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MECHANISMS OF ELIMINATION REACTIONS—XXVII

THE REACTIONS OF 1-ARYLETHYLDIMETHYLSULFONIUM BROMIDES WITH SODIUM ETHOXIDE IN ETHANOL[1]

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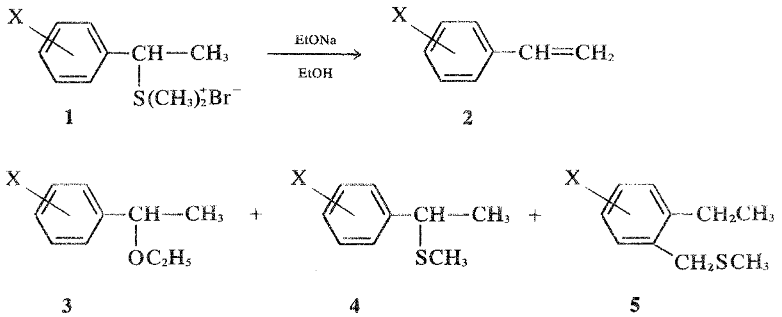
Abstract—Treatment of 1-phenylethyldimethylsulfonium bromide **1** with sodium ethoxide in ethanol at 35° affords four products by five reaction paths: styrene **2** by E2 and α'-β mechanisms, ethyl 1-phenylethyl ether **3** and methyl 1-phenylethyl sulfide **4** by the S_N2 mechanism, and methyl *o*-ethylbenzyl sulfide **5** by a Sommelet–Hauser rearrangement. Isotope effects of 5.9 and 3.5 for E2 and α'-β reactions were estimated by comparing the deuterium content of methyl sulfide from β-d_3 and α-d_7 (all α-positions exchanged) sulfonium salt. Product analyses on products from the unsubstituted, *p*-methyl, *p*-fluoro, *p*-bromo and *m*-chloro sulfonium salts were combined with overall rates to calculate partial rates for the formation of each product. These partial rates were fitted to the Hammett equation to give values for each product as follows: **2**, 0.95 ± 0.19; **3**, -0.63 ± 0.41; **4**, 0.95 ± 0.11; **5**, 4.84 ± 0.38. The mechanistic implications of the results are discussed.

The use of substituent effects and isotope effects to probe the structure of the transition state in bimolecular elimination reactions is by now widespread, and by far the most thoroughly-studied system has been 2-arylethyl.[3] Since the generality of conclusions drawn from a single type of structure is open to suspicion, we set out to examine substituent and isotope effects in the elimination reactions of 1-arylethyldimethylsulfonium ions for comparison with data on the 2-arylethyldimethylsulfonium ions.[4-11] The original aim was not extensively pursued because of the complexity of the reaction, but a study was made of the characteristics of the five different reaction paths followed in the reaction with sodium ethoxide in ethanol.

The desired compounds were synthesized by reaction of the corresponding 1-arylethyl bromides with methyl sulfide. We noted, as did Banthorpe, Hughes and Ingold,[12] the formation of trimethylsulfonium bromide as a byproduct. An attempted alternate synthesis, the reaction of the 1-arylethyl methyl sulfide with methyl bromide, gave a product which was even more difficult to purify. Under our reaction conditions the desired sulfonium salt was always >90% pure, and the trimethylsulfonium bromide did not interfere in the determination of the rate of reaction with base under pseudo-first-order conditions.

In the reaction of the unsubstituted compound **1a**, with base (eqn 1), we readily identified by GLC the three products reported by Banthorpe, Hughes and Ingold,[12] **2a**, **3a** and **4a**. Our GLC traces also revealed a fourth peak, 7–8% of the total product, which was identified by isolation and comparison with an authentic sample as the product of a Sommelet–Hauser rearrangement,[13-18] **5a**. The corresponding products from **1d** and **1e**, **5d** and **5e**, constituted over half of their reaction mixtures. Although not previously observed with compounds of the structure **1**, this reaction is well known with other benzylic sulfonium salts,[14,16,18] and has more recently been noted with azasulfonium salts.[19] Isolation and identification by NMR was also carried out for **5d**.

The rate of loss of starting material was determined by following the appearance of styrene spectrophotometrically.[20] In the presence of a large excess of base the overall reaction was cleanly first order, but the second-order rate constants calculated by dividing k_1 by the base concentration decreased with increasing base concentration, as shown in Table 1 for **1a** and **1e**. There appears to be no significant first-order component to the reactions. The two substrates most likely to solvolyze, **1a** and **1b**, had first order rate constants for solvolysis of 3.7×10^{-6} and 3.8×10^{-6} sec^{-1}, respectively, at 35°. This corresponds to *ca.* 1% of the rate of reaction with base



a: X = H; **b**: X = *p*-CH₃; **c**: X = *p*-F;
d: X = *p*-Br; **e**: X = *m*-Cl

Table 1. Apparent second-order rate constants for loss of starting material in the reaction of 1-arylethyldimethylsulfonium bromides with sodium ethoxide in ethanol at 35.0°

Ar	[OEt$^-$]	$k_2 \times 10^3$, l-mole^{-1} sec^{-1}
C_6H_5	0.0910	5.48 ± 0.08[a]
	0.1065	4.98 ± 0.08
	0.1228	4.58 ± 0.01
	0.1410	4.06 ± 0.01
m-ClC_6H_4	0.0915	42.9 ± 2.2
	0.1167	44.2 ± 1.1
	0.1336	34.7 ± 0.4
	0.1752	27.6 ± 1.0

[a] Average deviations for three simultaneous runs.

Table 2. Second-order rate constants for product formation in the reaction of 1-arylethyldimethylsulfonium bromides with sodium ethoxide at 35.0°

	$k_2 \times 10^3$ l-mole^{-1} sec^{-1} for product[a,b,d]			
Ar	**2**	**3**	**4**	**5**
p-MeC_6H_4	3.41	1.52	0.33	0.11
C_6H_5	3.76	0.57	0.49	0.39
p-FC_6H_4	6.47	1.14	0.68	1.00
p-BrC_6H_4	8.58	0.90	0.85	11.2
m-ClC_6H_4	10.0	0.52	1.08	31.7
C_6H_5-d_3[c]	0.67	0.60	0.39	0.41

[a] Rate constants are the overall rate constants (Table 1) interpolated to [OEt$^-$] = 0.1 M times the average mole fraction of the appropriate product (mole fractions at all [OEt$^-$] averaged, omitting seriously discordant values, and renormalized). [b] Combined uncertainties of rate constants and mole fractions *ca.* 5% in most cases. [c] 1-Phenylethyl-2,2,2-d_3-dimethylsulfonium bromide. [d] **2** is the styrene, **3** 1-arylethyl ethyl ether, **4** 1-arylethyl methyl sulfide, **5** *o*-ethylbenzyl methyl sulfide.

Table 3. Hammett correlations and isotope effects in the reactions of 1-arylethyldimethylsulfonium bromides with sodium ethoxide in ethanol at 35.0°

Reaction to give	k_H/k_D	ρ[b]	r[c]
2	5.6[a]	0.95 ± 0.19	0.94
3	0.95	− 0.63 ± 0.41	0.67
4	1.26	0.95 ± 0.11	0.98
5	0.93	4.84 ± 0.38	0.99

[a] Weighted average of k_H/k_D values for E2 reaction (5.9) and α'-β reaction (3.5) (see text). [b] Hammett reaction constant determined by linear regression, with standard deviation. [c] Correlation coefficient.

under our conditions, ignoring salt effects. Furthermore, the product composition from each substrate shows no trend with base concentration, which makes unlikely the possibility that a significant fraction of any single product could arise via a first-order reaction.

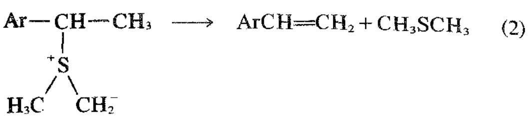
For these reasons, we consider the dependence of the second-order rate constants on base concentration to be a salt effect. An effect in this direction for reactions between oppositely-charged ions is predicted by the Hughes–Ingold theory of solvent effects,[21] and reported by Banthorpe, Hughes and Ingold[12] for reactions of **1a** and other sulfonium salts with base. Mamalis and Rydon[22] report that plots of log k_2 vs $\mu^{1/2}$ for the reaction of 2-aryloxyethyldimethylsulfonium iodides with hydroxide ion in water had slopes near −2.5. Similar plots for **1a** and **1e** (where μ = [OEt$^-$], since ethoxide is present in large excess) gave slopes of −1.7 and −1.8, respectively.

Before the rates for different substrates can be compared, it is necessary to interpolate to a common base concentration. We were faced with a choice of doing this at the outset and then partitioning the overall rate constants into partial rate constants for the formation of each product, or with calculating partial rate constants at each base concentration and then interpolating each of them to a common base concentration. We chose the former course, and a base concentration of 0.1 M. As noted above, there was no systematic dependence of product composition on base concentration, so we felt that the average of all product analyses for a given substrate would give more reliable figures for product composition than taking separately the results at each different base concentration and combining them with the corresponding k_2 values. While the salt effects on the rates of formation of all four products need not be the same, the constancy of product composition with base concentration indicates that in fact they do not differ within our experimental error. The rate constants for formation of the individual products are listed in Table 2.[23] The estimated overall uncertainty in the values is ±5% in most cases.

Rate constants for the formation of each product were fitted to the Hammett equation, and isotope effects were determined by comparing the rates for **1a** with rates for **1a**-2,2,2-d_3. The results are shown in Table 3. Since the formation of **2** is the only reaction involving cleavage of a β-carbon-hydrogen bond, one expects and observes a sizable primary isotope effect only in that case. For the reactions forming the other products, at most a small secondary effect is expected. The k_H/k_D values for formation of **3** and **5** are within experimental error of unity. That for formation of **4** is somewhat larger than the anticipated error, but there is no reason to expect a real effect of any significance, so we prefer to consider it the result of a chance accumulation of errors.[24]

The Hammett ρ value (0.95) for the elimination to give **2** is the same in sign as that for the corresponding reaction of 2-phenylethyldimethylsulfonium ion (*ca* 2.7[4,5]). It is difficult to see how electron-withdrawing groups on the α-carbon could facilitate departure of the leaving group, so we believe the positive ρ indicates an inductive effect on ease of removal of the β-hydrogen by base. Similar mild facilitation of elimination rates by electron-withdrawing substituents on an α-aryl group is observed with 1,2-diarylethyl chlorides[25,26] and 1-arylethyl bromides.[27] The combination of the positive ρ values and the substantial primary isotope effect point to a normal E2 reaction.[28]

One possible mechanism of elimination not excluded by the data so far presented is the α'-β, or ylid, mechanism (eqn 2).[29] Although it seemed unlikely that there would be a major contribution from the α'-β mechanism under our conditions, we carried out experiments in which the methyl sulfide from reaction of **1a**-2,2,2-d_3 was isolated and examined for deuterium content in the mass spectrometer. Two runs gave 7.3 and 4.1% deuteration, indicating, after allowance for the isotopically normal methyl sulfide formed in the reaction giving **3**, an average of 10.8% α'-β mechanism in the elimination reaction.



$$\mathrm{Ar{-}\underset{\underset{H_3C\quad CH_2^-}{\overset{|}{^+S}}}{CH}{-}CH_3 \longrightarrow ArCH{=}CH_2 + CH_3SCH_3} \qquad (2)$$

This figure is distinctly larger than the 0.9–2.6% α'–β reaction found with some simple secondary sulfonium salts and potassium *n*-butoxide in *n*-butyl alcohol.[29] Because **1a** appears to react substantially faster in the elimination reaction than do the simple substrates,[30] the increased importance of the α'–β path with **1a** cannot be ascribed to a slowing of the E2 path. Since conformational facilitation of the α'–β path seems to be important,[29] one could reasonably postulate that the aryl group favors a conformation of the intermediate ylid in which the negatively-charged methylene group is toward the β-methyl group and away from the aryl group.

The demonstration that the α'–β mechanism contributes to the total elimination reaction means that the values for k_H/k_D and ρ in Table 3 are weighted averages. The effort involved in attempting to dissect ρ seemed too great for the probable return, but a relatively simple method of estimating k_H/k_D for the α'–β reaction was devised. A sample of **1a** was allowed to equilibrate with ethanol-O-d and sodium ethoxide for one half life of the elimination reaction, the mixture acidified, and the solvent and all volatile products distilled off under vacuum. The residue, presumed to consist mainly of **1a** deuterated in the seven available α-positions, was then treated with sodium ethoxide in ethanol-O-d and the resulting methyl sulfide analyzed for deuterium. The content of d_5 material should measure the extent of the α'–β reaction when hydrogen is transferred, provided **1a** was completely deuterated in the α-positions, and provided the **1a**-d_7 reacted at the same rate as undeuterated **1a**. The results, unfortunately, gave some evidence that equilibration of **1a** with ethanol-O-d was not complete (see Experimental for details), but we can still arrive at an upper limit of 6.7% α'–β reaction which is probably fairly close to the true figure.

From the 10.8% and 6.7% α'–β reaction for **1a**-2,2,2-d_3 and **1a**-d_7, respectively, we can calculate that the E2 reaction proceeded with a k_H/k_D of 5.9, and the α'–β reaction with a k_H/k_D of 3.5. These figures are *a priori* quite reasonable, for the α'–β reaction must involve a non-linear proton transfer (C---H---C angle not far from 120°) if severe strain in the cyclic transition state is to be avoided. Model calculations give smaller isotope effects for non-linear than for linear proton transfers.[31,32] The k_H/k_D value for the E2 reaction is somewhat higher than that observed with 2-phenylethyldimethylsulfonium ion at 30° (5.1),[7] and is consistent with a linear proton transfer in which the proton is approximately half transferred in the transition state.

Table 4. Conditions and retention times for gas-chromatographic analysis of products from the reaction of 1-arylethyldimethylsulfonium bromides with sodium ethoxide in ethanol at 35.0°

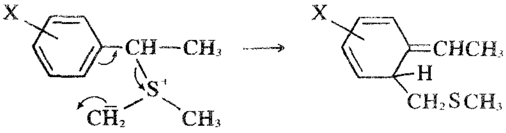
	T, °C[a]		Retention time for product, min[b,c,d]			
Ar	Initial	Final	**2**	**3**	**4**	**5**
p-MeC_6H_4	175	225	6.7	10.0	14.3	20.5
C_6H_5	200	200	1.5	4.0	10.0	21.5
p-FC_6H_4	170	210	4.5	8.5	12.5	22.0
p-BrC_6H_4	230	230	3.2	6.0	14.0	25.5
m-ClC_6H_4	210	230	2.2	4.0	8.0	14.5
C_6H_5-d_3[c]	200	200	1.5	4.0	10.0	21.5

[a]The temperature was raised rapidly (30°/min) to the final value after the styrene peak. [b]Analysis on a 3-ft × 0.125-in column of Chromosorb 101, 80–100 mesh, injector temperature 120°, hydrogen pressure 21.5 psi. [c,d]See corresponding footnotes, Table 2.

The S_N2 reaction producing **3** gives by far the poorest Hammett plot. The most striking feature is the slowness of **1a**, though on balance there seems a slight tendency for electron-withdrawing substituents to retard the reaction. Curved Hammett plots are fairly common in S_N2 reactions where the substituted phenyl group is attached to the α-carbon, and have been explained by postulating changes with substituent in the ratio of bond-making to bond-breaking in the transition state.[33] A particularly close analogy is afforded by the reaction of hydroxide ion with benzyldimethylsulfonium ions, where both the *p*-methyl and the *m*-chloro derivatives react faster than the unsubstituted compound.[34]

The other possible S_N2 process in this system involves attack at one of the *S*-methyl carbon atoms to give **4**, and occurs with a Hammett ρ value of 0.95. The sign of ρ is as expected for substitution in the leaving group in a displacement or solvolysis, and the magnitude is somewhat less than those observed in ethanolysis of methyl benzenesulfonates at 70° (1.3),[35] and the reaction of ethyl benzenesulfonates with ethoxide in ethanol at 35° (1.4).[36]

The Sommelet–Hauser rearrangement to give **5** has a large positive value of ρ. While a small part of the positive value could result from a substituent effect on the formation of the ylid precursor of the rearrangement product, the major factor is no doubt the substituent effect on attack by the ylid carbon at an *o*-position of the benzene ring (eqn 3). Indeed, the large positive ρ value requires that the rate-determining step of the reaction be eqn (3). Nucleophilic substitution reactions on aromatic rings by external nucleophiles have been extensively studied, and are found to have ρ values in the range of +3.5 to +5.0.[37,38]



(3)

EXPERIMENTAL

NMR spectra were determined on Varian or JEOL 60-MHz instruments and MS on an Atlas-MAT CH-4 instrument. Inorganic reagents were analytical reagent grade. B.p.s and m.p.s are uncorrected.

1-*Arylethanols* were prepared by reducing the corresponding acetophenones (Eastman Kodak White Label) with lithium aluminum hydride. The 1-phenylethanol-2,2,2-d_3 was prepared by reducing acetophenone which had been exchanged with deuterium oxide by a procedure reported for *o*-ferrocenylacetophenone.[39] One exchange of 0.08 moles of acetophenone with 1.5 moles of deuterium oxide gave 95% deuteration (NMR).

1-*Arylethyl bromides.* 1-Phenylethyl bromide was redistilled Eastman Kodak White Label material, b.p. 46–47° (2 mm) (lit.[40] 83–84° (10 mm)). Two other bromides were prepared by bubbling dry hydrogen bromide through the neat alcohol at 0°C until 15 min after the formation of an aqueous layer. The mixture was neutralized with 10% sodium bicarbonate, the organic layer extracted with ether and the extracts dried ($MgSO_4$). Removal of the ether and vacuum distillation gave the product.

1-*Phenylethyl*-2,2,2-d_3 *bromide* had b.p. 40–41° (0.25 mm) and 95% deuterium (NMR).

1-(p-*Fluorophenyl*)*ethyl bromide* had b.p. 75–78° (1.0 mm).

Anal. Calc. for C_8H_8BrF: C, 47.31; H, 13.34; Br, 39.35. Found: C, 47.19; H, 13.94; Br, 39.48%. The remaining bromides were prepared by adding 0.15 moles of phosphorus tribromide dropwise with stirring to 0.075 moles of the alcohol, followed by stirring for 1.5 h. The mixture was worked up as above.

1-(p-*Methylphenyl)ethyl bromide* had b.p. 57–58° (2 mm) (lit.[41] 105–106° (12 mm)).

1-(p-*Bromophenyl)ethyl bromide* had b.p. 89–91° (1.0 mm). Anal. Calc. for $C_8H_8Br_2$: C, 36.40; H, 3.05; Br, 60.55. Found: C, 36.30; H, 3.04, Br, 60.71%.

1-(m-*Chlorophenyl)ethyl bromide* had b.p. 93.5–94° (3.0 mm). Anal. Calc. for C_8H_8BrCl: C, 43.76; H, 3.67; Br, 36.39. Found: C, 43.64; H, 3.55; Br, 36.39%.

1-*Arylethyldimethylsulfonium bromides.* A mixture of 5 ml of dry nitromethane, 0.005 moles of the bromide and 0.0064 moles of methyl sulfide was allowed to stand in a stoppered test tube for 4–6 h at room temp. The mixture was poured into 100 ml of anhydrous ether and left overnight in a stoppered flask at 0°C. The resulting crystals were dissolved in a minimum of absolute ethanol, anhydrous ether added to the cloud point, a drop of anhydrous ethanol added, and crystallization allowed to proceed *ca.* 24 h at 0°C. The sulfonium salts were hygroscopic and were handled in a dry box. The salts were usually contaminated by small amounts (up to 10%) of trimethylsulfonium bromide (NMR) which did not interfere in the kinetic studies.

1-*Phenylethyldimethylsulfonium bromide* had m.p. 100° (dec) (lit.[42] 91.7–92.8°). A carefully purified sample was analyzed. Anal. Calc. for $C_{10}H_{15}SBr$: C, 48.59; H, 6.11; S, 12.97. Found: C, 48.47; H, 6.05; S, 12.92%.

1-*Phenylethyl-2,2,2-d_3-trimethylsulfonium bromide* had m.p. 102° (dec), and contained 95.6% of the calculated amount of deuterium (analysis by J. Nemeth, Urbana, Illinois).

1-(p-*Methylphenyl)ethyldimethylsulfonium bromide* had m.p. 96° (dec).

1-(p-*Bromophenyl)ethyldimethylsulfonium bromide* had m.p. 125° (dec).

1-(p-*Fluorophenyl)ethyldimethylsulfonium bromide* had m.p. 78° (dec).

1-(m-*Chlorophenyl)ethyldimethylsulfonium bromide* had m.p. 102° (dec).

Ethyl 1-phenylethyl ether was obtained from the reaction of 0.05 mole of 1-phenylethyl bromide with 0.1 mole of sodium ethoxide in 200 ml of absolute ethanol at 35° under dry nitrogen overnight. The mixture was diluted with 200 ml of water, extracted with ether, and the extracts dried ($MgSO_4$). Removal of the ether and distillation yielded 80% of product, b.p. 52° (7 mm) (lit.[43] 53–54°) (5 mm)). Identity was further checked by NMR and purity by GLC (>97%).

Methyl 1-phenylethyl sulfide was prepared by adding 0.125 mole of cold methanethiol to 0.1 mole of sodium ethoxide in 200 ml of ethanol under nitrogen in a flask equipped with a Dry-Ice condenser. To the mixture was added 0.05 mole of 1-phenylethyl bromide with stirring, and stirring continued overnight at room temperature. The same workup procedure as for ethyl 1-phenylethyl ether gave 67% of methyl 1-phenylethyl sulfide, b.p. 54° (1.0 mm) (lit.[44] 60° (0.3 mm)), shown to be >99% pure by GLC.

Styrene was freshly distilled Eastman Kodak White Label material, shown by GLC to be >99% pure.

Methyl o-*ethylbenzyl sulfide.* The method of Vogel[45] was used to convert *o*-ethylaniline to *o*-ethylbenzonitrile in 30% yield. The nitrile was hydrolyzed with sodium hydroxide[46] to 45% of *o*-ethylbenzoic acid, which in turn was reduced by lithium aluminum hydride in ether to give 90% of *o*-ethylbenzyl alcohol. Treatment with dry hydrogen bromide (see above) yielded *o*-ethylbenzyl bromide, which was treated with sodium methanethiolate (see procedure for methyl 1-phenylethyl sulfide preparation) to give methyl *o*-ethylbenzyl sulfide, NMR δ1.2 (3H, t, J = 8 Hz), 1.9 (2H, s), 2.8 (2H, q, J = 8 Hz), 3.8 (3H, s), 7.4 (4H, m). Analysis by GLC showed *ca.* 4% impurities.

Solvents and base solutions. Ethanol was dried over magnesium, and only material containing <0.05% water was used.[47] Ethanol-O-d (Stohler Isotopic Chemical Co.) was used without further purification. Comparison of the NMR peaks at δ 5.3 and 3.5 showed 2.7% of undeuterated ethanol. Base solutions were prepared by bubbling dry nitrogen through ethanol for 45 min, followed by addition of the calculated amount of freshly-cut, ethanol-washed sodium. A positive nitrogen pressure was maintained in the flask, and aliquots were withdrawn by syringe for standardization by titration or use in reactions.

Rate measurements were performed in the cell compartment of a Beckman DU spectrophotometer equipped with thermospacers through which water from a constant-temperature bath circulated. The temperature was kept at 35.0 ± 0.1°, or 0.05° within a run. The ethoxide solution (0.08–0.18 M) was equilibrated in four 1-cm stoppered quartz cells for 20 min, and 50 μl of freshly-prepared sulfonium-salt solution added quickly with a 0.1-ml syringe to three of the cells. The cells were stoppered, shaken and replaced in the cell compartment, and readings taken periodically at λ_{max} for the solution (unsubs., 248 nm; *p*-Me, 252 nm; *p*-Br, 255.5 nm; *p*-F, 252 nm; *m*-Cl, 250 nm). The sulfonium-salt concentration was *ca.* 10^{-5} M, or such that A_∞ was *ca.* 0.7. Pseudo first-order rate constants were determined graphically, and divided by ethoxide concentration to give k_2 values (Table 1).

Product composition was determined by GLC. The four products from the unsubstituted compound were identified by coinjection with authentic samples on a 9-ft column of squalene on firebrick at 150°, and a 3-ft Chromosorb 101 column, 80/100 mesh, at 200°. As a further check, the final peaks from both unsubstituted and *p*-bromo compoundus were isolated from a GLC separation and their NMR spectra examined. The former gave a spectrum identical to that of the authentic sample, the latter gave δ1.2 (3H, t, J = 8 Hz), 1.9 (3H, s), 2.75 (2H, q, J = 8 Hz), 3.65 (2H, s); 7.3 (3H, m). Quantitative product measurements were done on 5.0-ml samples of 0.08–0.18 M base in 175-mm test tubes sealed with rubber septa to which were added 0.05 ml aliquots of 0.1 M sulfonium salt solution. After ten half lives at 35.0 ± 0.1°, the base was neutralized with an excess of Dowex 50W–X8 strongly acid cation exchange resin. Products were analyzed on a Perkin–Elmer 900 instrument using a 3-ft × 0.125-in column of Chromosorb 101 under conditions listed in Table 4. Plots of mole fraction vs peak area fraction were drawn for the products from the unsubstituted sulfonium salt and assumed to apply to the other sulfonium salts. Two analyses on each of three samples (six values) were performed. Deviations from the mean of the mole fractions were 3% or less in virtually all cases, even for products comprising <10% of the mixture. Changing the injector temperature from 240° to 280° had no effect on product proportions (250° was the standard setting), nor did changing hydrogen pressure from 20 to 22 psi (standard setting 21.5 psi). Product proportions remained constant in the presence of sodium ethoxide for at least 24 h, and in the presence of excess Dowex 50W–X8 resin for at least 8 h.

Deuterium tracer experiments were carried out in a three-neck flask with a plug in the center neck, a septum on one side neck, and a condenser on the other. To the top of the condenser was attached a calcium chloride tube, which in turn was attached to a coil trap in a Dewar flask containing liquid nitrogen. The other side of the coil trap led to a mercury bubbler. In the flask 1.04 g of 1-phenylethyl-2,2,2-d_3-dimethylsulfonium bromide in 10 ml of dry ethanol was equilibrated at 35.0° and 10 ml of 1.29 M sodium ethoxide in ethanol at 35.0° added by calibrated syringe. A positive nitrogen pressure was maintained in the apparatus until reaction was complete. The mixture was diluted with 20 ml of water and nitrogen bubbled through the solution for about 1 h by means of a syringe needle inserted in the septum. The methyl sulfide in the trap was purified by GLC using a 10-ft column of 20% Ucon 50-HB5100 on Chromosorb P at room temperature. It was then degassed on a vacuum line and transferred to a mass spectrometer sample tube.

The second set of experiments used a similar apparatus. To the reaction flask was added by syringe 0.2 g of 1-phenylethyldimethylsulfonium bromide in 2 ml of ethanol-0-d, and 15 ml of 0.1 M sodium ethoxide in ethanol-0-d, both equilibrated to 35.0° as above, and the flask kept at 35.0°. Sufficient time for 50% reaction was allowed and the reaction quenched with hydrogen chloride gas. Vacuum was applied to the apparatus and the solvent and volatile products flash distilled into the trap. The trap was replaced, 15 ml of 0.1 M sodium ethoxide added to the reaction flask (presumed to contain 1-phenylethyl-1-d-dimethyl-d_6-sulfonium salt) and the reaction allowed to proceed, in one case to 50% and in the other to 100% reaction. The methyl sulfide produced was collected and purified as above. All samples of methyl sulfide were examined in an Atlas–MAT CH-4 mass spectrometer at 13 eV ionizing voltage, conditions shown to give only the parent peaks.

The methyl sulfide samples from 1-phenylethyl-2,2,2-d_3-dimethylsulfonium bromide gave the following peak ratios in two separate experiments: *m/e* 63/62, 0.1098, 0.740; 64/62, 0.0490, 0.0463, compared to *m/e* 63/62, 0.0320, 0.0317; 64/62, 0.0457, 0.0452 for Eastman Kodak White Label methyl sulfide. After correction for the normal abundance of heavier isotopes according to the method of Biemann,[48] these results indicate 7.3 and 4.1%, or an average of 5.7%, of methyl-d_1 sulfide in the two samples. This number must be corrected for the fact that methyl sulfide results when both styrene (32.4%) and 1-phenylethyl ethyl ether (28.8%) are produced. The methyl sulfide from the ether-forming reaction must be isotopically normal, so 10.8% of the methyl sulfide from the elimination reaction was deuterated.

The methyl sulfide from "1-phenylethyl-1-d-dimethyl-d_6-sulfonium bromide" (material exchanged with ethanol-0-d) was next examined. The sample from 50% reaction gave *m/e* 67/66, 2.557 and 68/66, 6.115, while that from 100% reaction gave 67/66, 7.038 and 68/66, 25.77. Evidently the sulfonium salt was not in complete isotopic equilibrium with the solvent at all times, in spite of the preliminary exchange. Taking the 100% sample as the better approximation, one calculates[48] 20.9% of dimethyl-d_5 sulfide and 3.0% of dimethyl-d_4-sulfide. Correction for hydrogen introduced by equilibration with 2.8% undeuterated ethanol in the solvent (2.7% originally +0.1% from the sulfonium salt at half reaction) gives 5.8% excess dimethyl-d_5 sulfide and 1.9% dimethyl-d_4 sulfide from the reaction. Assuming that the proportions of styrene (72.2%) and ethyl 1-phenylethyl ether (11.0%) are the same as from the undeuterated sulfonium salt, the methyl sulfide from the elimination reaction can be calculated to be 6.7% d_5 and 2.2% d_4. In view of the evidence above for incomplete equilibration of the sulfonium salt with the ethanol-0-d, these numbers should be regarded as upper limits. No attempts at further correction were made in view of the uncertainties involved and the likelihood that the correction would be small.

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