Mechanisms of Elimination Reactions. X. Substituent, Isotope, and Solvent Effects in E2 Reactions of Some 2-Arylethyltrimethylammonium Bromides[1]

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Abstract: Rates of reaction were determined for a number of 2-arylethyltrimethylammonium bromides with sodium ethoxide in ethanol and sodium *t*-butoxide in *t*-butyl alcohol. The reactions in ethanol followed a normal second-order rate law, but in *t*-butyl alcohol, an assumed order of 1.5 in 2-phenylethyltrimethylammonium bromide was required to give a steady rate constant. In the presence of excess benzyltrimethylammonium chloride, the reaction did show the expected first-order dependence on both substrate and base. It is suggested that the base is present as sodium *t*-butoxide ion pairs which are converted to the more reactive free *t*-butoxide ion by quaternary ammonium salt (eq 1). In both solvents, the rates for *para*-substituted 2-phenylethyltrimethylammonium bromides fit the Hammett equation. The ρ values and the β-deuterium isotope effects suggest that there is less proton transfer and less carbanion character in the transition state in *t*-butyl alcohol than in ethanol.

Rates and deuterium isotope effects in E2 reactions of substituted 2-phenylethyl derivatives have been used by us[2-5] and others[6,7] to study the structure of the E2 transition state. We observed that the ρ value for the sulfonium salts (+2.7 at 30°) was larger than that for the bromides (+2.1 at 30°), in agreement with the prediction that compounds with Hofmann-rule leaving groups should give transition states of higher carbanion character than compounds with Saytzev-rule leaving groups. Since quaternary ammonium salts show more extreme Hofmann-rule behavior than tertiary sulfonium salts, the 2-arylethyltrimethylammonium salts should give still higher ρ values than the 2-arylethyldimethylsulfonium salts. The present work was undertaken to test this prediction and to examine the effect of solvent on ρ and k_H/k_D.

The 2-arylethyltrimethylammonium bromides were prepared by standard procedures (see Experimental Section). The rates of reaction were determined by spectrophotometric analysis for styrene. For the relatively slow reactions in ethanol substrate concentrations were around 5×10^{-2} *M* and aliquots were diluted for measurement, but for the faster reactions in *t*-butyl alcohol much lower ($3\text{–}8 \times 10^{-5}$ *M*) concentrations of substrate and at least a tenfold excess of base were used and the reaction was followed directly in the thermostated cell compartment of the spectrophotometer. Even so, it proved impossible to obtain rates on substrates with electron-withdrawing substituents in the work in *t*-butyl alcohol. Good second-order rate constants were obtained in ethanol and are recorded, along with enthalpies and entropies of activation, in Table I. The kinetic behavior in *t*-butyl alcohol was rather complex.

Table I. Rate Constants and Activation Parameters for Eliminations from 2-Arylethyltrimethylammonium Bromides with Sodium Ethoxide in Absolute Ethanol

para subst	Temp,[a] °C	$k_2 \times 10^5$, l./mol sec[d]	ΔH^*, kcal/mol	ΔS^*, eu
Cl	60.00	3340[b]		
H	60.00	670 ± 14		
CH_3	60.00	233 ± 3		
CH_3O	60.00	90.0 ± 3.4		
Cl	50.00	977 ± 16		
H	50.00	178 ± 2[c]	27.5	+13.7
CH_3	50.00	56.4 ± 1.2	28.9	+15.8
CH_3O	50.00	20.5 ± 1.0	30.7	+19.3
Cl	40.00	291 ± 8	25.2	+10.0
H	40.00	44.5 ± 0.6		
CH_3	40.00	13.5 ± 0.3		
CH_3O	40.00	4.39 ± 0.17		
Cl	30.00	9.99[b]		
CH_3	30.00	2.79[b]		
CH_3O	30.00	0.831[b]		

[a] Temperature constant to ±0.02°. [b] Extrapolated from Arrhenius plot of data at other temperatures. [c] Lit.[2c] 179 ± 4.7. [d] Averages include at least two determinations with average deviations indicated.

A plot of log $[(D_\infty - D_t)/D_\infty]$ was expected to be linear in the presence of a large excess of base. Instead the plots were markedly curved (see curve a, Figure 1), the apparent first-order rate constant decreasing with time. When second-order dependence on substrate was assumed, the plot curved in the opposite direction. A linear plot up to 85% reaction (curve c, Figure 1) was obtained with an assumed order of 1.5 in substrate. Rate constants based on this assumption are given in Table II. At the lowest substrate concentrations (2×10^{-6} *M*), the order seemed to approach unity, but the marked increase in rate with decreasing substrate concentration made the data too imprecise for reliable conclusions.

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(1) This work was supported by the National Science Foundation. A. F. C. acknowledges the award of an ICI Fellowship for 1966–1967.

(2) W. H. Saunders, Jr., and R. A. Williams, *J. Am. Chem. Soc.*, **79**, 3712 (1957).

(3) W. H. Saunders, Jr., C. B. Gibbons, and R. A. Williams, *ibid.*, **80**, 4099 (1958).

(4) W. H. Saunders, Jr., and D. H. Edison, *ibid.*, **82**, 138 (1960).

(5) A. F. Cockerill, S. Rottschaefer, and W. H. Saunders, Jr., *ibid.*, **89**, 901 (1967).

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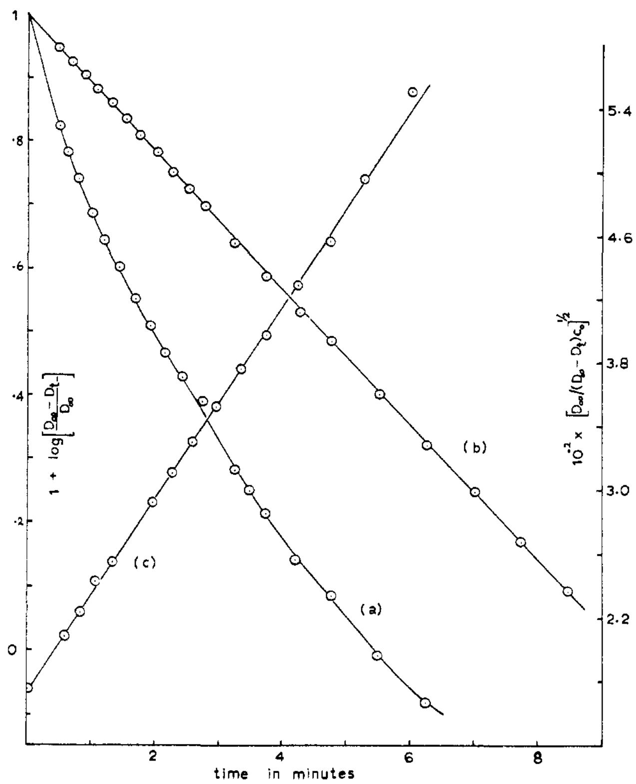

Figure 1. Rate data for reaction of 2-phenylethyl-2,2-d_2-trimethylammonium bromide with sodium *t*-butoxide in *t*-butyl alcohol at 30°. Curve a plots $1 + \log[(D_\infty - D_t)/D_\infty]$ *vs.* time for substrate 5.02×10^{-5} *M*, base 2.83×10^{-3} *M* (initial concentrations). Curve b plots $1 + \log[(D_\infty - D_t)/(D_\infty]$ *vs.* time for substrate 5.46×10^{-5} *M*, base 2.68×10^{-3} *M* (initial concentrations), benzyltrimethylammonium chloride 1.04×10^{-2} *M*. Curve c plots $[D_\infty/(D_\infty - D_t)C_0]^{0.5} \times 10^{-2}$ *vs.* time for substrate 3.52×10^{-5} *M*, base 1.33×10^{-3} *M* (initial concentration).

The immediately obvious explanation of such behavior is that the substrate exists partially as higher aggregates in solution, and that the monomer and the dimer are making comparable contributions to the observed rate. Since conductivity data (see below) provide no support for this hypothesis, we prefer a somewhat different explanation.

Table II. Pseudo-1.5-Order Rate Constants for Eliminations from 2-Arylethyltrimethylammonium Bromides with Sodium *t*-Butoxide in *t*-Butyl Alcohol at 30° [a]

Subst[b]	$RNMe_3Br$, $M \times 10^5$	*t*-BuONa, $M \times 10^3$	$k_{1.5}$, $l.^{0.5}/mol^{0.5}$ sec[c]
	4.11	1.33	3.33
2,2-d_2	3.52	1.33	0.514
p-MeO	3.65	1.33	0.490
	4.11	1.00	2.10
2,2-d_2	3.52	1.00	0.320
p-MeO	3.65	1.00	0.307
	8.13	1.33	1.29
2,2-d_2	6.96	1.33	0.224
p-MeO	7.22	1.33	0.198
	6.13	1.32	1.75
2,2-d_2	5.25	1.32	0.298
p-MeO	5.45	1.32	0.277
p-Me	7.60	1.32	0.358
p-Me	5.74	1.33	0.546
p-Me	3.85	1.33	0.938

[a] Controlled to ±0.1° or better. [b] Blanks refer to unsubstituted 2-phenylethyltrimethylammonium bromide. [c] Obtained from the slope of a plot of $[D_\infty/C_0(D_\infty - D_t)]^{0.5}$ (see Figure 1).

Table III. Conductance of Solutions in *t*-Butyl Alcohol at 30°

Solute	Concn, $M \times 10^2$	Cond $\times 10^6$ mho/cm
		0.330
t-BuONa	11.0	0.352
$PhCH_2NMe_3Cl$	0.226	0.972
$PhCH_2NMe_3Cl$	0.453	1.350
$PhCH_2NMe_3Cl$	0.509	1.476
$PhCH_2NMe_3Cl$	0.679	1.738
$PhCH_2NMe_3Cl$	0.792	1.831
$PhCH_2NMe_3Cl$	0.906	1.975
$PhCH_2NMe_3Cl$	1.132	2.384
$PhCH_2CH_2NMe_3Br$	0.253	1.167

Table III shows that sodium *t*-butoxide has very little effect on the conductivity of *t*-butyl alcohol, whereas much smaller concentrations of benzyltrimethylammonium chloride and 2-phenylethyltrimethylammonium bromide raise the conductivity markedly. In fact, a plot of conductance *vs.* concentration for benzyltrimethylammonium chloride has unit slope. These data suggest that sodium *t*-butoxide exists almost entirely as ion pairs and the quaternary ammonium salts to a considerable extent as free ions in *t*-butyl alcohol. A mixture of the base and the salt might thus contain both paired and free *t*-butoxide ions (eq 1).

$$t\text{-BuO}^-\text{M}^+ + \text{PhCH}_2\text{CH}_2\text{NMe}_3^+ + \text{Br}^- \rightleftharpoons \text{M}^+\text{Br}^- + \text{PhCH}_2\text{CH}_2\text{NMe}_3^+ + t\text{-BuO}^- \quad (1)$$

If free *t*-butoxide were the only effective base, a rate law *second* order in substrate is expected, since the substrate concentration determines the concentration of free *t*-butoxide according to eq 1. That the observed order is lower suggests that both paired and free *t*-butoxide are involved. Quantitative assessment of their relative importance is impossible because of lack of knowledge of the equilibrium constant of eq 1 and the evident variation of apparent 1.5-order rate constant with substrate concentration (lines 13–15, Table II). An alternative explanation for the deviation from second order in substrate is the imposition of a varying salt effect on the rate as the reaction proceeds and the concentration of ionic species decreases. Since the reaction is between oppositely charged ions, a decrease in ionic concentration would cause an upward drift in the second-order rate constant, as observed. The apparent order of 1.5 thus need not indicate a partial contribution from a first-order process. Indeed, it seems unlikely that sodium *t*-butoxide ion pairs could compete successfully with free *t*-butoxide unless present in very great excess, for benzyltrimethylammonium *t*-butoxide in *t*-butyl alcohol is reported to be at least 10^3 times as basic as potassium *t*-butoxide.[8] While we do not know the dependence of rate on medium basicity alone for this reaction, the rate of another E2 reaction (admittedly of different charge type) was found to increase considerably faster than basicity.[5]

Addition of benzyltrimethylammonium chloride in large excess over substrate provides strong evidence that free *t*-butoxide ions are involved. The reaction becomes cleanly first order in substrate (curve b, Figure 1), precisely as expected for a shift of the equilibrium of eq 1 to the right so as to give a sufficiently large excess of free *t*-butoxide that its concentration remains constant

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(8) D. Bethell and A. F. Cockerill, *J. Chem. Soc.*, *B*, 913 (1966).

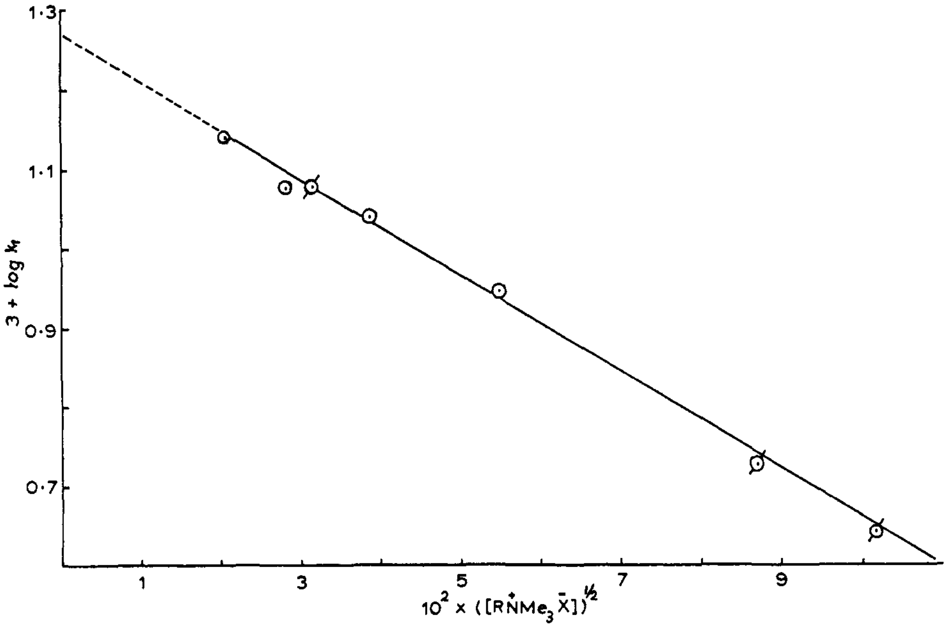

Figure 2. Effect of total quaternary ammonium salt concentration, $[RNMe_3X] = [PhCD_2CH_2NMe_3Br] + [PhCH_2NMe_3Cl]$, on rate of reaction of 2-phenylethyl-2,2-d_2-trimethylammonium bromide with sodium *t*-butoxide in *t*-butyl alcohol at 30°. Circles, lines 1–4, Table IV; circles with lines, other data in Table IV extrapolated to a base concentration of 2.93×10^{-3} *M* assuming that the rate depends on base concentration to the 0.84 power (as demonstrated by lines 16–18, Table IV).

during reaction. Rate constants are recorded in Table IV. Evidence that the equilibrium is still not entirely to the right is afforded by a comparison of lines 16–18 with lines 19–20 of Table IV. Potassium *t*-butoxide is still 1.6 times more effective than sodium *t*-butoxide, contrary to the equality of rates expected if the bases were completely converted to free *t*-butoxide in both cases.

Table IV. Pseudo-First-Order Rate Constants for Eliminations from 2-Arylethyltrimethylammonium Bromides with Sodium *t*-Butoxide in *t*-Butyl Alcohol at 30° [a] in the Presence of Added Benzyltrimethylammonium Chloride

Subst[b]	ArC_2H_4-NMe_3Br, $M \times 10^5$	$PhCH_2$-NMe_3Cl, $M \times 10^3$	*t*-BuONa, $M \times 10^3$	$k_1 \times 10^3$, sec^{-1} [c]
2,2-d_2	5.213	1.504	2.932	11.0
2,2-d_2	5.213	3.009	2.932	8.83
2,2-d_2	5.213	0.752	2.932	11.9
2,2-d_2	5.213	0.376	2.932	13.7
	6.023	1.612	2.617	79.6
2,2-d_2	5.589	1.612	2.617	10.9
p-MeO	5.988	0.967	0.873	4.82
p-Me	5.404	0.967	0.873	11.0
	6.023	0.967	0.873	30.6
2,2-d_2	5.589	0.967	0.873	4.37
p-MeO	5.988	3.760	1.062	3.83
p-Me	5.404	3.760	1.062	8.30
	6.023	3.760	1.062	25.3
	6.023	7.52	2.617	31.9
2,2-d_2	5.589	7.52	2.617	4.73
2,2-d_2	5.456	10.4	2.681	4.11
2,2-d_2	5.456	10.4	8.043	9.83
2,2-d_2	5.456	10.4	10.72	12.9
2,2-d_2	5.456	10.4	3.64[d]	8.87
2,2-d_2	5.456	10.4	7.27[d]	15.8

[a] Controlled to ±0.1° or better. [b] Dots refer to unsubstituted 2-phenylethyltrimethylammonium bromide. [c] From the slope of a plot of $\log [(D_\infty - D_t)/D_\infty]$ *vs.* time. [d] Base in these runs was potassium *t*-butoxide.

It is somewhat surprising that the rate of elimination remains in a measurable range when the concentration of free *t*-butoxide ion is increased markedly by excess benzyltrimethylammonium chloride. Evidently the rate-depressing salt effect counterbalances to a considerable extent the increase in active base concentration. The data in Table IV, lines 1–4, demonstrate the magnitude of the salt effect. With both reactants at constant initial concentration, an increase in concentration of added quaternary ammonium salt diminishes the rate (by 37% for an eightfold increase in concentration) even though the concentration of free *t*-butoxide must be increasing at the same time.

The form of the salt effect is interesting. The observed first-order rate constants decrease with increasing concentration of total ammonium salt (substrate plus benzyltrimethylammonium chloride) such that log *k* decreases linearly with the square root of ammonium salt concentration (Figure 2). Although this is the dependence predicted by the Debye–Hückel limiting law, it is unexpected that our complex nonideal system should follow such a simple theoretical treatment. Another possible source of the square-root dependence could be incomplete dissociation of the ammonium salt with the free ions responsible for the rate effect. The linear dependence of conductivity on the first power of ammonium salt concentration (see above and Table III) makes this explanation unlikely. In addition, slight dissociation would imply a small equilibrium constant for eq 1, which would make the striking effect of benzyltrimethylammonium chloride on reaction order difficult to explain. It is advisable at this stage not to make too much of the dependencies of log *k* or conductivity on concentration, for both studies covered only a fivefold range in concentration. Curvature might well have been found in one or both of the plots if a wider range had been easily attainable.

The Hammett ρ values (least-squares procedure of Jaffé[9]) derived from rates with *para* substituents meth-

Table V. Hammett Correlations and Kinetic Isotope Effects in Elimination Reactions of 2-Arylethyltrimethylammonium Bromides

Temp, °C	Solvent	ρ[a]	r[b]	k_H/k_D
30	EtOH	3.773 ± 0.212	0.997	
30	EtOH	3.943 ± 0.551[c]	0.990	
40	EtOH	3.579 ± 0.187	0.997	
40	EtOH	3.674 ± 0.504[c]	0.991	
50	EtOH	3.312 ± 0.156	0.998	2.98 ± 0.08[g]
50	EtOH	3.439 ± 0.405[c]	0.993	
60	EtOH	3.094 ± 0.149	0.998	
60	EtOH	3.191 ± 0.397[c]	0.992	
30	*t*-BuOH	3.070 ± 0.045[c,d]	0.997	7.03 ± 0.12
30	*t*-BuOH	3.111 ± 0.027[c,d]	0.999	
30	*t*-BuOH	2.954 ± 0.052[c,e]	0.996	6.90 ± 0.17
30	*t*-BuOH	3.036 ± 0.029[c,f]	0.998	

[a] By least-squares method[9] with indicated standard deviation. Substituents were *p*-Cl, H, *p*-Me, and *p*-MeO except where otherwise noted. [b] Correlation coefficient. [c] Based on *p*-MeO, *p*-Me, and H only. [d] Based on pseudo-1.5-order rate constants. The two values represent two different initial concentrations of substrate. [e] Based on pseudo-first-order rate constants in the presence of benzyltrimethylammonium chloride (9.67×10^{-4} *M*) with 8.73×10^{-3} *M* sodium *t*-butoxide. [f] Same as *e*, except benzyltrimethylammonium chloride was 3.76×10^{-3} *M* and sodium *t*-butoxide 1.062×10^{-3} *M*. [g] Reference 4.

oxyl, methyl, hydrogen, and chlorine are recorded in Table V. The very fast reaction of the *p*-chloro compound made determination of its rate of reaction in *t*-butyl alcohol impossible, so ρ values using only the first three substituents are recorded for the reactions in both *t*-butyl alcohol and ethanol. The value at 30° in ethanol is calculated with rate constants extrapolated from higher temperatures. Table II also contains k_H/k_D values for the reactions of 2-phenylethyltrimethylammonium ion.

The ρ value at 30° in ethanol is well above those previously observed[2,6] for the halides, tosylate, and sulfonium salt, and fully confirms our expectation that high sensitivity to the inductive effects of substituents is to be expected in eliminations from ammonium salts. The ρ value in *t*-butyl alcohol, while still fairly large, is considerably less than that in ethanol.

From these results we can conclude that the reaction in ethanol shows a high degree of carbanion character, and that the carbanion character becomes less pronounced in *t*-butyl alcohol. Even in ethanol the transition state is still well short of the E1cb end of the scale, for the nitrogen isotope effect is of substantial magnitude.[10] The decrease in ρ in *t*-butyl alcohol might be ascribed to less C–H stretching, or more C–N stretching, or both. The k_H/k_D values offer evidence that decreased C–H stretching is important. It seems probable that the low k_H/k_D in ethanol indicates a transition state in which proton transfer is more than half complete. If so, the accepted picture[11] requires that the larger k_H/k_D in *t*-butyl alcohol be the result of less complete proton transfer. In the absence of nitrogen isotope effects (probably very difficult to determine because of low solubility of the ammonium salt in *t*-butyl alcohol), no conclusions can be drawn about the extent of C–N stretching in *t*-butyl alcohol.

The decrease in carbanion character from ethanol to *t*-butyl alcohol is in contrast with our observation[12] that quaternary ammonium salts give a greater proportion of the less substituted (Hofmann rule) product in *t*-butyl alcohol than in ethanol. Evidently, the orientation is determined by factors other than carbanion character in these cases. The most plausible factor with these highly branched compounds would be a steric effect.[13]

Experimental Section[14]

2-Arylethanols. The following were prepared: 2-(*p*-tolyl)ethanol, 2-(*p*-anisyl)ethanol, and 2-(*p*-chlorophenyl)ethanol by the methods used previously.[2] Their properties agree well with those reported.[2]

2-Arylethyl *p*-toluenesulfonates were prepared in the usual fashion.[15]

2-(*p*-Tolyl)ethyl *p*-toluenesulfonate had mp 68.6–69.2. *Anal.* Calcd for $C_{16}H_{18}O_3S$: C, 66.18; H, 6.25. Found: C, 65.97; H, 6.21.

2-(*p*-Anisyl)ethyl *p*-toluenesulfonate had mp 58.3–59.0° (lit.[6] 58.6–59.6°).

2-(*p*-Chlorophenyl)ethyl *p*-toluenesulfonate had mp 79.5–80.1° (lit.[6] 79.3–80.3°).

Dimethyl-2-arylethylamines. Preparation was accomplished by treating the 2-arylethyl *p*-toluenesulfonate with anhydrous dimethylamine in anhydrous ether.[4] For the unsubstituted compound 2-phenylethyl bromide was used, but the procedure was otherwise closely similar.

Dimethyl-2-phenylethylamine had bp 100° (20 mm) (lit.[4] 110–111° (20 mm)). The picrate had mp 136.7–137.8° (lit.[4] 135°).

Dimethyl-2-(*p*-tolyl)ethylamine had bp 115° (18 mm), n^{25}D 1.4977. *Anal.* Calcd for $C_{11}H_{17}N$: C, 80.92; H, 10.50. Found: C, 81.02; H, 10.67.

Dimethyl-2-(*p*-anisyl)ethylamine had bp 100° (2 mm), n^{25}D 1.5079. *Anal.* Calcd for $C_{11}H_{17}NO$: C, 73.70; H, 9.56. Found: C, 73.45; H, 9.68.

Dimethyl-2-(*p*-chlorophenyl)ethylamine had bp 104–106° (1.2 mm), n^{25}D 1.5154. *Anal.* Calcd for $C_{10}H_{14}NCl$: C, 65.39; H, 7.68. Found: C, 65.45; H, 7.58.

2-Arylethyltrimethylammonium bromides were obtained by treating the amine in nitromethane solution with a twofold molar excess of methyl bromide. The mixture was allowed to stand at room temperature until the product crystallized, and the product was recrystallized from ethanol-ether.

2-Phenylethyltrimethylammonium bromide had mp 237.8–238.2° (lit.[4] 238–239°).

2-Phenylethyl-2,2-d_2-trimethylammonium bromide was prepared as above in two steps from a previously prepared sample of 2-phenylethyl-2,2-d_2 *p*-toluenesulfonate containing 1.95 atoms of D/molecule. The product had mp 238–239° (lit.[4] 238–239°). A second batch was obtained from phenylmalonic ester by the procedure of Saunders and Edison,[4] and was shown by nmr to contain at least 98% (1.96 atoms of D/molecule) of the theoretical amount of deuterium.

2-(*p*-Tolyl)ethyltrimethylammonium bromide had mp 200.5–201.0°. *Anal.* Calcd for $C_{12}H_{20}NBr$: C, 55.82; H, 7.81. Found: C, 55.91; H, 7.89.

2-(*p*-Anisyl)ethyltrimethylammonium bromide had mp 217.7–218.2°. *Anal.* Calcd for $C_{12}H_{20}NOBr$: C, 52.56; H, 7.35. Found: C, 52.60; H, 7.44.

2-(*p*-Chlorophenyl)ethyltrimethylammonium bromide had mp 242.3–242.6°. *Anal.* Calcd for $C_{11}H_{17}NBrCl$: C, 47.42; H, 6.15. Found: C, 47.36; H, 6.28.

Materials for Kinetic Runs. The ethanol and solutions of sodium ethoxide in ethanol were prepared and purified as described by Saunders and Williams.[2] The *t*-butyl alcohol and solutions of sodium and potassium *t*-butoxides in *t*-butyl alcohol were prepared as described by Cockerill, Rottschaefer, and Saunders.[5] The benzyltrimethylammonium chloride was obtained by neutralizing

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(9) H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953).

(10) A. N. Bourns and P. J. Smith, *Proc. Chem. Soc.*, 366 (1964).

(11) F. H. Westheimer, *Chem. Rev.*, **61**, 265 (1961).

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(13) H. C. Brown and I. Moritani, *J. Am. Chem. Soc.*, **75**, 4112 (1953); H. C. Brown, I. Moritani, and Y. Okamoto, *ibid.*, **78**, 2193 (1956).

(14) Melting points are corrected, boiling points uncorrected. Analyses by Micro-Tech Laboratories, Skokie, Ill.

(15) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

with hydrochloric acid a commercial 40% aqueous solution of the corresponding hydroxide. The sample was dried at 100° (0.01 mm) for 6 hr, recrystallized from a mixture of anhydrous ethanol and ether, and again dried *in vacuo* at 100°. It was stored in a desiccator.

Kinetic Measurements. The reactions in ethanol were carried out essentially by the procedure of Saunders and Williams[2] for the reactions of the corresponding sulfonium bromides with sodium ethoxide in absolute ethanol. Aliquots were taken periodically with a 1.0-ml calibrated hypodermic syringe and diluted twice to 25.0 ml with 95% ethanol (625-fold dilution). The optical density was determined at the absorption maximum for the styrene[2] and the concentration of the styrene calculated. Initial concentrations in the reaction mixtures were near 0.1 *M* in the sodium ethoxide and 0.05 *M* in the ammonium salt. Rate constants were calculated point by point, using the integrated form of the second-order rate law for unequal initial concentrations. Values in Table I are averages of at least two separate runs. Reactions were followed to at least two half-lives.

The runs in *t*-butyl alcohol were carried out in the thermostated cell compartment of a Beckman DU or Unicam S.P. 800 spectrophotometer as described by Cockerill, Rottschaefer, and Saunders[5] for the corresponding reactions of the 2-arylethyl bromides. Reagents and solutions were prepared in the same fashion as well. Substrate concentrations of 3–8 × 10^{-5} *M* were used, and the base concentration was always at least ten times the substrate concentration, though the high speeds of these reactions made necessary lower base concentrations than in the previous work. The pseudo-first-order rate constants were determined as before[5] from the experimental data. The pseudo-1.5-order rate constants were determined from a plot of $[(D_\infty - D)C_0/D_\infty]^{-0.5}$, which is equivalent to $C^{-0.5}$.

Conductivity Measurements. A Mullard conductivity cell (type E 7591/B) with platinized platinum electrodes was used. The cell was connected to a Pye conductance bridge (No. 11,700) with screened coaxial cable. Errors in the conductances given in Table III are ±0.003 × 10^6 mho/cm. We thank Mr. G. R. Taylor for use of this equipment.

Electrophilic Substitution at Saturated Carbon. XXXV. Mechanistic Components in Base-Catalyzed Racemization and Isotopic Exchange of 4-Biphenylylmethoxyphenylmethane in *t*-Butyl Alcohol-O-*d*[1]

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Abstract: The syntheses of optically active 4-biphenylylmethoxyphenylmethane (I-*h*) and 4-biphenylyldeuteriomethoxyphenylmethane (I-*d*) are described. The kinetics of racemization and isotopic exchange of (−)-I-*h* in *t*-butyl alcohol-O-*d*–potassium *t*-butoxide have been studied, as well as of racemization of (+)-I-*d* in the same medium. Rate constants for isotopic exchange of (±)-*I-h* and for racemization of (+)-I-*d* in this medium were determined. The variation with time of the optical activity of (−)-I-*h* was followed, and the results were demonstrated to be compatible with a kinetic model which provides for dissection of data into mechanistic pathways for isotopic exchange with retention and with inversion of configuration. The kinetic isotope effect for racemization in deuterated solvent at 116° was $(k^H/k^D)_\alpha = 2.7$. At this temperature, the rate constant for isotopic exchange with retention exceeded that for isotopic exchange with inversion by a factor of 33. The mechanisms of the exchange and racemization reactions are discussed.

A kinetic model has recently been developed[2] that allows dissection into specific components of rate data for base-catalyzed isotopic exchange and racemization reactions of carbon acids in proton-donating solvents. As applied to behavior of a starting protio acid in a deuterated solvent, the components are defined by the equations. The symbol H_+ refers to dextrorotatory protio carbon acid, and similar meanings extend to the other symbols. Exchange of *starting material* with retention of configuration (k_1), exchange with inversion (k_2), inversion without exchange or isoinversion (k_3), and inversion of *exchanged product* (k_4) are the four potentially identifiable components.

This model was tested by two experimentally independent methods with optically active and isotopically labeled 2-(N,N-dimethylcarboxamido)-9-methylfluorene. In the first method, partially exchanged and racemized carbon acid was reresolved and the mole fractions of H_+, H_-, D_+, and D_- were calculated. From these mole fractions and experimentally determined values of k_4, values of k_1, k_2, and k_3 were calculated. In a second method, values of k_1, k_2, k_3 were calculated solely from kinetic data. The two methods gave excellent agreement. This kinetic model has been applied only to cases in which net inversion or racemization was the observed result.[2,3] The present paper reports results of a study in which the kinetic model is applied to a system that undergoes isotopic exchange with high net retention of configuration.

$$\begin{array}{ll}
H_+ \xrightarrow{k_1} D_+ & H_- \xrightarrow{k_1} D_- \\
H_+ \xrightarrow{k_2} D_- & H_- \xrightarrow{k_2} D_+ \\
H_+ \xrightarrow{k_3} H_- & H_- \xrightarrow{k_3} H_+ \\
D_+ \xrightarrow{k_4} D_- & D_- \xrightarrow{k_4} D_+
\end{array}$$

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[2] (a) W. T. Ford, E. W. Graham, and D. J. Cram, *J. Am. Chem. Soc.*, **89**, 689, 690 (1967); (b) W. T. Ford, E. W. Graham, and D. J. Cram, *ibid.*, **89**, 4661 (1967).

[3] D. J. Cram and T. A. Whitney, *ibid.*, **89**, 4651 (1967).