(0.154 mole) of biphenyl were dissolved in 250 ml. of carbon disulfide, cooled and treated with 21.4 g. (0.160 mole) of anhyd. aluminum chloride over a 30-minute period employing efficient stirring. Working up the reaction mixture produced 34.9 g. (91% yield) of the ketone I, m.p. 85–86°, recrystallized from ethanol; $\lambda_{\max}$ 283 mμ (ϵ 24,200), γC=O 1680 cm.$^{-1}$.

Anal. Calcd. for $C_{19}H_{20}O$: C, 86.32; H, 7.63. Found: C, 86.03; H, 7.61.

This ketone I gave a 2,4-dinitrophenylhydrazone, m.p. 176–177°.

4-Biphenylyl 1-Bromocylohexyl Ketone (II).—A 45.9-g. (0.174 mole) sample of ketone I was heated between 80 and 85° with 28.0 g. (0.175 mole) of bromine in 350 ml. of gl. acetic acid for 30 minutes. The reaction mixture was cooled and poured over ice to precipitate the bromoketone II, 51.6 g. (86.5% yield), m.p. 109–110°, recrystallized from ethanol–benzene solution; $\lambda_{\max}$ 287 mμ (ϵ 19,400), γ C=O 1674 cm.$^{-1}$.

Anal. Calcd. for $C_{19}H_{19}BrO$: C, 66.48; H, 5.58; Br, 23.28. Found: C, 66.33; H, 5.66; Br, 23.42.

4-Biphenylyl 1-Cycohexenyl Ketone (III).—A 20.0-g. (0.0582 mole) sample of the bromoketone II was heated on the steam-bath for two hours with 50 ml. of 4-picoline. The reaction mixture was cooled and 50 ml. of dry ether added to precipitate 9.88 g. (97.8 % yield) of 4-picoline hydrobromide. The excess 4-picoline was removed from the filtrate by water and dil. hydrochloric acid washing. Evaporation of the ether gave the unsaturated ketone III, 14.74 g. (96.5% yield), m.p. 70–71°, recrystallized from ethanol; $\lambda_{\max}$ 281 mμ (ϵ 20,800), γ C=O 1647 cm.$^{-1}$.

Anal. Calcd. for $C_{19}H_{18}O$:C, 86.98; H, 6.91. Found: C, 86.76; H, 6.88.

Comparative Rates of Reaction of Bromoketone II with Pyridine Derivatives.—One-gram samples of II were dissolved in 10-ml. amounts of the amines (4-picoline, 3-picoline, γ-collidine) and heated in closed flasks at steam-bath temperature for 1.75 hours. The excess amine was then removed by vacuum distillation at steam-bath temperature over a period of 30 minutes. A 20-ml. portion of dry ether was added to each flask, the precipitated amine hydrobromide collected and weighed; 3-picoline hydrobromide, 0.48 g. (93.0% reaction); 4-picoline hydrobromide, 0.47 g. (93.0% reaction); γ-collidine hydrobromide 0.05 g. (8.51% reaction).

Reaction of Bromoketone II with Piperidine and Morpholine.—A 5.0-g. (0.0147 mole) sample of II was allowed to stand at room temperature for 72 hours with 2.75 g. (0.0323 mole) of piperidine in 20 ml. of benzene. From this reaction mixture was isolated 1.38 g. (56.6% yield) of piperidine hydrobromide and 2.18 g. (50.3% yield) of the unsaturated ketone III, m.p. 69–71°. No amino derivatives or acidic products were formed in isolable quantities in this reaction.

When 8.5 g. (0.0248 mole) of II was heated for two hours on the steam-bath with 5.9 g. (0.0693 mole) of piperidine in 20 ml. of benzene, a 97.3% yield of piperidine hydrobromide and a 71% yield of the unsaturated ketone III were isolated. After standing in 40 ml. of morpholine at room temperature for 22 hours, 5.0 g. (0.0147 mole) of II produced a 99% yield of morpholine hydrobromide and a 61% yield of the unsaturated ketone III. No hydrochloric acid or sodium hydroxide soluble materials were formed in this reaction.

Reaction of II with Silver Nitrate in Ethanol.—A 5.0-g. (0.0147 mole) sample of II was refluxed with 2.5 g. (0.0147 mole) of silver nitrate in 160 ml. of ethanol and 40 ml. of water for four hours in the absence of light. To the cooled reaction mixture was added 5 ml. of 6 *N* nitric acid and the silver bromide removed by filtration; 2.6 g. (95.7% yield). Dilution of the filtrate with water precipitated a product which was separated into a neutral and an acidic fraction by extraction with sodium hydroxide solution. The neutral fraction gave 2.61 g. (68.4% yield) of the unsaturated ketone III, m.p. 69–71°, while the acid fraction produced 1-(4-biphenylyl)-cyclohexane carboxylic acid (IV), 0.76 g. (18.7% yield), m.p. 177–178°, recrystallized from benzene.

Anal. Calcd. for $C_{19}H_{20}O_2$: mol. wt., 280.35; C, 81.39; H, 7.19. Found for IV: neut. equiv., 283; C, 81.05; H, 7.17.

4-Biphenylyl 1,2-Dibromocyclohexyl Ketone (V).—From 3.0-g. (0.0114 mole) of II and 1.83 g. (0.0114 mole) of bromine in 30 ml. of carbon tetrachloride was obtained 4.38 g. (91% yield) of the dibromoketone V, m.p. 137–138°, recrystallized from 60–70° b.p. petroleum ether; $\lambda_{\max}$ 289 mμ (ϵ 19,600), γ C=O 1680 cm.$^{-1}$.

Anal. Calcd. for $C_{19}H_{18}Br_2O$: C, 54.05; H, 4.30; Br, 37.86. Found: C, 54.02; H, 4.33; Br, 37.60.

Relative Rates of Reaction of Alicyclic α-Bromoketones with Alcoholic Silver Nitrate at 30°.—Solutions were prepared by dissolving 0.00200 molar amounts of the α-bromoketones in 95% ethanol in 100-ml. volumetric flasks. A 25-ml. aliquot sample of the ethanol solution of the α-bromoketone was mixed with 25 ml. of ethanol and 10 ml. of the alcoholic silver nitrate, which contained 0.00600 mole of $AgNO_3$, in glass stoppered flasks. The solutions were shaken at a constant temperature of 29.7° in the absence of light for four hours. To the reaction mixtures were added 3 ml. of 6 *N* nitric acid and the solutions filtered through weighed Gooch crucibles. The precipitates were washed with benzene and then very dil. nitric acid, dried at 80° for two hours and the crucibles weighed. Duplicate runs were made in each case. Under these conditions the amounts of silver bromide formed indicated a 6.32 ± 0.01% reaction for the bromoketone II, a 1.37 ± 0.07% reaction for 2-bromo-2-benzylindonone-1,[1] a 45.33 ± 0.68% reaction for 2-bromo-2-benzyl-4,4-dimethyl-1-tetralone[8] and no measurable reaction for 2-bromo-4,4-dimethyl-1-tetralone.[9]

LINCOLN, NEBR.

(b) H. E. Baumgarten, F. A. Bower and T. T. Okamoto, THIS JOURNAL, **79**, 3148 (1957).

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

Mechanisms of Elimination Reactions. IV. Deuterium Isotope Effects in E2 Reactions of Some 2-Phenylethyl Derivatives[1]

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Kinetic deuterium isotope effects have been determined for E2 reactions of the compounds $C_6H_5CD_2CH_2X$. The values of k_H/k_D with sodium ethoxide in ethanol are in the order Br > OTs > SMe_2 > NMe_3. A change of base and medium to potassium *t*-butoxide in *t*-butyl alcohol increases the isotope effect with the bromide and the tosylate. Experiments with sodium hydroxide in water on the onium salts show no clear pattern. The relation of the present work to other recent studies on the nature of the transition state in E2 reactions is discussed. Some rate constants given earlier[1] for 2-(*p*-acetylphenyl)-ethyldimethylsulfonium bromide are shown to be in error. An interesting case of anomalous orientation in a Friedel–Crafts acylation is reported.

The E2 reaction usually has been considered a completely synchronous process. Although this appears true in the sense that no intermediates can be detected, evidence has accumulated that the ratio of the extent of C–H and C–X bond stretch-

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[1] Paper III in this series: W. H. Saunders, Jr., C. B. Gibbons and R. A. Williams, THIS JOURNAL, **80**, 4099 (1958).

[2] Du Pont Fellow 1957–1958.

ing in the transition state may vary with changes in the leaving group, the solvent and the base. This evidence includes eclipsing effects,[3] substituent effects[1,4,5] and sulfur isotope effects.[6]

None of these approaches except the isotope effect gives a direct measure of the extent to which either bond is broken. Consequently a study of deuterium isotope effects in E2 reactions of β-deuterated 2-phenylethyl derivatives were undertaken. Knowledge of the strength of the C–H bond in the transition state, we hoped, would aid interpretation of the earlier results.

A method for preparing 2-phenylethanol-2,2-d_2 (I) in quantity has been previously reported.[7] This procedure involves the hydrolysis and subsequent decarboxylation of the sodium salt of phenylmalonic ester in deuterium oxide. The resulting deuterated phenylacetic ester is then reduced to I with lithium aluminum hydride.

TABLE I

RATE CONSTANTS AND OLEFIN YIELDS FOR ELIMINATIONS FROM 2-PHENYLETHYL DERIVATIVES

Y	Solvent[a]	T, °C.	Olefin yield, %[b]	$k_E \times 10^5$, l./mole-sec.[c]
		$C_6H_5CY_2CH_2Br$		
H	EtOH	30.00	100	41.3 ± 0.57
D	EtOH	30.00	84.6	5.81 ± 0.11
H	EtOH	40.00	100	129 ± 2.9
D	EtOH	40.00	86.0	19.0 ± 0.31
H	EtOH	50.00	100	358 ± 4.7
D	EtOH	50.00	86.0	59.4 ± 0.70
H	*t*-BuOH	30.00	100	776 ± 15.9
D	*t*-BuOH	30.00	100	98.5 ± 5.5
		$C_6H_5CY_2CH_2OTs$		
H	EtOH	30.00	38.6	4.26 ± 0.039
D	EtOH	30.00	9.8	0.754 ± 0.011
H	*t*-BuOH	30.00	100	181 ± 4.8
D	*t*-BuOH	30.00	86.0	22.6 ± 0.69
		$C_6H_5CY_2CH_2S(CH_3)_2Br$		
H	EtOH	30.00	100	527 ± 4.8
D	EtOH	30.00	100	104 ± 4.3
H	H_2O	60.00	100	13.7 ± 0.15
D	H_2O	60.00	100	2.91 ± .08
H	H_2O	70.00	100	42.3 ± .72
D	H_2O	70.00	100	9.8 ± .26
H	H_2O	80.00	100	122 ± 2.0
D	H_2O	80.00	100	29.5 ± 0.72
		$C_6H_5CY_2CH_2N(CH_3)_3Br$		
H	EtOH	50.00	[d]	179 ± 4.7
D	EtOH	50.00	[d]	60.1 ± 0.70
H	[e]	50.00	[d]	1.63 ± .037
D	[e]	50.00	[d]	0.572 ± .012

[a] In ethanol the base was sodium ethoxide, in water sodium hydroxide and in *t*-butyl alcohol potassium *t*-butoxide. Initial concentrations were *ca.* 0.1 *M* in base and 0.05 *M* in substrate. [b] Each figure is the average of two or more runs. Olefin yields within experimental error (1–2%) of 100% are listed as 100%. [c] Each figure is the average of two or more runs with average deviations, $k_E = k_2 \times$ (olefin yield)/100, where k_2 is the titrimetric second-order rate constant. [d] Rate constant determined by direct spectrophotometric analysis for styrene. [e] Solvent in these runs was 50% (by volume) ethanol–water.

Conversion of I to the desired 2-phenylethyl derivatives was accomplished *via* reactions selected so as to minimize the possibility of isotope exchange or isotope-position rearrangement. Compound I was first converted to the *p*-toluenesulfonate II from which the remaining derivatives were prepared. The synthetic scheme is given in Fig. 1.

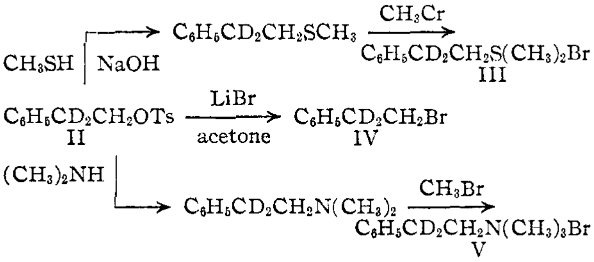

Fig. 1.—Synthesis of deuterated 2-phenylethyl derivatives.

The rate of E2 reactions of II-V and their undeuterated analogs are recorded in Table I. In most cases the rate was determined acidimetrically and the olefin yield spectrophotometrically as before.[4] The elimination reaction of the ammonium salt was followed directly by spectrophotometric analysis for styrene.

The change in rate with leaving group goes in the order Br > OTs and $\overset{\oplus}{S}Me_2 > \overset{\oplus}{N}Me_3$. Comparison of the charged and uncharged leaving groups is rendered uncertain by differing solvent effects. The sulfonium salt, for example, reacts faster than the bromide in ethanol, but this arises from a favorable entropy of activation which more than compensates for a higher energy of activation.[4] In a more polar solvent the bromide undoubtedly would react faster than the sulfonium salt. The order Br > OTs is in agreement with the recent observations of Bishop and DePuy[8] on the reactivity of tosylates in displacements and eliminations.

With the tosylates and bromides, some substitution accompanies the elimination. The bromides are more reactive than the tosylates in elimination, but less reactive in substitution. For the tosylate an isotope effect on substitution, k_H/k_D, of 0.98 can be calculated. This is obviously within experimental error of unity, in agreement with Shiner's observations on isopropyl-d_6 bromide.[9]

Values of the kinetic isotope effect on elimination are given in Table II. The effects are of the magnitude expected for rate-determining proton abstractions. The largest effect observed, 8.0 at 30°, is appreciably greater than that calculated (*ca.* 6.8) for complete loss of the C–H stretching vibration in the transition state.[10] Probably C–H bending vibrations are affected as well, but other explanations must be considered. A secondary isotope effect arising from the other β-deuterium

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

[4] W. H. Saunders, Jr., and R. A. Williams, *ibid.*, **79**, 3712 (1957).

[5] C. H. DePuy and D. H. Froemsdorf, *ibid.*, **79**, 3710 (1957).

[6] W. H. Saunders, Jr., and S. Ašperger, *ibid.*, **79**, 1612 (1957).

[7] W. H. Saunders, Jr., S. Ašperger and D. H. Edison, *ibid.*, **80**, 2421 (1958).

[8] C. A. Bishop and C. H. DePuy, *Chemistry & Industry*, 297 (1959).

[9] V. J. Shiner, Jr., THIS JOURNAL, **74**, 5285 (1952).

[10] K. B. Wiberg, *Chem. Revs.*, **55**, 713 (1955).

atom could be involved, although our k_H/k_D for 2-phenylethyl-2,2-d_2 bromide at 25° is the same as that found by Shiner and Smith[11] for 2-phenylpropyl-2-*d* bromide (7.5). Another possibility would be a quantum-mechanical tunnelling effect, which is more probable for hydrogen than for deuterium.[12] The temperature dependence of the isotope effect (Table III) is the product of a too-large energy of activation and a partially compensating entropy of activation as predicted by Bell for the tunnel effect.[12,13]

TABLE II

ISOTOPE EFFECTS IN THE ELIMINATION REACTIONS OF 2-PHENYLETHYL DERIVATIVES

Leaving group, X	Solvent[a]	T, °C.	k_H/k_D[b]
Br	EtOH	30.00	7.11 ± 0.17
Br	EtOH	40.00	6.79 ± .19
Br	EtOH	50.00	6.03 ± .11
Br	*t*-BuOH	30.00	7.89 ± .46
OTs	EtOH	30.00	5.66 ± .52
OTs	*t*-BuOH	30.00	8.01 ± .32
SMe_2Br	EtOH	30.00	5.07 ± .22
SMe_2Br	H_2O	60.00	4.71 ± .09
SMe_2Br	H_2O	70.00	4.32 ± .14
SMe_2Br	H_2O	80.00	4.14 ± .12
SMe_2Br	H_2O	30.00	5.93[c]
SMe_2Br	H_2O	50.00	5.05[c]
NMe_3Br	EtOH	50.00	2.98 ± .08
NMe_3Br	[d]	50.00	3.02 ± .09

[a] See footnote *a*, Table I. [b] Ratios of rates of elimination; deviation = $(k_H/k_D)\,[(r_H/k_H)^2 + (r_D/k_D)^2]^{1/2}$, where r is the deviation in k. [c] Extrapolated from data at higher temperatures. [d] See footnote *e*, Table I.

TABLE III

ENTHALPIES AND ENTROPIES OF ACTIVATION FOR ELIMINATIONS FROM 2-PHENYLETHYL DERIVATIVES, $C_6H_5CY_2CH_2X$

Y	X	Solvent	$\Delta H^{\ddagger}$, kcal./mole[a]	$\Delta S^{\ddagger}$, cal./mole-°C.[b]
H	Br	EtOH	20.4[c]	−6.8[c]
D	Br	EtOH	22.0	−5.4
H	SMe_2Br	H_2O	24.9[d]	−1.7[d]
D	SMe_2Br	H_2O	26.4	−0.1

[a] Calculated from the slope (method of least squares) of a log k *vs.* $1/T$ plot and the equation $\Delta H^{\ddagger} = E_a - RT$. [b] Calculated from the intercept (method of least squares) of a log k *vs.* $1/T$ plot. [c] Lit.[4] reports $\Delta H^{\ddagger} = 19.6$, $\Delta S^{\ddagger} = -9.2$. [d] Lit.[1,6] reports $\Delta H^{\ddagger} = 24.0$, 24.8 and $\Delta S^{\ddagger} = -4.2$, -1.9, respectively.

Variation of k_H/k_D with the leaving group is in the order Br > OTs > SMe_2 > NMe_3. This is probably the order of increasing difficulty of heterolytic cleavage of the C–X bond (see above). The most reasonable interpretation is that cleavage of the C–X bond provides some driving force for cleavage of the C–H bond. The larger isotope effects with the better leaving groups recall the observation that the tritium isotope effect in enolization is greater for a protonated than an unprotonated ketone.[14] Our results also provide added evidence that the suggested parallelism of activation energy and isotope effect[10] may break down when bonds other than the C–H bond are altered in the rate-determining step.

Earlier evidence[1,4-6] had emphasized the carbanion character of the transition states for eliminations from 2-phenylethyl derivatives, but the effect of the leaving group on k_H/k_D makes it apparent that some double-bond character is retained. The Hammett ρ for sulfonium salts is substantially greater than for bromides, suggesting that the β-carbon has more carbanion character in the transition state for the sulfonium salt.[4] Other factors being equal, more carbanion character requires more C–H bond stretching and hence a larger isotope effect, contrary to fact. Again, therefore, we have evidence that the C–X bond is to some degree weakened in the transition state. The low sulfur isotope effect found in the E2 reaction of 2-phenylethyldimethylsulfonium bromide suggests that C–X bond weakening is still small compared to C–H bond weakening for this compound and probably for the other 2-phenylethyl derivatives as well.[6] The sulfonium salt does not exchange deuterium with the solvent during the reaction in harmony with our conclusion that there is not a discrete carbanion intermediate.

The influence of the solvent is a composite of two factors: solvation effects and the strength of the conjugate base of the solvent. The larger isotope effect observed in *t*-butyl alcohol most probably results mainly from the greater base strength of *t*-butoxide ion compared to ethoxide ion. In water *vs.* ethanol the situation is more complex. The sulfonium salt appears to give a smaller isotope effect in ethanol than in water and the ammonium salt shows no significant change in isotope effect from ethanol to 50% water–ethanol. Since the water–ethanol comparisons are made with charged substrates and the ethanol–*t*-butyl alcohol comparisons with uncharged substrates, any conclusions are necessarily tentative. The reactions of the charged substrates should be much more sensitive to solvation effects, however, and it seems reasonable that such effects might overpower the base strength.[15]

In the course of this work some earlier kinetic studies[1] on 2-(*p*-acetylphenyl)-ethyldimethylsulfonium bromide were found to be in error. The corrected rate constants[16] are recorded in Table IV. The error with ethoxide ion in ethanol arose from a solvent-promoted elimination which occurred while the sulfonium salt was being brought into solution. In water this solvolytic reaction was negligible over the time in which the base-promoted reaction was followed. We have at present no satisfactory explanation of the error in water.

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(11) V. J. Shiner, Jr., and M. L. Smith, THIS JOURNAL, **80**, 4095 (1958).

(12) R. P. Bell, J. A. Fendley and J. R. Hulett, *Proc. Roy. Soc.* (*London*), **235**, 453 (1956).

(13) Actually our differences in energies and entropies of activation are barely beyond experimental error. The fact that they form a consistent pattern with earlier results, whatever the ultimate explanation, gives them added weight.

(14) C. G. Swain, E. C. Stivers, J. F. Reuwer, Jr., and L. J. Schaad, THIS JOURNAL, **80**, 5885 (1958).

(15) The solvation effect should be in the right direction. A more polar solvent stabilizes the ground state relative to the transition state for reactions between oppositely charged ions (C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 347, 457). *If* the parallelism between activation energy and isotope effect[10] holds under these circumstances, the larger isotope effect should be observed in the more polar solvent.

(16) We are indebted to Dr. Rudolf Glaser for providing an independent check of our values on some of these constants.

TABLE IV

RATE CONSTANTS FOR ELIMINATIONS FROM ACETYL-SUBSTITUTED 2-PHENYLETHYLDIMETHYLSULFONIUM BROMIDES

Isomer	Solvent	T, °C.	$k_E \times 10^5$, l./mole-sec.[a]
Para	EtOH	0.00	2855 ± 42[b]
Para	EtOH	10.35	7700[c]
Para	H_2O	30.00	135 ± 3.1
Para	H_2O	40.00	383 ± 5.8[d]
Para	H_2O	50.00	1035 ± 11[e]
Ortho	EtOH	0.00	24.4 ± 0.81[f]
Ortho	H_2O	50.00	30.9 ± 0.46[f]

[a] See footnotes *a–c*, Table I. [b] The data of ref. 1 give 2810 when recalculated allowing for solvolysis. [c] Not a new run—recalculated from data of ref. 1, allowing for solvolysis. [d] Ref. 1 gives 288 ± 4.9. [e] Ref. 1 gives 552 ± 9.4. [f] Olefin yields were not determined but assumed to be 100%.

In both solvents the new rate constants give more "normal" energies and entropies of activation. The new values are $\Delta H^{\ddagger} = 14.4$ kcal./mole and $\Delta S^{\ddagger} = -12.6$ cal./mole-°C. in ethanol and $\Delta H^{\ddagger} = 19.2$ kcal./mole and $\Delta S^{\ddagger} = -8.4$ cal./mole-°C. in water. The figures in ethanol are still somewhat out of line compared with those for other sulfonium salts,[4] but at least some of this discrepancy may arise from systematic errors in following the very fast reactions.

An observation which was interesting, although apparently unconnected with the error, was made about the same time. In an attempt to improve the yield in the acetylation, the ratio of aluminum chloride to methyl 2-phenylethyl sulfide was increased from 2:1 to 3:1. The product (67% yield) was converted to the sulfonium salt and the salt proved, on oxidation to the corresponding phthalic acid, to be entirely the *o*-isomer. Repetition of the earlier procedure (2:1 ratio) gave again the *p*-isomer in 28% yield (79% based on unrecovered starting material). Mixtures of the two sulfonium salts showed marked melting point depressions. No careful search for other isomers was made on the liquid acetylated sulfides, so we can only say that the isomer isolated in each case was the predominant product. The mixed melting points of the sulfonium salts make it unlikely that contamination with other isomers played a role in the erroneous kinetic results.

A search of the literature revealed no precedent for the orientation effect, although "anomalous" orientations in the form of unexpectedly large amounts of *m*-isomer have been found in some Friedel–Crafts acylations.[17] Possibly our reaction proceeds *via* a cyclic mechanism with simultaneous coördination of the aluminum halide to the acetyl chloride and the sulfide sulfur. One could then postulate that the uncoördinated sulfide is the major reactant in the normal reaction but that the coordinated sulfide takes over this role as the aluminum chloride concentration is increased.

Experimental[18]

Ethyl Phenylacetate-α,α-d_2.—Several modifications in the previously published procedure[7] gave improved isotopic purity. A solution of 100 g. of diethyl phenylmalonate in 500 ml. of AR petroleum ether (b.p. 30–60°) was filtered through a bed of adsorption alumina and then added over 6 hr. to a well-stirred mixture of 200 ml. of petroleum ether and 20 g. of a 50% dispersion of sodium hydride in mineral oil (Metal Hydrides, Inc.). The white, amorphous solid was collected by filtration after another hour of stirring and washed well with petroleum ether. The solid was then placed in a vacuum desiccator and residual solvent removed by continuous pumping for 6 hours.

One hundred grams of the dried sodium salt was added to 80 g. of deuterium oxide (99.5%) and the mixture refluxed for 8 hours under nitrogen. The organic layer was separated and the aqueous layer extracted twice with ether. The combined extracts and organic layer were dried over anhydrous magnesium sulfate. Removal of the ether and distillation of the residue through a short Vigreux column gave 32 g. (52%) of ethyl phenylacetate-α,α-d_2, b.p. 73–74° (0.5 mm.), 1.94 atoms D/molecule.

2-Phenylethanol-2,2-d_2 was prepared by reduction of ethyl phenylacetate-α,α-d_2 with lithium aluminum hydride. The reaction mixture was worked up by the procedure of Amundsen and Nelson[19] to yield 88% of 2-phenylethanol-2,2-d_2, b.p. 110° (20 mm.), 1.96 atoms D/molecule.

2-Phenylethyl-2,2-d_2 *p*-Toluenesulfonate.—Treatment of the alcohol with *p*-toluenesulfonyl chloride in pyridine[7,20] gave the *p*-toluenesulfonate in 85% yield, m.p. 37.4–38.0° (lit.[7] 37.5–38.2°), 1.95 atoms D/molecule.

2-Phenylethyl-2,2-d_2 Bromide.—A solution of 17 g. of 2-phenylethyl-2,2-d_2 *p*-toluenesulfonate and 10.5 g. of lithium bromide in 100 ml. of dry acetone was allowed to stand at room temperature for two days. The solution was concentrated to 25 ml. under reduced pressure, 75 ml. of water was added, and the resulting mixture was extracted three times with ether. The combined extracts were dried over anhydrous sodium sulfate. The ether was removed and the residue distilled to yield 8.0 g. (71%) of 2-phenylethyl-2,2-d_2 bromide, b.p. 94° (15 mm.), 1.92 atoms D/molecule.

Methyl 2-Phenylethyl-2,2-d_2 Sulfide.—To 0.2 mole of sodium methyl mercaptide in absolute ethanol (prepared by adding methyl mercaptan to sodium ethoxide in ethanol) was added 0.1 mole of 2-phenylethyl-2,2-d_2 *p*-toluenesulfonate and the mixture allowed to stand for 24 hours at room temperature. The precipitated sodium *p*-toluenesulfonate was removed by filtration and about 75% of the ethanol was removed under reduced pressure. The residue was diluted with five volumes of water and extracted five times with ether. The extracts were combined, dried, and the ether evaporated. Distillation gave a 75% yield of methyl 2-phenylethyl-2,2-d_2 sulfide, b.p. 121° (75 mm.), 1.94 atoms D/molecule.

2-Phenylethyldimethylsulfonium-2,2-d_2 bromide was prepared in 79% yield, m.p. 136.5–137° dec. (lit.[6] 135.5°), 1.94 atoms D/molecule, by reaction of methyl 2-phenylethyl-2,2-d_2 sulfide with methyl bromide in nitromethane.[21]

Dimethyl 2-Phenylethylamine-2,2-d_2.—A solution of 0.1 mole of 2-phenylethyl-2,2-d_2 *p*-toluenesulfonate and 0.2 mole of anhydrous dimethylamine in 200 ml. of anhydrous ether was allowed to stand at room temperature for two days. A little absolute ethanol was added occasionally to keep the mixture homogeneous. The reaction mixture was then concentrated to 50 ml. under reduced pressure and poured into 150 ml. of water. The solution was extracted with ether and the ether solution in turn extracted with 10% hydrochloric acid. The acid solution was made basic with sodium hydroxide and extracted with ether. The extract was dried over sodium sulfate, the ether removed, and the residue distilled. There resulted 78% of dimethyl 2-phenylethylamine-2,2-d_2, b.p. 111° (20 mm.), m.p. of picrate 136° (lit.[22] 135–136°), 1.96 atoms D/molecule.

2-Phenylethyltrimethylammonium-2,2-d_2 bromide was prepared by treating dimethyl 2-phenylethylamine-2,2-d_2 with methyl bromide in nitromethane. The product was obtained in 90% yield, m.p. 238–239°, 1.98 atoms D/mole-

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[17] See, for example, D. Papa, E. Schwenk and A. Klingsberg, THIS JOURNAL, **68**, 2133 (1946).

[18] Melting points and boiling points are uncorrected. Analyses by Miss A. Smith.

[19] L. H. Amundsen and L. S. Nelson, THIS JOURNAL, **73**, 242 (1951).

[20] R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

[21] E. D. Hughes, C. K. Ingold and G. A. Maw, *J. Chem. Soc.*, 2072 (1948).

[22] K. Kindler, *Ann.*, **431**, 219 (1923).

cule. The corresponding undeuterated substance (prepared in the same way) was a new compound.

Anal. Calcd. for $C_{11}H_{18}NBr$: C, 54.10; H, 7.43. Found: C, 54.21; H, 7.78.

Kinetic Measurements.—Anhydrous ethanol was prepared by the method of Smith as modified by Manske.[23] The *t*-butyl alcohol (Eastman Kodak Co. white label) was treated with potassium and distilled. Both alcohols were shown to contain less than 0.05% water by the method of Henle.[24] Standard aqueous solutions of acid and base were prepared in the usual manner. Solutions of alkoxides were prepared by dissolving the appropriate metal in the alcohol. They were stored in polyethylene bottles and standardized just prior to use.

Reactions were carried out in a thermostat that held within 0.05° of the stated temperature. The thermometer was calibrated at the boiling and freezing points of water and at 32.38° (transition temperature of sodium sulfate decahydrate). The procedures and apparatus were essentially as described by Saunders and Williams.[4]

Styrene analyses were performed spectrophotometrically as previously described.[4] Results were usually reproducible to within 1%. With 2-phenylethyl tosylate allowance was made for the ultraviolet absorption of the predominating substitution product. The kinetics of elimination from 2-phenylethyltrimethylammonium bromide was followed by analysis for styrene, since the trimethylamine generated in the reaction precludes titrimetric analysis.

Deuterium analyses were performed by the "falling drop" method. The procedure and apparatus were essentially as described by previous workers.[25] Duplicate determinations usually agreed to within 1%.

Deuterium Exchange Study on 2-Phenylethyldimethylsulfonium-2,2-d_2 Bromide.—An ethanol solution 0.0492 *M* in sulfonium salt and 0.0983 *M* in sodium ethoxide was placed in a thermostat at 30.00° just as in the kinetic runs. Aliquots were withdrawn, quenched in 0.1001 *N* hydrochloric acid and reduced to dryness *in vacuo* with a rotary evaporator. The residues were washed with ether and analyzed for deuterium. The results were (% reaction, atoms D/molecule): 0%, 1.96; 35.9%, 1.98; 44.2%, 1.94; 62.2%, 1.94.

Reinvestigation of Kinetic Measurements on the Acetyl-substituted Sulfonium Salts.—Experimental procedures were as outlined under "Kinetic Measurements." In ethanol with the *p*-acetylsulfonium salt plots of log $[b(a - x)/a(b - x)]$ *vs.* time gave negative time intercepts. The actual concentrations at $t = 0$ were evaluated from these plots and used in recalculation of the rate constants. That solvolysis of the *p*-acetylsulfonium salt did occur was confirmed in semi-quantitative experiments. When a 0.05 *M* solution of the sulfonium salt in ethanol was allowed to stand at room temperature, spectrophotometric analysis revealed 4% styrene in 20 min. and 8% styrene in 60 min. In contrast, a solution of the sulfonium salt in water at 50° showed no detectable solvolysis in 60 min. Since an unexplained conflict with earlier work existed for the *p*-acetylsulfonium salt in water, these results were checked independently by two workers (D. H. E. and Dr. R. Glaser). They agreed with each other within experimental error.

Acetylation of Methyl 2-Phenylethyl Sulfide.—The general procedure of Foreman and McElvain[26] was followed as before.[4] With two moles of aluminum chloride per mole of sulfide the monoacetyl sulfide was obtained in 28% overall yield, or 79% based on unrecovered starting material. This sulfide gave a single sulfonium salt in 80% yield, m.p. 121° dec. (lit.[1] m.p. 121–121.5° dec.). Oxidation of the sulfonium salt with potassium permanganate[27] gave 91% of terephthalic acid which had an infrared spectrum (potassium bromide pellet) identical with that of an authentic sample.

With three moles of aluminum chloride per mole of sulfide, a monoacetyl sulfide was obtained in 67% yield. This gave a single sulfonium salt in 86% yield, m.p. 115–116° dec.

Anal. Calcd. for $C_{12}H_{17}BrOS$: C, 49.82; H, 5.92. Found: C, 50.18; H, 5.93.

Oxidation with potassium permanganate gave 72% of phthalic acid, identified by melting point and infrared spectrum.

Melting points of some mixtures of the *o*- and *p*-acetyl sulfonium salts were (% *para*, melting range in °C.): 100, 121–122°; 90, 97–112°; 50, 95–101°; 15, 100–105°; 0, 114–115°. Other mixtures not quoted followed the same general pattern, the melting range remaining about the same from 25–75% *para*. Obviously neither isomer could contain an appreciable proportion of the other without a noticeable effect on the melting point. Each sulfonium salt behaved satisfactorily in the kinetic studies (Table IV).

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

Mechanisms of Elimination Reactions. XXI. The Alkaline Dehydrochlorination of *meso*- and *dl*-Stilbene Dichlorides[1]

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The dehydrochlorinations of *meso*- and *dl*-stilbene dichlorides with sodium hydroxide in 92.6 wt. % ethanol are shown to be first order in base and first order in dichloride, and to follow the normal concerted elimination mechanism. Second-order rate constants are given at 34.40, 43.90 and 53.30°. Entropies and energies of activation have been calculated. The data have been discussed in terms of recent concepts of transition states for bimolecular elimination reactions.

Introduction

Differences in the reactivity of diastereoisomers have been observed for many years.[2] Young and his co-workers[3] were the first to measure accurately the reactivity difference of a pair of diastereoisomers undergoing a concerted bimolecular elimination.[3b,d] They studied the iodide ion-initiated debromination of a series of *dl*- (Ia) and *meso*- (IIIa) alkylene dibromides.

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[1] Previous paper in series: S. J. Cristol and L. E. Rademacher, THIS JOURNAL, **81**, 1600 (1959).

[2] (a) A. Michael, *J. prakt. Chem.*, **52**, 305 (1895); (b) J. Wislicenus and F. Seeler, *Ber.*, **28**, 2693 (1895); (c) P. Pfeiffer, *Z. physik. Chem.*, **48**, 40 (1904); (d) P. F. Frankland, *J. Chem. Soc.*, 654 (1912).

[3] (a) R. T. Dillon, W. G. Young and H. J. Lucas, THIS JOURNAL, **52**, 1953 (1930); (b) W. G. Young, D. Pressman and C. D. Coryell, *ibid.*, **61**, 1641 (1939); (c) S. Winstein, D. Pressman and W. G. Young, *ibid.*, **61**, 1645 (1939); (d) W. G. Young, S. J. Cristol and T. Skei, *ibid.*, **65**, 2099 (1943); (e) W. G. Young, Abstracts of the Eighth National Organic Symposium, St. Louis, Mo., December, 1939.