromatic protons.

Preparation of 2-Iodo-2-phenylethanol. To an ice-cooled, stirred mixture of 25.0 g (0.208 mole) of styrene oxide and 25 ml of water was added 53.6 ml (0.208 mole) of 47% hydriodic acid over a period of 5 min. After 10 min, a solid was filtered and washed with water. The yellowish crystals were crystallized from 80% ethanol to yield 17 g (33%) of white crystals, mp 73–74° (lit.[18] 79°).

Preparation of α-(Hydroxymethyl)benzyldimethylsulfonium 2,4,6-Trinitrobenzenesulfonate (5). To a 20-ml solution of 4.80 g (0.0194 mole) of 2-iodo-2-phenylethanol in 80% methanol was added 1.5 ml (0.0145 mole) of methyl sulfide. The reaction was allowed to stand 3 days at room temperature. The dark reaction mixture was extracted five times with ethyl ether to give a colorless aqueous solution. To the aqueous solution was added 5 g of 2,4,6-trinitrobenzenesulfonic acid dissolved in 15 ml of water to yield a whitish precipitate. The precipitate was washed with water and dried (yield 5.5 g, 79%). The crude product was crystallized from methanol and yielded 3.25 g of white crystals, mp 156.5–158.5°. The 60-MHz proton nmr spectrum (ppm shielding relative to internal TMS) exhibits a 2 H singlet at −8.84 (2,4,6-trinitrobenzenesulfonate), a 5 H singlet at −7.51 (C_6H_5), a 1 H triplet (J = 5.8 Hz) at −4.94 (CH), a 2 H doublet (J = 5.8 Hz) ($W_{1/2}$ ~ 3 Hz, ~1.5 Hz after addition of D_2O) at −4.16 (CH_2), a 3 H singlet at −2.94 (S^+–CH_3), a 3 H singlet at −2.57 (S^+–CH_3), and a 1 H broad absorption at −5.9 (OH). The infrared spectrum (mull, Nujol–Fluorolube) shows absorptions (cm^{-1}) at 3385 (OH), 1318 and 1294 ($S^+(CH_3)_2$), and 1062 (primary C–OH). This spectral information confirms the structure of sulfonium 5. *Anal.* Calcd for $C_{16}H_{17}N_3O_{10}S_2$: C, 40.4; H, 3.61; N, 8.84; S, 13.49. Found: C, 40.4; H, 3.68; N, 8.61; S, 13.55.

Conversion of α-(Hydroxymethyl)benzyldimethylsulfonium 2,4,6-Trinitrobenzenesulfonate (5) to α-(Hydroxymethyl)benzyldimethylsulfonium Chloride (6). A solution of 2.03 g (0.043 mole) of α-(hydroxymethyl)benzyldimethylsulfonium 2,4,6-trinitrobenzenesulfonate dissolved in 150 ml of 98% methanol was exchanged on a 2 cm × 20 cm column containing 20 ml of Dowex 1-X2, 50–100 mesh, Cl^- form. The solution was eluted with 250 ml of 98% methanol. The effluent was concentrated to a yellowish liquid on a rotary evaporator at water pump pressure. Water was added to bring the volume to 10 ml. An aliquot sample of α-(hydroxymethyl)benzyldimethylsulfonium chloride was potentiometrically titrated with silver nitrate to determine the concentration of chloride ion as 0.38 *M*.

Reaction of Aqueous Benzyldimethylsulfonium Chloride (1), Formaldehyde, and Sodium Hydroxide to Low Yields of Styrene Oxide. To a 250-ml, three-necked flask equipped with a stirrer, reflux condenser, thermometer, and dropping funnel were added 5.70 ml (0.020 mole) of 3.50 *M* benzyldimethylsulfonium chloride, 1.60 ml (0.020 mole) of 36.6% formaldehyde, 30 ml of water, and 10.0 ml of toluene. To the stirred mixture preheated to 54° was added 1.00 ml (0.0195 mole) of 19.45 *N* sodium hydroxide plus 1.0 ml of water. The temperature rose to 55°, and the mixture was maintained at 55° for 2.0 min. The reaction was quenched with 25 g of ice. The toluene layer was separated and washed twice with water. The toluene solution was dried over anhydrous $MgSO_4$ and gave a volume of 7.3 ml. The styrene oxide content was analyzed by vpc under the following conditions: instrument, F & M 810; column, 16 ft × 1/8 in., 15% E4000 on 40–60 mesh, WI support at 150°; injection port, 180°; detector, 280°; He, 60 cc/min; and sensitivity, 150 ma. The styrene, oxide rearranged completely to phenylacetaldehyde under these vpc conditions. This rearrangement was substantiated by infrared analysis of an authentic sample of styrene oxide. The retention time of styrene oxide (phenylacetaldehyde) was 25.0 min. The infrared analysis of the vpc fraction of styrene oxide from the reaction mixture confirmed the identity of the styrene oxide (rearranged to phenylacetaldehyde). The average yield of styrene oxide for four runs was 0.079 mmole (0.4% based on NaOH).

The Determination of the Disappearance of Formaldehyde in the Synthesis of Styrene Oxide (Low Yield). To a 250-ml, three-necked flask equipped with a stirrer, reflux condenser, thermometer, and dropping funnel were added 14.1 ml (0.0493 mole) of 3.50 *M* benzyldimethylsulfonium chloride, 3.94 ml (0.0498 mole) of 36.6% formaldehyde, and 74.0 ml of water. To the stirred solution preheated to 54° were added 20.0 ml of toluene and 2.50 ml (0.0453 mole) of 18.13 *N* sodium hydroxide. The temperature rose to 55° and remained at 54–55° for 2.0 min. Aliquot samples of the aqueous layer were taken and were treated immediately with excess standard acid. The samples were neutralized and the formaldehyde content was determined as 0.0459 mole by the sodium sulfite method.[19] Approximately 8% of formaldehyde disappeared during the reaction. The remaining reaction mixture was quenched with 25 g of ice. The toluene layer was separated and washed twice with water. The solution was dried over anhydrous $MgSO_4$ and filtered. The styrene oxide content was analyzed by vpc (under conditions described earlier) as 0.000190 mole (0.4%).

Reaction of α-(Hydroxymethyl)benzyldimethylsulfonium Chloride (6) with Sodium Hydroxide in the Absence and the Presence of Benzyldimethylsulfonium Chloride (1) and Formaldehyde. These reactions were run under identical conditions as the two preceding experiments at 54–55° for 2.0 min and analyzed in a similar manner. (a) To a solution of 3.00 ml of 0.38 *M* (0.00114 mole) α-(hydroxymethyl)benzyldimethylsulfonium chloride (6), 33 ml of water, and 10.0 ml of toluene at 54° was added 1.00 ml of 19.45 *N* sodium hydroxide (0.0195 mole). The styrene oxide was identified by vpc retention time and infrared and nmr analyses. The yield was 0.00110 mole (96.5%). (b) To a solution of 3.00 ml of 0.38 *M* (0.00114 mole) α-(hydroxymethyl)benzyldimethylsulfonium chloride (6), 5.7 ml (0.020 mole) of 3.50 *M* benzyldimethylsulfonium chloride (1), 1.60 ml (0.020 mole) of 36.6% formaldehyde, 30 ml of water, and 10.0 ml of toluene at 54° were added 1.00 ml of 19.45 *N* sodium hydroxide (0.0195 mole) plus 1 ml of water. The styrene oxide was identified by vpc retention time and infrared and nmr analyses. The yield was 0.00112 mole. Correcting for the average yield of styrene

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[16] Melting points were taken on a Fisher-Johns melting point apparatus and are uncorrected. The elemental analyses were performed by L. E. Swim of The Dow Chemical Company, Midland, Mich.

[17] F. E. Critchfield, "Organic Functional Group Analysis," Pergamon Press, The MacMillan Co., New York, N. Y., 1963, pp 133, 136.

[18] M. Tiffeneau and E. Fourneau, *Compt. Rend.*, **146**, 697 (1908).

[19] J. F. Walker, "Formaldehyde," 3d ed, Reinhold Publishing Corp., New York, N. Y., 1964, p 486.

Table III

Temp °C	Time, min	NaOH, mole	HCHO, mole	Acetone, mole	β,β'-Dimethylstyrene oxide, mole	Styrene oxide, mole
49	0	0.159	0.122	0.108	...	...
54	0.5	0.056	0.009	0.077	0.0022	0.019
57	1.5	0.052	0	0.086	0.0061	0.025
54	5.3	0.022	0	0.069	0.015	0.025
50	8.8	0.009	0	0.063	0.023	0.022

oxide from the reaction of benzyldimethylsulfonium chloride, formaldehyde, and sodium hydroxide established in the previous experiment, the α-(hydroxymethyl)benzylmethylsulfonium chloride gave a product yield of 0.00104 mole (91.2%). (c) To a solution containing 0.00099 mole of dried α-(hydroxymethyl)benzyldimethylsulfonium chloride (**6**), 30 ml of 99.8% D_2O, and 5.0 ml of toluene at 54° (in a system protected from external H_2O vapor with Drierite) was added 1.30 ml of 13.0 *N* sodium deuterioxide in 99.7% D_2O. The styrene oxide content was analyzed by vpc as 0.000985 mole (99.5%), and was identified by vpc retention time and infrared and nmr analyses. Proton nmr analysis indicated approximately 75% deuteration in the α position and no observable deuteration in the β position.

The Competitive Reaction of 3-Chlorobenzaldehyde and Formaldehyde for Dimethylsulfonium Benzylide (2). To a mixture of 28.6 ml of 3.5 *M* (0.10 mole) benzyldimethylsulfonium chloride (**1**), 11.4 ml (0.15 mole) of formaldehyde, 21.1 g (0.15 mole) of 3-chlorobenzaldehyde containing 32% 2,6-dichlorobenzaldehyde, 30 ml of toluene, and 30 ml of ethanol stirred and heated to 55° was added 16 g (0.4 mole) of sodium hydroxide in 30 ml of water. The reaction temperature rose and peaked at 65°. After 2.0 min, 50 g of ice was added to quench the reaction. The reaction mixture was washed three times with water, separated, and dried over anhydrous $MgSO_4$. The mixture was concentrated to 28.1 g by a simple distillation at 36–44° (55 mm). Analysis of the residue by mass spectrometry, nmr, and infrared indicated that the major product was 1-(3-chlorophenyl)-2-phenyloxirane plus 1-(2,6-dichlorophenyl)-2-phenyloxirane. The oxirane content of the residue was determined by the morpholine method[17] to be 0.073 mole. The mass spectrometric analysis of the residue indicated a styrene oxide content of 0.002 mole. Thus, the product ratio of 1-(3-chlorophenyl)-2-phenyloxirane plus 1-(2,6-chlorophenyl)-2-oxirane to styrene oxide was 35:1.

The Reaction of α-(Hydroxymethyl)benzyldimethylsulfonium Chloride (6) with Sodium Hydroxide in the Presence of Excess 3-Chlorobenzaldehyde. To a mixture of 24 ml (0.018 mole) of α-(hydroxymethyl)benzyldimethylsulfonium chloride solution, 20 ml of ethanol, 20 ml of toluene, and 7.6 g (0.054 mole) of 3-chlorobenzaldehyde containing 32% 2,6-dichlorobenzaldehyde heated to 55° was added 2.48 g (0.062 mole) of sodium hydroxide in 20 ml of water. The reaction mixture was stirred at 55° for 2 min. The reaction was quenched with 50 g of ice. The toluene layer was washed three times with water, separated, and dried over anhydrous $MgSO_4$. The mixture was concentrated to 9.62 g by a simple distillation at 36–44° (55 mm). Analyses of the residue by mass spectrometry and vpc indicated no detectable quantity of 1-(3-chlorophenyl)-2-phenyloxirane or 1-(2,6-dichlorophenyl)-2-phenyloxirane. The lower limit of the vpc detection was less than 0.004 mole %. Styrene oxide was identified by mass spectrometry and vpc retention time. The styrene oxide content was determined by the morpholine method[17] to be 0.017 mole (94.5%).

The Competitive Reaction of Acetone and Formaldehyde for Dimethylsulfonium Benzylide (2). To a 500-ml, three-necked flask equipped with a stirrer, reflux condenser, dropping funnel, thermometer, and syringe needle for removing samples were added 220 ml (1.04 moles) of 4.73 *M* benzyldimethylsulfonium chloride, 6.28 g (0.108 mole) of distilled acetone, 10.0 g (0.112 mole) of 36.6% formaldehyde, and 60 ml of toluene. The stirred mixture was heated to 49° and a sample of starting material was taken. Then, 8.20 ml (0.159 mole) of 19.45 *N* sodium hydroxide was added. Samples were taken at the indicated times and temperatures. The aliquot samples (see Table III) of the reaction mixture were quenched with 20 g of ice and immediately titrated with 1.0 *N* HCl to a thymolphthalein end point. The samples were frozen in a deep freeze. The toluene layer was poured off and dried over anhydrous $MgSO_4$.

Method of Analyses. a. Formaldehyde. The aqueous layer was thawed out and was analyzed by the sodium sulfite method.[19] Formaldehyde content could be determined in the presence of a large excess of acetone if only a threefold excess of sodium sulfite over that of the anticipated formaldehyde content was used.

b. Acetone and Methanol in the Aqueous Phase by Vpc Analyses. Conditions were as follows: instrument, F & M 810; column, 4 ft × 0.25 in. Porpak Q, 80–120 μ; initial temperature, 70°; rate, 10°/min; final temperature, 145° hold; sensitivity, 150 ma; He, 40 cc/min; detector, 282°; injection port, 145°; vpc retention time, min: H_2O, 4.5; methanol, 7.0; acetone, 13.8; methyl sulfide, 15.4; *t*-butyl alcohol, 20.4 (internal standard). A factor of 1.25 (determined experimentally) was used to correct for the solubility of methanol and acetone in the toluene phase under the conditions of the work-up and analyses.

c. Styrene Oxide and β,β'-Dimethylstyrene Oxide by Vpc Analyses. Conditions were as follows: instrument, F & M 810; column, 16 ft × $^1/_8$ in., 15% E4000 on WI, 40–60 mesh; column temperature, 150°; detector, 280°; injection port, 160°; He, 60 cc/min; and sensitivity, 150 ma; vpc retention time, min: toluene, 2.8; anisole (internal standard), 8.4; β,β'-dimethylstyrene oxide (β,β'-DMSO (I)); 19.8; β,β'-DMSO (II), 22.8; and β,β'-DMSO (III) and styrene oxide, 29.0. The vpc fractions of the reaction mixture were compared with the vpc fractions of authentic styrene oxide and β,β'-dimethylstyrene oxide by infrared analyses and were reported to be identical. The infrared analyses indicated that under these conditions styrene oxide rearranged to phenylacetaldehyde and β,β'-dimethylstyrene oxide gave an unrearranged product, an aldehyde, and a conjugated ketone. A correction for β,β'-DMSO (III) in the styrene oxide fraction, 29.0 min, was applied in the analysis.

Preparation of Benzyldimethylsulfonium Chloride (1) in 99.8% D_2O. To a 250-ml, three-necked flask equipped with a stirrer, thermometer, and condenser (protected against atmospheric water by Drierite) were added 19.0 g (0.15 mole) of benzyl chloride, 10.2 g (0.165 mole) of dimethyl sulfide, and 30.0 ml of 99.83% D_2O. The reaction mixture was heated to 34° and stirred rapidly for 17 hr. The reaction was far from complete as indicated by the presence of a large organic layer. The heating was increased to refluxing (37–40°), and the mixture was stirred vigorously. After 24 hr the organic layer nearly disappeared. The organic layer was completely removed with a syringe, leaving 51.0 ml of D_2O solution. The D_2O solution was extracted several times with toluene. Proton nmr analysis of the D_2O solution indicated aromatic protons, −7.70 ppm from TMS, OH and methylene protons (one peak), −4.75 ppm, and methyl protons, −2.97 ppm in the following ratio; 4.0:2.08:6.15. On the addition of dimethyl sulfoxide-d_6, the H_2O and methylene protons were split, shifting the methylene protons to −4.81 ppm and OH to −4.59 ppm. The ratio of aromatic: methylene:methyl protons was now calculated to be 5.0:2.0:6.1, suggesting that D_2O did not exchange with benzyldimethylsulfonium chloride to any detectable extent. An aliquot sample of the solution was titrated with 0.10 *N* sodium hydroxide and indicated a negligible acid content. The benzyldimethylsulfonium chloride concentration of 2.60 *M* was determined by potentiometric titration with 1.0 *M* $AgNO_3$. The yield, based on 51.0 ml of solution, was 0.133 mole (88%).

Preparation of Methanol-d_1. To 35 ml of 99.83% D_2O was added slowly with cooling 31.5 g (0.60 mole) of 95% sodium methoxide. The solution was distilled at 66–68° and redistilled at 65–67° to yield 8.2 g of methanol-d_1. Proton nmr analysis indicated that the mixture contained more than 99.3 mole % of methanol-d_1.

Preparation of Formaldehyde in D_2O-Methanol-d_1. Approximately 50 g of paraformaldehyde was depolymerized at 180–200° under a slow stream of nitrogen. The formaldehyde was trapped in a mixture of 4.0 g of methanol-d_1 and 17.5 g of 99.5% D_2O. The turbid mixture was centrifuged to yield 30.0 g of clear 34% formaldehyde solution.

Preparation of Styrene Oxide in 99% D_2O. To a 500-ml, three-necked flask equipped with condenser (protected with Drierite), stirrer, thermometer, and wide-bore dropping funnel were added 34.6 ml (0.090 mole) of benzyldimethylsulfonium chloride (99.3% D_2O), 27.0 g (0.27 mole) of formaldehyde (98.6% D_2O–CH_3OD), and 30.0 ml of toluene. To the stirred mixture preheated to 50° was added 27.7 ml (0.36 mole) of 13.0 *N* sodium deuterioxide (99.7% D_2O). The reaction temperature rose immediately to 72°. The temperature was kept between 64 and 70° for 30 min. Then, the dark yellow organic layer was separated from the aqueous layer and was extracted with water. The organic layer was dried over anhydrous $MgSO_4$ and was filtered to yield 41.0 ml of toluene solution. The determination of the oxirane content of the toluene solution by the pyridine-HCl method[17] indicated a 62% yield based on benzyldimethylsulfonium chloride. The distillation of the solution at 59–60° (5 mm) gave 6.5 g (60%) of styrene oxide, and the mass spectrometric analysis is listed in Table I. Proton nmr analysis indicated 88% deuteration in the α position and 5–6% deuteration in the β position. Infrared analysis indicated a C–D absorption at 2230 cm^{-1}. The distillation residue of 1.3 g was analyzed by vpc and mass spectrometry and the results are shown in Table II. The mass spectrometric analysis of the cold trap of the above distillation indicated the presence of toluene and methyl sulfide. The methyl sulfide was deuterated to the extent of 82.4% according to the following distribution: d_0, 4.2%; d_1, 0.6%; d_2 0.95%; d_3, 3.5%; d_4, 13.4%; d_5, 35.1%; and d_6, 42.0%. The ratio of d_6/d_5, 1.3, was calculated by E. B. Baker from deuterium analyses by nmr. Infrared analysis confirmed the presence of deuterium with C–D absorptions at 2300 and 2260 cm^{-1}.

Attempted Deuteration of Methyl Sulfide with D_2O and Sodium Hydroxide. To 1.86 g (0.03 mole) of methyl sulfide in 10 ml of toluene was added a solution of 4.8 g (0.12 mole) of NaOH and 1.75 g (0.03 mole) of NaCl in 25 ml of 99.5% D_2O. The stirred mixture was heated to 70° and refluxed at 60–65° for 30 min. The reaction mixture was separated. The organic layer was extracted three times with water and dried over anhydrous $MgSO_4$. Mass spectrometric and infrared analyses did not detect any deuteration of the methyl sulfide.

Acknowledgment. We wish to express our sincere appreciation to the following persons of The Dow Chemical Company, Midland, Mich., for the spectroscopic analyses: E. B. Baker and J. P. Heeschen, nmr; L. Westover, G. Kallos, and J. C. Tou, mass spectrometry; and R. A. Nyquist, infrared.

A New Reaction of Thionyl Chloride with a Carboxylic Acid in the Presence of a Tertiary Amine. An X-Ray Crystallographic Proof of Structure of α-Chloro-α-chlorosulfenyl-4-nitro-2,5-dimethoxyphenylacetyl Chloride

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Abstract: When 4-nitro-2,5-dimethoxyphenylacetic acid was treated with thionyl chloride and a small amount of tertiary amine, a sulfur-containing product, $C_{10}H_8NO_5SCl_3$, was obtained. A single-crystal three-dimensional X-ray crystallographic study showed the structure of this product to be α-chloro-α-chlorosulfenyl-4-nitro-2,5-dimethoxyphenylacetyl chloride. Some chemical and physical properties of this unusual compound are reported and discussed. That this novel reaction may be general is suggested by the fact that phenylacetic acid gives an analogous compound, $C_8H_5OSCl_3$.

Although the use of thionyl chloride with a tertiary amine is a well-known method for the preparation of carboxylic acid chlorides, we wish to report a new reaction arising from attempted application of this method,[2] for which little precedent has been found. When 4-nitro-2,5-dimethoxyphenylacetic acid was treated with excess thionyl chloride and 0.3–0.4 equiv of pyridine (or triethylamine), the expected 4-nitro-2,5-dimethoxyphenacetyl chloride was not obtained. The beautifully crystalline yellow product, isolated in 75% yield, was found to contain sulfur as well as a high percentage of chlorine. The analysis of the product (C, H, N, S, O, Cl, mol wt, OMe) corresponded to the formula $C_{10}H_8NO_5SCl_3$ ($2OCH_3$). The structure and some chemical reactions of this compound are the subjects of this report.

Physical Evidence for the Structure of the $C_{10}H_8NO_5SCl_3$ Compound

The infrared spectrum (Figures 1 and 2) showed the presence of the nitro group (1346, 1527 cm^{-1}), the methoxyl groups (1224 cm^{-1}) as well as the aromatic ring (1624, 1580, 1495 cm^{-1}), and a relatively complicated pattern in the carbonyl region, with a strong peak at 1766 cm^{-1}, inflections at 1783 and 1800 cm^{-1}, and a medium-strength peak at 1808 cm^{-1} (in carbon tetrachloride). The spectrum taken in KBr was very little different in this region. The presence of an acid chloride was strongly indicated although the material did not appear to be degraded by the water usually present in an ordinary KBr pressing. This stability to water will be discussed further below.

The proton magnetic resonance spectra were clear-cut and readily interpretable. There were only two pairs of singlets, at 3.97 and 4.03 ppm and at 7.47 and 7.57 ppm, in the ratio 3:1. The high-field pair could be assigned to the methoxyl protons, and the low-field pair to two protons on the aromatic ring.

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[1] (a) Polaroid Corp., Cambridge, Mass. (b) Harvard University, Cambridge, Mass.

[2] (a) P. Carré and D. Liebermann, *Compt. Rend.*, **199**, 1422 (1934); *ibid.*, 200, 1215 (1935); (b) J. P. E. Human and J. A. Mills, *Nature*, **158**, 877 (1946); (c) W. Gerrard and A. M. Thrush, *J. Chem. Soc.*, 741, (1952); 2117 (1953); J. A. Cade and W. Gerrard, *Nature*, 172, 29 (1953).