[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF ROCHESTER]

Mechanisms of Elimination Reactions. II. Rates of Elimination from Some Substituted 2-Phenylethyl Bromides and 2-Phenylethyldimethylsulfonium Bromides[1]

BY WILLIAM H. SAUNDERS, JR., AND RICHARD A. WILLIAMS[2]

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A series of *p*-substituted 2-phenylethyl bromides and 2-phenylethyldimethylsulfonium bromides has been prepared. The rates of their reactions with sodium ethoxide in ethanol were determined over a range of temperatures and the enthalpies and entropies of activation calculated. All of the compounds studied gave quantitative yields of the corresponding styrenes. The data fit the Hammett equation satisfactorily, giving $\rho = +2.15$ for the bromides and $+2.64$ for the sulfonium salts when the substituents are *p*-methoxyl, *p*-methyl, hydrogen and *p*-chloro. The substituents *p*-acetyl and *p*-nitro require the use of σ-values derived from the reactions of phenols and anilines. Factors affecting the balance and timing of the bond-making and bond-breaking processes in E2 eliminations are discussed, and some applications of these ideas to previous results are made.

Recent studies of base-promoted elimination reactions have suggested the need for revision of some commonly accepted ideas. For instance, the usual marked preference for *trans* elimination may be greatly reduced when electron-withdrawing substituents are present on the β-carbon atom[3] or when the four centers involved (H–C–C–X) cannot achieve coplanarity.[4] Reactivities of diastereomeric 1,2-diphenyl-1-propyl derivatives show that the degree of eclipsing in the transition state may be greatly modified by changes in the leaving group, the solvent and the base.[5] The absence of an appreciable sulfur isotope effect in eliminations from 2-phenylethyldimethylsulfonium bromide has been taken as indicating a transition state possessing considerable carbanion character.[1]

These and other results provide evidence that many E2 eliminations may depart rather widely from the conventional picture of a synchronous *trans* process. Recent evidence that steric[6] as well as electronic factors may be important in elimination reactions also calls for a reconsideration of former concepts. We felt that a systematic study of electronic influences on rates of eliminations might shed further light on these problems. Consequently, the preparation of a series of *p*-substituted 2-phenylethyl bromides and 2-phenylethyldimethylsulfonium bromides was undertaken and the rates of their reactions with sodium ethoxide in absolute ethanol were determined. It was anticipated that the direction and magnitude of substituent effects would lead to information on the electron distribution in the transition state.

Syntheses of the desired compounds were accomplished by conventional procedures. The reactions employed in most cases are summarized in Fig. 1. A considerable number of the intermediates and products were unknown prior to this investigation. Details on these and other aspects of the synthetic approach are given under Experimental. Some departures from the general scheme were necessary. Direct acetylation[7] of IIIa and IVa yielded IIIe and IVe, respectively. Nitration[7] of IIIa gave IIIf. Attempts to prepare Vf were unsuccessful and were abandoned when it became apparent that the reaction of Vf with base would be too fast to measure.

The compounds examined in the kinetic studies were IIIa-f in the bromide series and Va-d in the sulfonium bromide series. The corresponding styrenes (VI) were, for the most part, obtained by treatment of the sulfonium salts with aqueous sodium hydroxide, followed by isolation and careful distillation of the styrenes. The ultraviolet absorption spectra of the styrenes were determined in absolute ethanol. Extinction coefficients at the maxima used for analysis are recorded in Table I. These values were used in the calculation of olefin yields in the kinetic experiments.

TABLE I

ULTRAVIOLET ABSORPTION OF *p*-SUBSTITUTED STYRENES IN 95% ETHANOL

Cpd.[a]	λ_{max}, mμ	Molar extinction $\times 10^{-4}$
VIa	248	1.38[b]
VIb	252	1.69
VIc	258	1.92
VId	253	1.97
VIe	280	2.07[c]
VIf	300	1.37[d]

[a] See Fig. 1 for numbering of compounds. [b] Lit.[1] 1.35×10^4. [c] G. Baddeley, E. Wrench and R. Williamson, *J. Chem. Soc.*, 2110 (1953), give 2.15×10^4. [d] M. J. Kamlet and D. J. Glover, THIS JOURNAL, **77**, 5696 (1955), give 1.39×10^4.

The rates of the reactions of III and V with sodium ethoxide in absolute ethanol were followed acidimetrically. Olefin yields were calculated from the ultraviolet absorption of the reaction mixtures at the appropriate maxima. Rate constants and olefin yields are collected in Table II. The olefin yields are obviously within experimental error of 100% and thus the rate constants are attributable entirely to elimination.[8] The reactions were all

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(1) Paper I in this series: W. H. Saunders, Jr., and S. Ašperger, THIS JOURNAL, **79**, 1612 (1957).

(2) American Cyanamid Fellow, 1955–1956; Beaunit Mills Fellow, Summer, 1956.

(3) J. Weinstock, R. G. Pearson and F. G. Bordwell, THIS JOURNAL, **78**, 3468 (1956).

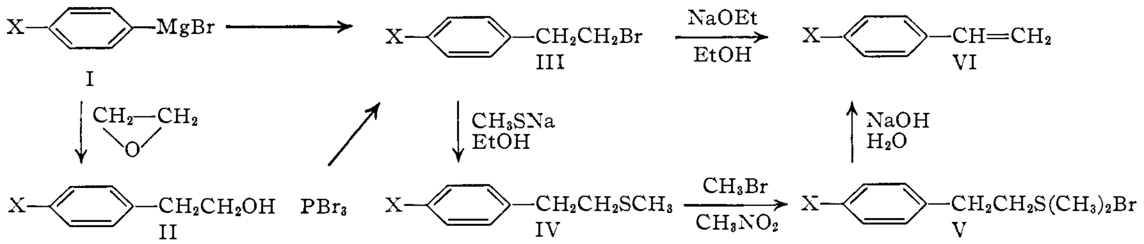
(4) S. J. Cristol and N. L. Hause, *ibid.*, **74**, 2193 (1952); S. J. Cristol and R. P. Arganbright, Abstracts of Papers, 130th Meeting of the American Chemical Society, Atlantic City, N. J., September 16–21, 1956.

(5) D. J. Cram, F. D. Greene and C. H. DePuy, THIS JOURNAL, **78**, 790 (1956).

(6) H. C. Brown and I. Moritani, *ibid.*, **78**, 2203 (1956), and preceding papers.

(7) E. L. Foreman and S. M. McElvain, *ibid.*, **62**, 1435 (1940).

(8) The styrene yield from IIIa is reported to be 94.6% by E. D. Hughes, C. K. Ingold, S. Masterman and B. J. McNulty, *J. Chem. Soc.*, 899 (1940). The sulfonium iodide corresponding to Va is reported to give 89.1% olefin by E. D. Hughes, C. K. Ingold and G. A. Maw, *ibid.*, 2072 (1948). Their analyses employed the bromine-addition



a, X = H; b, X = CH_3; C, X = CH_3O; d, X = Cl; e, X = CH_3CO; f, X = NO_2

Fig. 1.—Synthetic scheme.

cleanly second order and the constants were steady to a precision of 1–2% in practically all cases. The data were fitted to log *k vs.* $1/T$ plots by the method of least squares and the enthalpies and entropies of activation calculated. These values are recorded in Table III.

TABLE II

RATE CONSTANTS AND OLEFIN YIELDS FOR ELIMINATIONS FROM 2-ARYLETHYL BROMIDES AND 2-ARYLETHYLDIMETHYLSULFONIUM BROMIDES WITH SODIUM ETHOXIDE IN ABSOLUTE ETHANOL

Cpd.[a]	T, °C.	$k_2 \times 10^5$, l. mole^{-1} sec.$^{-1}$[c]	Olefin yield, %[c]
IIIa	59.40	814 ± 9.4	99.7 ± 0.3
IIIa	50.20	342 ± 4.3	99.5 ± .3
IIIa	40.75	133 ± 2.1	99.6 ± .4
IIIa	30.05	41.7 ± 0.66	99.6 ± .1
IIIb	59.40	494 ± 6.0	100.1 ± .2
IIIb	50.20	202 ± 3.3	99.6 ± .4
IIIb	40.75	75.0 ± 1.14	100.0 ± .1
IIIb	30.05	22.8[b]	....
IIIc	59.40	378 ± 4.7	99.3 ± 0.4
IIIc	50.20	151 ± 1.5	100.5 ± .3
IIIc	40.75	52.8 ± 0.71	99.8 ± .3
IIIc	30.05	16.2[b]	....
IIId	50.20	1410 ± 22	99.1 ± 0.5
IIId	40.75	585 ± 11.9	99.4 ± .4
IIId	30.05	191 ± 3.3	99.0 ± .1
IIIe	30.05	3720[b]	....
IIIe	20.10	1340 ± 27	100.4 ± 0.3
IIIe	10.35	464 ± 5.1	100.0 ± .2
IIIe	0.0	135 ± 2.4	100.2 ± .1
IIIf	30.05	74200[b]	....
IIIf	10.35	9140 ± 280	99.0 ± 0.7
IIIf	0.0	2680 ± 24	99.4 ± .5
Va	40.75	1970 ± 26	99.4 ± .2
Va	30.05	500 ± 7.5	99.4 ± .3
Va	20.10	133 ± 1.1	99.4 ± .2
Vb	40.75	1000 ± 12	99.5 ± .4
Vb	30.05	232 ± 2.3	99.9 ± .3
Vb	20.10	55.1 ± 0.69	100.2 ± .2
Vc	40.75	484 ± 3.6	99.5 ± .4
Vc	30.05	111 ± 1.4	99.3 ± .2
Vd	30.05	2440 ± 38	99.0 ± .2
Vd	20.10	680 ± 12	99.2 ± .3
Vd	10.35	177 ± 3.8	99.0 ± .1

[a] See Fig. 1 for numbering of compounds. [b] Extrapolated from the Arrhenius plot of data at other temperatures. [c] Deviations listed are average deviations.

Inspection of the rate constants shows that the elimination reaction in both series is strongly accelerated by electron-withdrawing substituents. Activation enthalpies for the sulfonium salts run 3–5 kcal. higher than for the bromides, but the reactions of the sulfonium salts are actually faster because of a compensating difference in entropies of activation. The much larger entropies of activation for the sulfonium salts probably can be ascribed mainly to entropies of solvation. Since the reaction is between oppositely charged ions, solvent molecules should be released on going to the transition state. The variation in entropy of activation among the bromides (except IIIf) appears to be within experimental error. The difference for IIIf may have mechanistic significance, but we cannot exclude the possibility of systematic errors in the rate constants aggravated by the high speed of the reaction. Entropies of activation for the sulfonium salts are spread over a wider range (*ca.* 5 e.u.), and there is a tendency for high $\Delta S^{\ddagger}$ to be associated with high $\Delta H^{\ddagger}$.[9]

TABLE III

ENTROPIES AND ENTHALPIES OF ACTIVATION FOR ELIMINATIONS FROM 2-ARYLETHYL BROMIDES AND 2-ARYLETHYLDIMETHYLSULFONIUM BROMIDES

Cpd.	T, °C.[a]	$\Delta H^{\ddagger}$,[b] kcal.-mole^{-1}	$\Delta S^{\ddagger}$,[c] cal.-mole^{-1}, °C.$^{-1}$
IIIc	50	20.8	−7.3
IIIb	50	20.3	−8.2
IIIa	45	19.6	−9.2
IIId	40	18.7	−9.2
IIIe	20	17.6	−7.0
IIIf	5	17.7	−0.8
Vc	45	25.4	11.6
Vb	30	25.0	12.2
Va	30	23.3[d]	7.7
Vd	20	22.2	7.2

[a] Mid-point of the temperature range of the data. [b] Calculated from the slope (method of least squares) of a log k *vs.* $1/T$ plot and the equation $\Delta H^{\ddagger} = E_a - RT$. [c] Calculated from the intercept (method of least squares) of a log k *vs.* $1/T$ plot. [d] lit.[8] reports E_a = 23.9 kcal., which is equivalent to $\Delta H^{\ddagger}$ = 23.3 kcal.

Rate constants at 30° (some extrapolated from data at other temperatures) for the *p*-substituents methoxyl, methyl, hydrogen and chlorine in each series were fitted to the Hammett equation[10] by the method of least squares, using the σ-values tabulated by Jaffé.[10b] Table IV records the results of these calculations. Reaction constants for the entire series of bromides IIIa to IIIf are also tabulated. It is evident that the calculations employ-

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method. The reasons for the discrepancies are not entirely clear, but chances of loss of product should be greater in the chemical than in the spectrophotometric analyses.

(9) J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955), discusses such relationships and quotes many examples.

(10) (a) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book, Co., Inc., New York, N. Y., 1940, Chap. VII; (b) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

TABLE IV

HAMMETT CORRELATION OF RATES OF ELIMINATION[a]

Cpd.	ρ	s^e	r^f	$-\log k_0{}^g$
IIIa-d	2.154 ± 0.242[d]	0.091	0.987	3.269
IIIa-f[b]	2.342 ± .115	.154	.996	3.270
IIIa-f[c]	3.505 ± .338	.308	.982	3.148
Va-d	2.639 ± .157	.059	.996	2.365

[a] Calculations by the least squares procedure as outlined in ref. 10b. [b] Using σ^*-values for *p*-nitro and *p*-acetyl. [c] Using ordinary σ-values for *p*-nitro and *p*-acetyl. All σ-values are from ref. 9b. [d] Standard deviation of ρ. [e] Standard deviation of experimental points from the least squares line. [f] Correlation coefficient. [g] Calculated value of the intercept.

ing σ^*-values[10b] (those derived from the reactions of phenols and anilines) give a far better fit with the *p*-acetyl and *p*-nitro groups. Figure 2 shows that the use of ordinary σ-values for these two substituents produces marked curvature.[11]

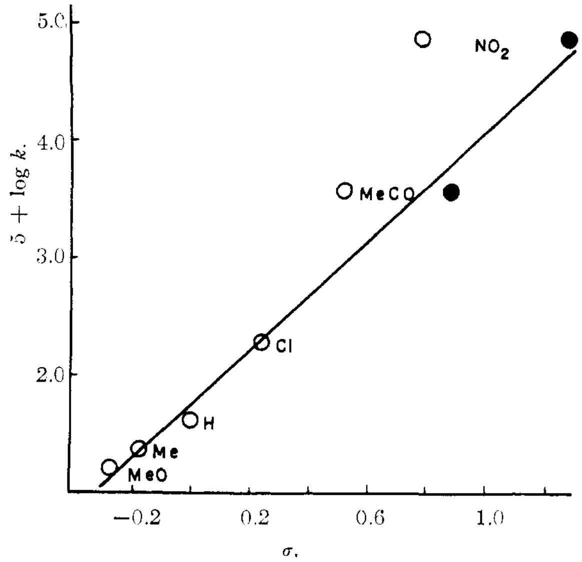
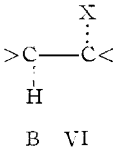


Fig. 2.—Hammett plot of rate constants for eliminations from *p*-substituted 2-phenylethyl bromides. The straight line is constructed from data given in line 2, Table IV. Open circles, ordinary σ-values; solid circles, σ^*-values.

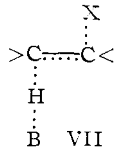
The results of the Hammett correlation clearly show that eliminations from the sulfonium salts are more sensitive to electronic effects than are eliminations from the bromides. The rather large positive values of ρ suggest that the carbon atom adjacent to the ring (the β-carbon) acquires considerable negative charge in the transition state[12] and that this increase in charge density is greater for the sulfonium salts than for the bromides. Further support for this view is found in the necessity of using σ^*-values for *p*-nitro and *p*-acetyl, since these are derived from cases where strong resonance interaction of a negative charge or an unshared pair with the substituent is possible.[13] Since the two systems under discussion have leaving groups of different charge types, the objection might be raised that this factor in itself influences the value of ρ. What ρ measures, however, is a *difference* in electron density at the β-carbon between the ground state and the transition state. The effect of charge type should therefore cancel, particularly in view of independent evidence[1] that the C–S bond is little disturbed on going to the transition state.

The nature of the transition state in E2 eliminations can be discussed best in terms of the structures VI–VIII.[5] In this representation VII is the



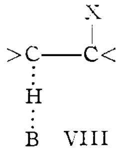
$$\begin{array}{ll} & X \\ & \vdots \\ >C—&C< \\ \vdots & \\ H & \\ & \\ B & \end{array}$$

VI



$$\begin{array}{ll} & X \\ & \vdots \\ >C\cdots&C< \\ \vdots & \\ H & \\ \vdots & \\ B & \end{array}$$

VII



$$\begin{array}{ll} & X \\ & | \\ >C—&C< \\ \vdots & \\ H & \\ \vdots & \\ B & \end{array}$$

VIII

conventional E2 transition state. Appropriate changes in reaction variables could, however, shift the mechanism either toward the E1 (VI) or the E1cb (VIII) end of the scale. The manner in which the solvent, the base and the nature of the group "X" affect the transition state already has been discussed by Cram.[5]

The larger ρ-value for the sulfonium salts than for the bromides is in harmony with the greater ease of heterolysis of a C–Br bond than a C–$\overset{+}{S}R_2$ bond.[14] The positive charge on sulfur would also increase the ease of heterolysis of the C–H bond *via* an electrostatic effect. Both of these factors would increase the contribution of VIII. Our evidence leads to the somewhat surprising conclusion that even with the bromides the transition state is closer to VIII than to VII. If simple alkyl halides are assumed to react *via* a transition state similar to VII, this means that a β-phenyl group shifts the mechanism toward the E1cb end of the scale. Comparison of our results with those of Cram[5] suggests that an α-phenyl group has the opposite effect.[15] It should be remembered, however, that the *p*-substituents themselves probably affect the nature of the transition state. The calculated ρ thus represents an average over the range of compounds studied and is not necessarily a good measure of electron distribution in the unsubstituted case. The systems studied by Weinstock, Pearson and Bordwell[3] probably react *via* a carbanion-like transition state because of the strongly electron-withdrawing β-sulfone grouping. The low preference for *trans* over *cis* elimination supports this view, since a transition state with a large contribution from VIII and only a small contribution from VII would not be very dependent on a *trans–anti* arrangement of the β-hydrogen and the leaving group. Another example of an electron-withdrawing group reducing the preference for *trans* elimination has been given by Cristol and Norris.[16]

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(11) The compound Ve was also examined kinetically at 0 and 10°. The extrapolated rate constant appeared to fit the σ^*-value better, but the measured constants were very imprecise due to the high speed of reaction. Discussion will therefore be reserved until contemplated studies in aqueous solution are completed.

(12) See C. G. Swain and W. P. Langsdorf, Jr., THIS JOURNAL, **73**, 2813 (1951), for an excellent discussion of the reasoning in this interpretation of reaction constants.

(13) The σ^*-values also apply to activated nucleophilic aromatic substitution. Here, too, ability to delocalize a negative charge should be important. See J. F. Bunnett, F. Draper, Jr., P. R. Ryason, P. Noble, Jr., R. G. Tonkyn and R. E. Zahler, *ibid.*, **75**, 642 (1953).

(14) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 339.

(15) Reference 1, footnote 17.

(16) S. J. Cristol and W. P. Norris, THIS JOURNAL, **76**, 3005 (1954).

There are only a few examples in the literature of other applications of the Hammett equation to elimination reactions.[17] Eliminations from IX and X have been studied with sodium hydroxide in

Ar_2CHCCl_3 IX $\qquad$ $Ar_2CHCHCl_2$ X

92.6% ethanol.[18] Recalculation of these data at our temperature (30°) and using only our substituents (*p*-methoxyl, *p*-methyl, hydrogen and *p*-chloro) gives ρ = 2.43 for IX and 2.26 for X. These ρ-values are larger than for the phenylethyl bromides. The result is not unexpected, since both the additional β-aryl group and the substitution of chlorine for bromine as the leaving group should increase the carbanion character of the transition state. Comparison of our results with the data of Simonetta and Favini[19] on the 2-arylethyl chlorides is more difficult because they used different temperatures (60 and 70°), different substituents (*p*-methoxyl, *m*-methoxyl and hydrogen) and a much more aqueous solvent (2:1 ethanol–water). Since variations in the kind and number of substituents alone may change ρ considerably (*cf.* Table IV), conclusions would be unwise.

Finally, the present results provide additional support for the Hughes–Ingold explanations of the empirical rules of orientation in elimination reactions. In their interpretation the Hofmann rule is a consequence of electrostatic influences on the acidity of the β-hydrogen,[20] while the Saytzeff rule is a consequence of hyperconjugative stabilization of the partial double bond in the transition state.[21] An increased contribution to the transition state from VIII would result in an increased sensitivity to electrostatic effects. Since there should be a concomitant decrease in the contribution of VII, a decreased sensitivity to hyperconjugative effects is also expected. Our evidence shows that sulfonium salts, which follow the Hofmann rule, are more sensitive to electrostatic effects than bromides, which follow the Saytzeff rule.

No mention of steric effects has been made in this discussion, because our results provide neither positive nor negative information on their possible importance. Undoubtedly there are many situations where such effects are important. It should be noted, however, that Brown's[6] arguments are based on VII as a model for the transition state and may therefore require some modification.

Experimental[22]

Preparation of 2-Arylethanols.—The appropriate arylmagnesium bromide was treated with ethylene oxide according to the general procedure of Houston and Agett,[23] using a 10% molar excess of ethylene oxide. Compounds prepared by this procedure are listed below.

2-(*p*-Tolyl)-ethanol: 65% yield, b.p. 110–111° (10 mm.), $n^{24}\mathrm{D}$ 1.5279 (lit.[24] b.p. 105° (4 mm.), $n^{21}\mathrm{D}$ 1.5275).

2-(*p*-Anisyl)-ethanol: 76% yield, b.p. 142–145° (15 mm.), $n^{25}\mathrm{D}$ 1.5397 (lit.[25] b.p. 148° (19 mm.)).

2-(*p*-Chlorophenyl)ethanol: 50% yield, b.p. 77–78° (0.5 mm.), $n^{25}\mathrm{D}$ 1.5482 (lit.[26] b.p. 110° (0.5 mm.)).

Preparation of 2-Arylethyl Bromides.—The arylethanol was treated with phosphorus tribromide, using a procedure similar to that of Rupe.[27] The bromides obtained by this and other procedures are as follows.

2-(*p*-Tolyl)-ethyl bromide: 81% yield, b.p. 43.5° (0.3 mm.), $n^{22}\mathrm{D}$ 1.5490 (lit.[28] b.p. 103.5–105° (11 mm.)).

2-(*p*-Anisyl)-ethyl bromide: 50% yield, b.p. 63° (0.15 mm.), $n^{21}\mathrm{D}$ 1.5595 (lit.[29] b.p. 147–149° (22 mm.)).

2-(*p*-Chlorophenyl)-ethyl bromide: 61% yield, b.p. 86.5° (1.6 mm.), $n^{25}\mathrm{D}$ 1.5697.

Anal. Calcd. for C_8H_8BrCl: C, 43.76; H, 3.67. Found: C, 43.82; H, 3.75.

2-Phenylethyl bromide was redistilled commercial material of b.p. 66° (2 mm.), $n^{26}\mathrm{D}$ 1.5542 (lit.[30] $n^{24}\mathrm{D}$ 1.5549).

2-(*p*-Acetylphenyl)-ethyl bromide was obtained by the acetylation of 2-phenylethyl bromide with acetyl chloride in the presence of aluminum chloride.[8] The product, obtained in 71% yield, had b.p. 111–112° (0.3 mm.), $n^{24}\mathrm{D}$ 1.5722 (lit.[7] b.p. 117–118° (0.1 mm.), $n^{25}\mathrm{D}$ 1.5724).

2-(*p*-Nitrophenyl)-ethyl Bromide.—The nitration of 2-phenylethyl bromide with nitric acid in acetic anhydride[7] gave 33% of a product of m.p. 69–69.5° (lit.[7] 69–70°).

Preparation of Methyl 2-Arylethyl Sulfides.—The 2-arylethyl bromides were converted to methyl 2-arylethyl sulfides by treatment with a solution of methyl mercaptan in ethanolic sodium hydroxide according to a procedure given by Fehnel and Carmack[31] for ethyl 2-phenylethyl sulfide. The sulfides prepared are described below.

Methyl 2-phenylethyl sulfide: 95% yield, b.p. 70–71° (11 mm.), $n^{24.5}\mathrm{D}$ 1.5494 (lit.[32] b.p. 111° (12 mm.)).

Methyl 2-(*p*-tolyl)-ethyl sulfide: 93% yield, b.p. 49–50° (0.3 mm.), $n^{21}\mathrm{D}$ 1.5450. *Anal.* Calcd. for $C_{10}H_{14}S$: C, 72.23; H, 8.49. Found: C, 72.24; H, 8.54.

Methyl 2-(*p*-anisyl)-ethyl sulfide: 83% yield, b.p. 102–103° (2 mm.), $n^{25}\mathrm{D}$ 1.5522. *Anal.* Calcd. for $C_{10}H_{14}OS$: C, 65.89; H, 7.74. Found: C, 65.70; H, 7.84.

Methyl 2-(*p*-chlorophenyl)-ethyl sulfide: 87% yield, b.p. 83–85° (0.6 mm.), $n^{25}\mathrm{D}$ 1.5630. *Anal.* Calcd. for $C_9H_{11}SCl$: C, 57.90; H, 5.97. Found: C, 57.82; H, 6.12.

Methyl 2-(*p*-Acetylphenyl)-ethyl Sulfide.—Methyl 2-phenylethyl sulfide was acetylated by the procedure of Foreman and McElvain,[7] using 2 moles of aluminum chloride per mole of sulfide. The product (88% yield) had b.p. 131–132° (1.0 mm.), $n^{24}\mathrm{D}$ 1.5670.

Anal. Calcd. for $C_{11}H_{14}OS$: C, 67.99; H, 7.26. Found: C, 67.69; H, 7.23.

Preparation of 2-Arylethyldimethylsulfonium Bromides.—The sulfide was treated with methyl bromide in nitromethane solution[8b] and the product recrystallized from ethanol–ether.

2-Phenylethyldimethylsulfonium bromide: 70% yield, m.p. 135–135.5° dec. (cor.) (lit.[1] m.p. 135.5°).

2-(*p*-Tolyl)-ethyldimethylsulfonium bromide: 65% yield, m.p. 106.5–107° dec. (cor.). *Anal.* Calcd. for $C_{11}H_{17}SBr$: C, 50.57; H, 6.56. Found: C, 50.80; H, 6.66.

2-(*p*-Anisyl)-ethyldimethylsulfonium bromide: 50% yield, m.p. 133–133.5° dec. (cor.). *Anal.* Calcd. for $C_{11}H_{17}OSBr$: C, 47.65; H, 6.18. Found: C, 47.81; H, 6.34.

2-(*p*-Chlorophenyl)-ethyldimethylsulfonium bromide: 63% yield, m.p. 126–126.5° dec. (cor.). *Anal.* Calcd.

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(17) We learned recently that Dr. C. H. DePuy is engaged in studies similar to ours. We thank Dr. DePuy for information in advance of publication and for several helpful discussions. See C. H. DePuy and D. H. Froemsdorf, Abstracts of Papers, 130th Meeting of American Chemical Society, Atlantic City, N. J., September 16–21, 1956; C. H. DePuy and D. H. Froemsdorf, THIS JOURNAL, **79**, 3705 (1957).

(18) S. J. Cristol, N. L. Hause, A. J. Quant, H. W. Miller, K. R. Eilar and J. S. Meek, THIS JOURNAL, **72**, 3333 (1952); S. J. Cristol, *ibid.*, **67**, 1494 (1945).

(19) M. Simonetta and G. Favini, *J. Chem. Soc.*, 1840 (1954).

(20) W. Hanhart and C. K. Ingold, *ibid.*, 997 (1927).

(21) E. D. Hughes and C. K. Ingold, *Trans. Faraday Soc.*, **37**, 657 (1941).

(22) Melting points and boiling points are uncorrected unless otherwise noted. Analyses by Miss A. Smith.

(23) R. C. Houston and A. H. Agett, *J. Org. Chem.*, **6**, 123 (1941).

(24) N. V. Shorygina, *Zhur. Obshchei Khim.*, **21**, 1273 (1951).

(25) G. M. Bennett and M. Hafaz, *J. Chem. Soc.*, 652 (1941).

(26) G. Baddeley and G. M. Bennett, *ibid.*, 1819 (1935).

(27) H. von Rupe, *Ann.*, **395**, 114 (1913).

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for $C_{10}H_{14}SClBr$: C, 42.64; H, 5.01. Found: C, 42.74; H, 5.27.

2-(*p*-Acetylphenyl)-ethyldimethylsulfonium bromide: 74% yield, m.p. 121–121.5 dec. (cor.). *Anal.* Calcd. for $C_{12}H_{17}OSBr$: C, 49.82; H, 5.92. Found: C, 49.53; H, 5.82.

Preparation of Styrenes.—The sulfonium bromide was dissolved in water, treated with 10% sodium hydroxide solution and the mixture warmed gently on the steam-bath. The cessation of methyl sulfide evolution indicated completion of the reaction. The styrene was decanted, dried over Drierite and fractionated in the presence of a small amount of *p*-*t*-butylpyrocatechol.

Styrene: 87% yield, b.p. 38° (15 mm.), $n^{25}D$ 1.5433 (lit.[33] $n^{25}D$ 1.5433).

***p*-Methylstyrene:** 87% yield, b.p. 50° (13 mm.), $n^{25}D$ 1.5395 (lit.[34] $n^{25}D$ 1.5402).

***p*-Methoxystyrene:** 92% yield, b.p. 85° (14 mm.), $n^{23}D$ 1.5595 (lit.[35] $n^{20}D$ 1.5608).

***p*-Chlorostyrene:** 93% yield, b.p. 38° (2.2 mm.), $n^{20}D$ 1.5650 (lit.[36] $n^{20}D$ 1.5648).

***p*-Acetylstyrene:** 88% yield, m.p. 33–33.5° (lit.[37] m.p. 33°).

***p*-Nitrostyrene** was obtained by treating 2-(*p*-nitrophenyl)-ethyl bromide with warm alcoholic sodium hydroxide for 15 min. The mixture was poured into a saturated salt solution and the organic layer taken up in ether and dried. Removal of the ether left a solid which was recrystallized from petroleum ether. There was obtained 70% of *p*-nitrostyrene, m.p. 29° (lit.[38] m.p. 28°).

Styrene Analysis.—Ultraviolet absorption spectra of the freshly distilled styrenes in 95% ethanol solution were determined on a Cary recording spectrophotometer. The optical densities at the maxima used for analysis (around 250 mμ) were then carefully determined on a Beckman DU spectrophotometer. Molar extinction coefficients at these maxima are listed in Table I. Beer's law was obeyed over the concentration ranges used, and the solutions underwent no changes in concentration over a period of at least 48 hr.

Samples of the reaction mixtures at "time infinity" were appropriately diluted and optical densities determined, from which the olefin concentrations were calculated. In some of the slower reactions there appeared to be a slow depletion of the styrene, so the determinations were made on aliquots taken after one or two half-lives. Under the conditions of the measurements the styrene precursors (bromides or sulfonium bromides), sodium ethoxide, sodium bromide and methyl sulfide did not contribute appreciably to the observed ultraviolet absorption. Olefin yields in Table II are averages of two or three analyses with indicated average deviations.

Kinetic Measurements.—Reactions were carried out in a 100-ml. volumetric flask to which was attached, above the calibration mark, a side-arm bearing a 10-ml. bulb sealed with a rubber ampoule-stopper. This could be covered with a ground-glass cap so that the entire vessel could be immersed in the constant-temperature bath. Runs were carried out in a thermostat with temperature control to ±0.05°. Runs at 0° were performed in a well-stirred ice-water slurry.

For the bromides (mostly liquids), 50.0 ml. of *ca.* 0.2 *M* sodium ethoxide in absolute ethanol (at bath temperature) was diluted to 99.0 ml. with thermally equilibrated absolute ethanol. To this was added a weighed portion of the bromide (0.005 mole, *ca.* 1 ml.). The reactor was agitated in the bath for two minutes following the addition. Aliquots were withdrawn periodically with a calibrated 5-ml. hypodermic syringe and delivered into excess aqueous hydrochloric acid. The quenched sample was diluted fivefold with water and titrated to the phenolphthalein end-point with standard sodium hydroxide. The sodium ethoxide solution was sampled at bath temperature and standardized before each run.

A weighed quantity of a sulfonium salt (*ca.* 0.005 mole) was dissolved in slightly less than 50 ml. of absolute ethanol and the solution allowed to equilibrate thermally. To this solution was added by pipet 50.0 ml. of thermally equilibrated ethoxide solution, the volume adjusted to 100 ml. and the vessel agitated for 1 minute. Sampling and analysis were carried out as with the bromides.

Compounds used had the physical constants indicated under their preparation. Absolute ethanol was obtained by the procedure of Smith as modified by Manske.[39] All solutions were frequently restandardized to ensure that rate constants would be comparable. Each run consisted of at least 10 points and the rate constants from the integrated second-order equation were arithmetically averaged. Values recorded in Table II are the averages of two or more runs with average deviations. Whenever there was a departure from the usual concentrations, ionic strength was maintained with added sodium bromide. Most runs covered two or three half-lives and no serious drifts were noted.

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ROCHESTER 20, N. Y.