Appendix

$\Delta H_f°(g)$ has been measured for trimethyl orthoformate;[11] for trimethyl orthoacetate, $\Delta H_f°(g)$ was calculated using the bond–bond interaction scheme of Pihlaja.[12] The standard entropies of the gaseous ortho esters were estimated using the standard entropies of the corresponding hydrocarbons and the correction factor proposed by Stull, *et al.*[13] (it was assumed that this factor should be applied for each oxygen[14]). $S°(g)$ for methyl acetate was estimated from the value of $S°(g)$ for ethyl acetate,[13] using the difference in $S°(g)$ for ethanol and methanol[13] ($\Delta S° = 10.25$).

In Table V are collected the thermochemical data used in this paper, as well as the free energies of formation in aqueous solution estimated for ortho acid derivatives. To calculate $\Delta G_f°(aq)$ values it was necessary to evaluate free energies of transfer, ΔG_t, from standard state (g, 1 atm) to standard state (aq, 1 *M*); the data used to evaluate ΔG_t are found in Table VI.

Most of the relative methyl basicities found in Table I are calculated from equilibrium constants for reaction of carbonyl compounds; the equilibria which were used are found in Table VII.

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(11) K. Pihlaja and M.-L. Tuomi, *Acta Chem. Scand.*, 25, 465 (1971).

(12) K. Pihlaja, *Acta Chem. Scand.*, 25, 451 (1971).

(13) D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds," Wiley, New York, N. Y., 1969.

(14) No standard entropy data are available for any ortho ester; the only acetal for which $S°(g)$ is available is dimethoxymethane[12] for which $S°(g)$ estimated as described is within 0.6 eu of the observed value.

The Solvent System Ethanol–2,2,2-Trifluoroethanol as a Medium for Solvolytic Displacement

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Abstract: A comparative rate study of the solvolyses of benzyl bromide and chloride and their *m*-fluoro and *p*-methyl derivatives in various mixtures of ethanol and 2,2,2-trifluoroethanol has been conducted. The reactivity of *p*-methylbenzyl chloride increases and that of *m*-fluorobenzyl chloride decreases with increasing trifluoroethanol content of the medium; benzyl chloride is relatively insensitive to changes in solvent composition. These reactivity differences reflect the electronic influence of substrate ring substituents on the extent to which solvent is involved as a nucleophile and as an electrophile in rate-determining processes. These differences are also reflected in the influences of changes in solvent composition on the composition of reaction product (ethyl ether *vs.* trifluoroethyl ether) as the ring substituents of the reacting halides are changed. The reactivity ratios of the substituted benzyl bromides and the corresponding benzyl chlorides are insensitive to changes in ring substituents when ethanol is the medium but increase significantly with increasing trifluoroethanol content of the medium. The variations in the observed solvent influence on bromide–chloride reactivity ratios are ascribed to differences in disposition of the bromides and chlorides to solvolyze by processes which are subject to internal return.

In accounting for the response of substrate reactivity to change in the medium, eq 1, as formulated by

$$\mathrm{d}\log k = \left(\frac{\partial \log k}{\partial Y}\right)_N \mathrm{d}Y + \left(\frac{\partial \log k}{\partial N}\right)_Y \mathrm{d}N \qquad (1)$$

Winstein, Grunwald, and Jones,[1] is frequently applied. This equation relates variations in solvolysis rate constant (k) to variations in ionizing power (Y) and nucleophilic character (N) of the solvent. The term $(\partial \log k/\partial Y)_N$ has been equated with the Grunwald–Winstein[2] m value (eq 2), as measured by the slope of a plot of

$$\log k = mY + \log k_0 \qquad (2)$$

values of log k *vs.* Y for reactions in media which are comparable in nucleophilicity but variable in ionizing power, *e.g.*, ethanol–water mixtures.

The Y value of a solvent is defined as the logarithm of the solvolysis rate ratio for reaction of *tert*-butyl chloride in that solvent and in 80% aqueous ethanol, and k_0 is the rate constant for reaction of the substrate in 80% aqueous ethanol. Substrates which have m values close to that for *tert*-butyl chloride (unity) are considered as prone to solvolyze by processes in which there is a high degree of bond breaking and correspondingly extensive involvement of the solvent as an electrophile, at the transition state. As their m values diminish, the substrates presumably become increasingly sensitive to changes in solvent nucleophilicity.

The components of the binary mixtures generally used in connection with the Grunwald–Winstein correlation differ significantly in dielectric constant as well as in their capacities to solvate the departing anion, *e.g.*, halide ion in alkyl halide solvolysis. The dielectric constant of the medium is thus built into the Y value. Therefore the m value reflects the sensitivity of substrate reactivity to changes in the dielectric constant of the solvent as well as in its electrophilic character.

In the current investigation, consideration has been given to the means of eliminating the dielectric constant as a variable in assessing the influence of medium changes as reflected in solvolysis rate. Experimental attention has focused on the solvent system ethanol–

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(1) S. Winstein, E. Grunwald, and H. W. Jones, *J. Amer. Chem. Soc.*, 73, 2700 (1951).

(2) E. Grunwald and S. Winstein, *ibid.*, 70, 846 (1948).

2,2,2-trifluoroethanol. The two alcohols, which differ significantly in nucleophilic and electrophilic character,[3-5] have dielectric constants which are closely similar[6] (24.32 and 26.14, respectively, at 25°), and the values for their mixtures fall between these two figures. A comparative rate study of the reactions of benzyl chloride and bromide and their *p*-methyl and *m*-fluoro analogs in various mixtures of the two solvents has been conducted. The influence of changes in medium on the composition of products obtained from the benzyl bromides has also been investigated. The results reflect rather dramatically the electronic influences of the ring substituents on structure at the transition states for reactions of the benzyl halides.

Experimental Section

Materials. Samples of Eastman Organic Chemicals *tert*-butyl chloride (bp 50–51°), benzyl bromide (bp 112–114° (16 mm)), and benzyl chloride (bp 66–68° (10–14 mm)) were distilled before use. The *p*-nitrobenzyl bromide (mp 98–100°), *p*-nitrobenzyl chloride (mp 70–72°), and 2,6-lutidine (bp 142–144°) were obtained from the same supplier and employed in rate work without further purification. Samples of Aldrich Chemical Co. *m*-fluorobenzyl bromide (bp 85–88° (15–18 mm)), *m*-fluorobenzyl chloride (bp 70–72° (15–18 mm)), and *p*-methylbenzyl chloride (bp 88–89° (16 mm)) were distilled prior to use. Matheson Coleman and Bell *p*-methylbenzyl bromide (bp 82–84° (14–15 mm)) was also distilled before use.

p-Methoxybenzyl bromide was prepared by bubbling anhydrous hydrogen bromide through an ice-cooled solution of anisyl alcohol in benzene. The solution of the bromide was washed with sodium carbonate solution and dried over sodium sulfate. The product was recovered by distillation (bp 111–114° (8–10 mm)) and used immediately in rate studies since it is subject to decomposition in storage.[7]

p-Methoxybenzyl chloride was prepared through dropwise addition of thionyl chloride to a solution of anisyl alcohol in benzene under reflux. The product was recovered by distillation [bp 116–120° (14–15 mm) (lit.[8] bp 92.5° (1.5 mm))].

Solvents. Commercial absolute ethanol was further dried through refluxing with sodium and ethyl succinate,[9] followed by distillation. A fraction collected at 78–79° was used in rate studies.

2,2,2-Trifluoroethanol (Halocarbon Products Co.) was dried over Linde 4A molecular sieves (Union Carbide Corp.) and distilled.[4] The fraction collected at 73.5–74.0° was used in rate work.

In preparing ethanol–trifluoroethanol mixtures of x vol % of the latter, x volumes of trifluoroethanol were mixed with $100 - x$ volumes of ethanol at 25°.

The Solvolysis Rate Studies. In a typical rate run, a sample of organic halide sufficient to provide a substrate concentration of 0.005–0.030 *M* was weighed into a volumetric flask. 2,6-Lutidine, if it was used, was introduced in 10–15% molar excess of the halide. The flask was filled to the mark with solvent, which in runs at temperatures below 45° was previously equilibrated to reaction temperature, and the mixture was shaken to accomplish solution. For runs at 45° and higher temperatures, 5-ml samples of the reaction mixtures were sealed in glass ampoules and these were simultaneously immersed in a constant-temperature bath. From time to time an ampoule was withdrawn from the bath and cooled in ice. The contents of the cooled ampoules were added to 40 ml of acetone, and additional acetone was used to rinse the ampoules in completing the transfer. The acetone solutions were titrated for hydrogen halide with standard aqueous sodium hydroxide to the bright greenish end point of Bromothymol Blue (four drops of a solution of 0.5 g of the indicator in 15 ml of ethanol and 85 ml of water).

In making a run at a temperature below 45°, the volumetric flask containing the weighed sample of organic halide and lutidine, if used, was immersed in the constant-temperature bath. Solvent that had been equilibrated to bath temperature was added to the mark of the reaction flask and the mixture was shaken briefly and returned to the bath. At appropriate time intervals, 5-ml samples of the resultant solution were withdrawn, added to acetone, and titrated as described above. In fast reactions, the rate samples were added to acetone which had been cooled to 0°, and these solutions were stored at −10° pending titration.

The runs in general were followed to at least 75% completion. In no case was there evidence that the first-order rate constants for solvolysis were dependent on the lutidine concentration. The reported rate constants for organic halide (RX) solvolysis (eq 3)

$$-\mathrm{d}[\mathrm{RX}]/\mathrm{d}t = k[\mathrm{RX}] = k([\mathrm{RX}]_{\mathrm{i}} - [\mathrm{HX}]) \qquad (3)$$

were calculated from slopes of plots of values of log [RX] *vs.* time. In most cases these plots were linear to high percentages of completion of reaction. The experimental rate constants for solvolysis of *m*-fluorobenzyl bromide in 100% trifluoroethanol diminish rapidly with time even for early phases of the reaction. It has not, therefore, been possible to evaluate the rate constant for this reaction.

Solvolysis Products. The compositions of ether mixtures formed in the solvolyses of benzyl bromide and its *m*-fluoro and *p*-methyl analogs in various mixtures of ethanol and trifluoroethanol were established through analysis of samples removed from solutions of products, as generated in connection with the rate studies. In all cases the reactions had proceeded to at least 75% completion prior to removal of the samples. The 15 μl of each product solution which was withdrawn was subjected to gas–liquid chromatography on a 15-ft Carbowax 20 M column. An Aerograph Model A-90-P gas chromatograph was used with column, detector, and injector temperatures of 175, 230, and 210°, respectively. The flow rate of the carrier gas, helium, was 6.5 ml/10 sec. Under these conditions, retention times in minutes of the various ethers obtained as products were: *m*-$FC_6H_4CH_2OCH_2CF_3$ (12.0), $C_6H_5CH_2OCH_2CF_3$ (12.6), *p*-$CH_3C_6H_4CH_2OCH_2CF_3$ (14.2), $C_6H_5CH_2OCH_2CH_3$ (14.6), *m*-$FC_6H_4CH_2OCH_2CH_3$ (17.4), and *p*-$CH_3C_6H_4CH_2OCH_2CH_3$ (19.0). The identities of the emerging ethers were established through addition of small amounts (50–100 μl) of the ethers of interest to 1-ml portions of appropriate reaction product mixtures. Samples of the product mixtures were chromatographed before and after addition of the pure ethers, and observed increases in peak heights were interpreted as signifying that the peaks in question were characteristic of the added ethers. The relative molar quantities of ethyl and trifluoroethyl ethers in the product mixtures were calculated from the relative peak areas of the two in the chromatogram of those mixtures. The appropriateness of equating relative peak areas to product composition was confirmed by chromatographing ether mixtures of known composition.

Samples of the pure ethyl ethers were prepared through several hours of reflux of solutions of 0.1 mol of sodium and 0.05–0.07 mol of the appropriate benzyl chloride in 50 ml of ethanol. The product mixtures were diluted with water and extracted with diethyl ether. The ethers were recovered from the extracts by distillation. Benzyl ethyl ether, bp 88–90° (18–19 mm) (lit.[10] bp 184° (1 atm)), was obtained in 83% yield: nmr (CCl_4, chemical shifts downfield from $(CH_3)_4Si$) δ 1.16 (t, 3 H), 4.35 (s, 2 H), and 7.12 (m, arom, 5 H).

Anal. Calcd for $C_9H_{12}O$: C, 79.42; H, 8.82. Found: C, 79.07; H, 9.16.

p-Methylbenzyl ethyl ether, bp 92–94° (18–19 mm), was obtained in 80% yield: nmr (CCl_4) δ 1.12 (t, 3 H), 2.20 (s, 3 H), 3.35 (q, 2 H), 4.30 (s, 2 H), and 7.02 (m, arom, 4 H).

Anal. Calcd for $C_{10}H_{14}O$: C, 80.00; H, 9.33. Found: C, 79.85; H, 9.35.

m-Fluorobenzyl ethyl ether, bp 83–84° (18–19 mm), was obtained in 71% yield: nmr (CCl_4) δ 1.14 (t, 3 H), 3.40 (q, 2 H), 4.31 (s, 2 H), and 7.00 (m, arom, 4 H).

Anal. Calcd for $C_9H_{11}FO$: C, 70.14; H, 7.14. Found: C, 69.99; H, 6.98.

Samples of the 2,2,2-trifluoroethyl ethers were prepared by refluxing mixtures of 0.04–0.05 mol of the appropriate benzyl chloride, 0.06–0.1 mol of sodium carbonate, and 50 ml of 2,2,2-trifluoroethanol. The refluxing time varied from 18 hr in the reaction of *p*-methylbenzyl chloride to 2 weeks in the case of *m*-fluoro-

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(3) V. J. Shiner, Jr., W. Dowd, R. D. Fischer, S. R. Hartshorn, M. A. Kessick, L. Milakovsky, and M. W. Rapp, *J. Amer. Chem. Soc.*, **91**, 4838 (1969).

(4) G. A. Dafforn and A. Streitwieser, Jr., *Tetrahedron Lett.*, 3159 (1970).

(5) M. D. Bentley and J. A. Lacadie, *ibid.*, 741 (1971).

(6) L. M. Mukherjee and E. Grunwald, *J. Phys. Chem.*, **62**, 1311 (1958).

(7) E. S. Huyser, Dow Chemical Co., U. S. Patent 3,190,825 (1965); *Chem. Abstr.*, **65**, 8818a (1966).

(8) C. G. Swain and W. P. Langsdorf, *J. Amer. Chem. Soc.*, **73**, 2813 (1951).

(9) L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath, New York, N. Y., 1955, p 287.

(10) J. B. Senderens, *C. R. Acad. Sci.*, **178**, 1412 (1924).

Table I. Solvolysis Rate Constants of Benzyl Halides (RX) in Ethanol–Trifluoroethanol Mixtures

$10^3[RX]_i$,[a] M	Temp, °C	10^6k, sec^{-1}	Solvent, vol % trifluoroethanol
	p-$CH_3C_6H_4CH_2Br$		
13.8–15.7	50.0	32.4	0
10.5–11.8	65.0	132	0
	85.0	713[b]	0
14.8–33.0	50.0	41.5	20
15.9	65.0	153	20
	85.0	735[c]	20
21.8	85.0	960	50
17.0	50.0	104	80
15.2–17.7	65.0	354	80
	85.0	1540[d]	80
13.0–22.3	35.0	65.4	100
12.5–15.2	50.0	284	100
	85.0	5433[e]	100
	$C_6H_5CH_2Br$		
10.4–17.4	65.0	40.2	0
15.2–15.9	85.0	192	0
11.9	85.0	184	20
14.9–19.1	85.0	186	50
16.9–17.5	85.0	111	80
14.5–15.6	85.0	48.6	100
	m-$FC_6H_4CH_2Br$		
9.2–13.5	65.0	12.0	0
10.0–12.8	85.0	61.8	0
19.6	85.0	56.1	20
19.4	85.0	42.5	50
14.1	85.0	21.0	80
	p-$CH_3C_6H_4CH_2Cl$		
9.7–14.7	65.0	6.17	0
15.5–15.7	85.0	30.0	0
12.8–17.8	85.0	44.0	20
14.0–25.9	85.0	90.9	50
14.2–16.4	85.0	352	80
9.8–17.0	50.0	84.2	100
11.5–17.3	65.0	346	100
	85.0	1900[f]	100
	$C_6H_5CH_2Cl$		
	65.0	1.76[g]	0
11.4–16.8	85.0	8.89	0
10.9–16.5	100.0	26.7	0
12.3–19.7	85.0	10.1	20
16.2–18.0	85.0	13.6	50
14.4	85.0	11.8	80
14.0–18.0	85.0	9.9	100
	m-$FC_6H_4CH_2Cl$		
	65.0	0.429[h]	0
9.1–23.7	85.0	2.58	0
8.2–17.0	100.0	8.74	0
	85.0	2.40[i]	20
20.4	100.0	8.13	20
15.1	115.0	25.1	20
	85.0	2.20[j]	50
11.5	100.0	7.57	50
23.6	115.0	23.7	50
	85.0	1.67[k]	80
10.7	100.0	4.78	80
13.3	115.0	12.6	80
	85.0	0.235[l]	100
17.9	100.0	0.624	100
15.2–19.6	115.0	1.54	100
	p-$NO_2C_6H_4CH_2Br$		
10.5–13.7	65.0	4.13	0
	p-$CH_3OC_6H_4CH_2Br$		
	25.0	176[m]	0
13.6–22.7	35.0	699	0
	65.0	26,900[n]	0
	p-$NO_2C_6H_4CH_2Cl$		
9.50	65.0	0.175	0
	p-$CH_3OC_6H_4CH_2Cl$		
10.9	25.0	16.7	0
15.6	45.0	159	0
	65.0	1150[o]	0

[a] Where a range of values is listed, more than one run was conducted. The reported k value is the average of that calculated from the results of those runs. In most cases 2,6-lutidine was included in the rate samples to trap HBr; in no instance was there evidence that it had any influence on the solvolysis rate constant. [b] Calculated using an E_a value of 20.3 kcal/mol, as evaluated from solvolysis rate constants reported at other temperatures; $\Delta S^{\ddagger} = -19$ eu. [c] Calculated using $E_a = 18.9$ kcal/mol; $\Delta S^{\ddagger} = -22$ eu. [d] Calculated using $E_a = 17.7$ kcal/mol; $\Delta S^{\ddagger} = -24$ eu. [e] Calculated using $E_a = 19.4$ kcal/mol; $\Delta S^{\ddagger} = -17$ eu. [f] Calculated using $E_a = 20.5$ kcal/mol; $\Delta S^{\ddagger} = -16$ eu. [g] Calculated using $E_a = 19.5$ kcal/mol; $\Delta S^{\ddagger} = -30$ eu. [h] Calculated using $E_a = 21.6$ kcal/mol; $\Delta S^{\ddagger} = -26$ eu. [i] Calculated using $E_a = 21.6$ kcal/mol; $\Delta S^{\ddagger} = -26$ eu. [j] Calculated using $E_a = 21.9$ kcal/mol; $\Delta S^{\ddagger} = -26$ eu. [k] Calculated using $E_a = 18.6$ kcal/mol; $\Delta S^{\ddagger} = -36$ eu. [l] Calculated using $E_a = 17.3$ kcal/mol; $\Delta S^{\ddagger} = -43$ eu. [m] E. C. F. Ko and A. J. Parker, *J. Amer. Chem. Soc.*, **90,** 6447 (1968). [n] Calculated using $E_a = 25.2$ kcal/mol; $\Delta S^{\ddagger} = -21$ eu. [o] Calculated using $E_a = 21.2$ kcal/mol; $\Delta S^{\ddagger} = -11.5$ eu.

benzyl chloride. The products were isolated as described above for preparation of the ethyl ethers. Benzyl 2,2,2-trifluoroethyl ether, bp 84–85° (17–18 mm), was obtained in 69% yield: nmr (CCl_4) δ 3.66 (q, 2 H), 4.53 (s, 2 H), and 7.24 (s, arom, 5 H).

Anal. Calcd for $C_9H_9F_3O$: C, 56.85; H, 4.73. Found: C, 57.20; H, 4.89.

p-Methylbenzyl 2,2,2-trifluoroethyl ether, bp 95–96° (20–21 mm), was obtained in 73% yield: nmr (CCl_4) δ 2.20 (s, 3 H), 3.56 (q, 2 H), 4.40 (s, 2 H), and 7.00 (m, arom, 4 H).

Anal. Calcd for $C_{10}H_{11}F_3O$: C, 58.87; H, 5.39. Found: C, 59.28; H, 5.47.

m-Fluorobenzyl 2,2,2-trifluoroethyl ether, bp 85–86° (17–18 mm), was obtained in 46% yield: nmr (CCl_4) δ 3.70 (q, 2 H), 4.52 (s, 2 H), and 7.02 (m, arom, 4 H).

Anal. Calcd for $C_9H_9F_4O$: C, 52.05; H, 3.84. Found: C, 51.65; H, 3.73.

The analyses reported were made by Chemanalytics, Inc., Tempe, Arizona 85281.

Results

In Table I a summary is presented of the results of the rate studies of solvolysis of the benzyl bromides and chlorides of current interest in ethanol–2,2,2-trifluoroethanol mixtures. Because of wide variations in substrate reactivities it was not feasible to conduct all rate runs at a single temperature. In making comparisons of the differences in reactivity of benzyl bromide and chloride and their p-methyl and m-fluoro analogs as influenced by changes in medium composition, a reference temperature of 85.0° was chosen since a substantial number of the rate constants could be obtained by direct measurement at 85.0°. The remaining rate constants at 85° were calculated from activation energies as determined from the results of rate studies at other temperatures.

For use in correlating the variations in reactivity of the benzyl halides with medium changes, the influence of those same medium changes on the solvolysis rate constants of *tert*-butyl chloride (at 25°) were also in-

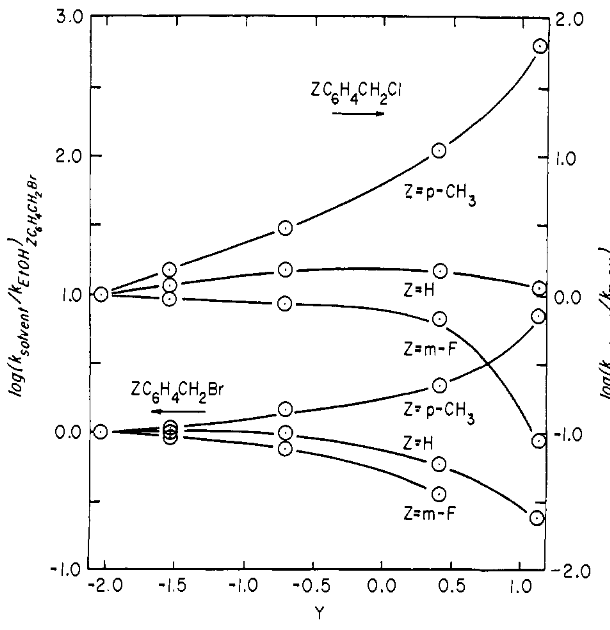

Figure 1. Variations in log ($k_{\text{solvent}}/k_{\text{EtOH}}$) at 85.0° with Y for solvolysis of several substituted benzyl halides. The upper set of three curves for the system $ZC_6H_4CH_2Cl$ is based on the right-hand ordinate scale. The lower set of three curves for the system ZC_6H_4-CH_2Br is based on the left-hand ordinate scale.

Table II. Rate Constants for Solvolysis of *tert*-Butyl Chloride in Ethanol–Trifluoroethanol Mixtures at 25°

10^3 × [*t*-BuCl]$_i$, *M*	10^6k, sec^{-1}	Solvent, vol % trifluoroethanol	Solvent *Y* value[a]
	0.086	0	−2.033
19.5	0.283	20	−1.515
16.0	2.39	50	−0.588
10.5	23.6	80	0.406
	130[b]	100	1.147

[a] Calculated using the rate constant reported by A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **78**, 2770 (1956), for solvolysis of *tert*-butyl chloride in 80% aqueous ethanol at 25.0° (9.26 × 10^{-6} sec^{-1}). [b] V. J. Shiner, Jr., W. Dowd, R. D. Fischer, S. R. Hartshorn, M. A. Kessick, L. Milakowsky, and M. W. Rapp, *J. Amer. Chem. Soc.*, **91**, 4838 (1969), report a value of 104 × 10^{-6} sec^{-1}.

Table III. Benzyl Halide Solvolysis Rates in Ethanol–Trifluoroethanol Mixtures Relative to Those in Ethanol (85.0°)

Solvent, vol % trifluoroethanol	$k_{\text{solvent}}/k_{\text{ethanol}}$ for $ZC_6H_4CH_2Br$, Z = *p*-CH$_3$	Z = H	Z = *m*-F	$k_{\text{solvent}}/k_{\text{ethanol}}$ for $ZC_6H_4CH_2Cl$, Z = *p*-CH$_3$	Z = H	Z = *m*-F
0	1.00	1.00	1.00	1.00	1.00	1.00
20	1.03	0.96	0.91	1.47	1.14	0.93
50	1.35	0.97	0.69	3.03	1.53	0.85
80	2.16	0.58	0.34	11.7	1.33	0.65
100	7.62	0.25		63.3	1.11	0.091

vestigated. From the results, which are summarized in Table II, *Y* values were calculated for the several ethanol–trifluoroethanol mixtures.

In Table III a list is given of the solvolysis rates of benzyl chloride and bromide and their *p*-methyl and *m*-fluoro derivatives in various ethanol–trifluoroethanol mixtures relative to their reaction rates in pure ethanol. In Figure 1 the logarithms of these ratios are plotted *vs.* the solvent *Y* values. Although this graphical analysis of the data may at first glance appear to be an application of the Grunwald–Winstein correlation (eq 2), linear plots are not obtained and in fact are not to be expected inasmuch as the nucleophilicities of the media used change radically with their composition. As revealed both by the tabulated data and the plots, the reactivity of *p*-methylbenzyl chloride is significantly increased as the medium changes from ethanol to trifluoroethanol, a fact which reflects the disposition of the halide as influenced by the electron releasing methyl group, to undergo bond breaking as opposed to bond making at the transition state.[11] The ring substituent of *m*-fluorobenzyl chloride is substantially electron withdrawing in character and correspondingly its solvolysis rate, in contrast to that of its *p*-methyl analog, drops off as the medium becomes less favorably constituted to engage in bond-making processes. Benzyl chloride is relatively insensitive to the changes in the capacity of the solvent to serve as an electrophile and as a nucleophile, which places it in that group of substrates which are intermediate in their disposition to undergo solvolysis by limiting and S$_N$2 like processes. The proportionate increase in reactivity of *p*-methylbenzyl bromide with increasing trifluoroethanol content of the medium is by no means as great as is observed for the corresponding chloride. In the case of benzyl bromide, the reactivity of the halide drops considerably as the medium is changed from ethanol to trifluoroethanol. That is, these two bromides respond less favorably (unfavorably in the case of benzyl bromide) to the change in solvent from ethanol to trifluoroethanol than do the two chlorides. The proportionate changes in reactivity of *m*-fluorobenzyl chloride and bromide to the solvent change are similar. Possible reasons for differences in the responses of the chlorides and their corresponding bromides to medium changes are considered below.

The preceding analysis of the influence of changes in medium and ring substituents on substrate reactivity deserves amplification in recognition of the fact that it is now rather generally accepted that ion pair formation along the reaction coordinate is characteristic of solvolytic displacements.[12–14] Certainly this is the case for reactions in which the substrates form relatively stable carbonium ions. There is good evidence

[11] For evidence of the high degree of effectiveness of trifluoroethanol as a hydrogen-bonding solvent in promoting solvolytic processes as reflected in the rates of reaction of 7-methyl-7-norbornyl tosylate in trifluoroethanol–water mixtures see: D. Sienko, I. Szele, and M. Tornic, *Tetrahedron Lett.*, 1827 (1972).

[12] W. G. Young, S. Winstein, and H. L. Goering, *J. Amer. Chem. Soc.*, 73, 1958 (1951).

[13] S. Winstein and G. C. Robinson, *ibid.*, 80, 169 (1958).

[14] S. Winstein, B. Appel, R. Baker, and A. Diaz, *Chem. Soc., Spec. Publ.*, No. 19, 109 (1965).

at hand that two types of ion pairs, the intimate or tight ion pair and the solvent separated ion pair,[13–15] may precede a carbonium ion on the reaction coordinate (eq 4) and that the solvent may enter the picture as a

$$\mathrm{RX} \rightleftarrows \underset{\substack{\text{intimate}\\ \text{ion pair}}}{\mathrm{R^+X^-}} \rightleftarrows \underset{\substack{\text{solvent}\\ \text{separated}\\ \text{ion pair}}}{\mathrm{R^+\|X^-}} \rightleftarrows \mathrm{R^+} + \mathrm{X^-} \tag{4}$$

nucleophile at any of the several stages of reaction, depending on the nature of the substrate and solvent. Sneen and Larsen[16] have, in fact, proposed that all nucleophilic displacements, even those considered to be truly SN2 like in character (*e.g.*, those involving methyl halides as substrates), proceed by a mechanism in which the nucleophile attacks an ion pair in the slow step.

In reviewing the course of benzyl substrate solvolyses, Shiner[17,18] has presented arguments based on the effect of α deuteration on reactivity[19] that in trifluoroethanol–water mixtures of high trifluoroethanol content *p*-methylbenzyl chloride solvolyzes by a process in which a tight ion pair is converted to a solvent-separated ion pair in the slow step.[3] Presumably the solvent does not become involved as a nucleophile until later non-rate-determining stages of reaction. Shiner reviews other evidence (*e.g.*, diminution in the magnitude of the α-deuterium effect) that as the solvent becomes more nucleophilic and as the substrate is altered so that the corresponding carbonium ion is less stable, as occurs when the substrate is changed to benzyl brosylate and to its *p*-CF_3 and *p*-NO_2 derivatives, the product-forming step shifts to one in which the solvent, functioning as a nucleophile, attacks the tight ion pair in a process which may be rate limiting. In the extreme case the reaction may become truly SN2 in character. That is, as the substrate becomes less prone to form a carbonium ion, as in the present work when it is changed from *p*-methylbenzyl halide to benzyl and to *m*-fluorobenzyl halide, involvement of the solvent as a nucleophile will occur earlier along the reaction coordinate. In this regard values of $\log (k_{\mathrm{CF_3CH_2OH}}/k_{\mathrm{EtOH}})$ appear to be of potential use in establishing in a relative sense when such involvement occurs. By way of illustration, the values for *tert*-butyl chloride, *p*-methylbenzyl chloride, benzyl chloride, and *m*-fluorobenzyl chloride at 85° are respectively 3.2, 1.8, 0.0, and -1.0.

Recently Bentley, Schadt, and Schleyer[20] have developed a method for evaluating solvent nucleophilicity (N), as defined in eq 5 (*cf.* eq 1 and 2), which depends

$$\log (k/k_0) = lN + mY \tag{5}$$

on the use of two reference substrates. The one, 2-adamantyl tosylate, is used as a model of a compound which solvolyzes without involvement of the solvent as a nucleophile in rate-determining processes.[21] The other, methyl tosylate, is selected as a reference standard of a substrate displaying SN2 like behavior. At the suggestion of a referee, measurements, to be regarded as preliminary, have been conducted to determine the so called N_{BS} values (as defined by Bentley, Schadt, and Schleyer[20]) of various mixtures of trifluoroethanol with ethanol. Solvolysis rate constants for methyl tosylate ($k_{50°}$) determined in this connection are 0.83×10^{-6}, 3.5×10^{-6}, and 6.3×10^{-6} sec^{-1} respectively in 80, 50, and 20% trifluoroethanol (in trifluoroethanol–ethanol mixtures). Corresponding values of N_{BS} are -1.62, -0.63, and -0.09 as compared with the N_{BS} value of $+0.09$ for ethanol as reported by Bentley, Schadt, and Schleyer.[20] Rate constants for reactions in mixtures of high trifluoroethanol content (80%) were observed to drift downward somewhat with time. A value of $N_{\mathrm{BS}} = -2.1$ is therefore assigned tentatively to pure trifluoroethanol on the grounds that good experimental evidence exists that this solvent is closely comparable in nucleophilicity to formic acid.[21,22] There is a fair linear correlation between Y and N_{BS} values for ethanol–trifluoroethanol mixtures, and when the ordinate of Figure 1 is changed to N_{BS}, the plots obtained are similarly shaped but in a mirrored orientation to those shown for cases in which Y is used as the ordinate.

The Products of Solvolysis of the Benzyl Bromides. The results of the study of the influence of changes in composition of ethanol–trifluoroethanol solvent mixtures on the composition of products obtained in the reaction of benzyl bromide and its *m*-fluoro and *p*-methyl derivatives are summarized in Table IV. The *m*-fluoro bromide displays a strong disposition to form the ethyl ether, this being the case even when the medium is 80 vol % trifluoroethanol. This is consistent with the view that the halide is prone to solvolyze with early involvement of solvent as a nucleophile along the reaction coordinate, a process in which ethanol (rather than trifluoroethanol) apparently participates preferentially even when it is a minor component of the solvent. As the substrate is changed from *m*-fluorobenzyl bromide to benzyl bromide and to its *p*-methyl derivative, the reactions become less selective as concerns the production of ethyl ether (in preference to the trifluoroethyl ether). It is noteworthy, however, that in a mixture which is 50% by volume trifluoroethanol, *p*-methylbenzyl bromide reacts to form mainly the ethyl ether.

Table IV. Distribution of Products of Solvolysis of Benzyl Bromides ($ZC_6H_4CH_2Br$) in Ethanol–Trifluoroethanol Mixtures at 85.0°

Solvent, vol % trifluoroethanol	Mole fraction of trifluoroethyl ether in product ($ZC_6H_4CH_2OCH_2CF_3$)/($ZC_6H_4CH_2OCH_2CF_3$ + $ZC_6H_4CH_2OCH_2CH_3$)		
	Z = *m*-F	Z = H	Z = *p*-CH_3
0	0.00	0.00	0.00
20	0.00	0.00	0.00
50	0.00	0.00	0.04
80	0.00	0.13	0.41
100	1.00	1.00	1.00

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(15) H. L. Goering and H. Hopf, *J. Amer. Chem. Soc.*, **93**, 1224 (1971).

(16) R. A. Sneen and J. W. Larsen, *ibid.*, **91**, 362, 6031 (1969).

(17) V. J. Shiner, Jr., "Isotope Effects in Chemical Reactions," C. J, Collins and N. S. Bowman, Ed., Van Nostrand-Reinhold, New York, N. Y., 1970, pp 90–159.

(18) For a pertinent review of the role of ion pairs in processes which fall between SN1 and SN2 extremes see: D. J. Raber and J. M. Harris, *J. Chem. Educ.*, **49**, 60 (1972).

(19) V. J. Shiner, Jr., M. Rapp, and H. R. Pinnick, Jr., *J. Amer. Chem. Soc.*, **92**, 232 (1970).

(20) T. W. Bentley, F. L. Schadt, and P. v. R. Schleyer, *ibid.*, **94**, 992 (1972).

(21) J. L. Fry, C. J. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *ibid.*, **92**, 2538 (1970).

(22) M. D. Bentley and J. A. Lacadie, *Tetrahedron Lett.*, 741 (1971).

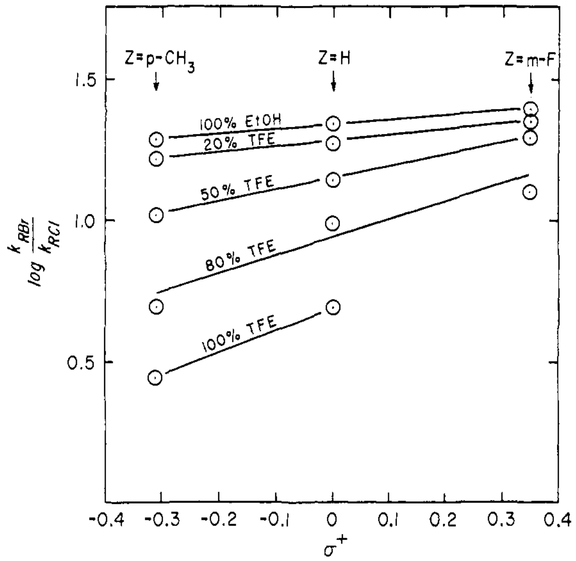

Figure 2. Changes in log (k_{RBr}/k_{RCl}) with σ^+ for the system $ZC_6H_4CH_2X$ in ethanol–trifluoroethanol solutions (EtOH–TFE) at 85.0°.

This again is a reflection of the relative nucleophilicities of the solvent components, in this instance most likely a manifestation of differences in their capacities to compete for an intermediate in which there is significant development of positive charge at the reaction center. A more definitive statement concerning the relationship between solvent composition and the structure of the species which solvent attacks in product-forming steps is not justified on the basis of evidence currently available.[23]

Bromide–Chloride Rate Ratios as a Function of Solvent Composition. When the solvent is pure ethanol, the changes in reactivity of substituted benzyl bromides with changes in ring substituents are more or less parallel to those for the corresponding benzyl chlorides. This is illustrated in Table V which summarizes the rate studies of ethanolysis (65°) of benzyl bromide and chloride and their *p*-nitro, *m*-fluoro, *p*-methyl, and *p*-methoxy derivatives. The values of log (k_{RBr}/k_{RCl}) are relatively insensitive to changes in σ^+ values of the ring substituents; the Hammett ρ value, as determined from the slope of a plot of log (k_{RBr}/k_{RCl}) *vs.* σ^+, is very small (about 0.1).

Table V. Changes in Log (k_{RBr}/k_{RCl}) with σ^+ for the System $ZC_6H_4CH_2X$ in Ethanol (65.0°)

Z	10^6k_{RBr}, sec^{-1}	10^6k_{RCl}, sec^{-1}	Log (k_{RBr}/k_{RCl})	$\sigma^{+\,a}$
p-NO$_2$	3.71	0.192	1.286	0.79
m-F	11.2	0.443	1.403	0.35
H	36.5	1.66	1.342	0.00
p-CH$_3$	113	5.88	1.284	−0.31
p-CH$_3$O	24,400	962	1.404	−0.78

[a] H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4879 (1958); Y. Okamoto, T. Inukai, and H. C. Brown, *ibid.*, **80**, 4969 (1958).

As the trifluoroethanol content of the medium is increased, the bromide–chloride ratio appears to become increasingly sensitive to changes in the ring substituent. This is illustrated in Figure 2 in which log (k_{RBr}/k_{RCl}) values for reaction of the benzyl halides and their *m*-fluoro and *p*-methyl derivatives in various ethanol–trifluoroethanol mixtures (85°) are plotted *vs.* the σ^+ values of the ring substituents. As mentioned above, the slope of the plot (ρ) for reaction in pure ethanol is of the order of 0.1; the slope for reaction in pure trifluoroethanol is of the order of 0.8.

In accounting for the drop in values of k_{RBr}/k_{RCl} which accompanies the change in ring substituent from *m*-F to *p*-CH$_3$ in a medium of high trifluoroethanol content, the relative importance of bond breaking at the transition state (without involvement of the solvent as a nucleophile) for solvolysis of the latter again comes to mind. It is conceivable that in a solvent which is an unusually effective hydrogen bonder, *i.e.*, trifluoroethanol, *p*-methylbenzyl chloride may approach *p*-methylbenzyl bromide in reactivity because of differences in disposition of chlorine and bromine to form hydrogen bonds.[24,25] Yet ethanol is functionally capable of acting as an electrophile through hydrogen bonding in solvation processes, though granted it is less effective than trifluoroethanol in this capacity. Nonetheless, the fact that the ratio k_{RBr}/k_{RCl} for reaction in ethanol does not change greatly as the substrate is changed from *m*-fluoro to *p*-methylbenzyl halide suggests that the difference in susceptibility of bromine and chlorine to engage in hydrogen bonding is not primarily responsible for the drop in that ratio for solvolysis when there is a substantial amount of trifluoroethanol in the medium. Alternatively, it is proposed that the change in slope of the plots of Figure 2 with increasing trifluoroethanol content of the medium is associated with ion pair return. Such return is more characteristic of reactions of bromides than of chlorides and is encountered in situations in which the medium, in this instance trifluoroethanol, is a poor nucleophile and in reactions in which bond breaking at the transition state is extensive.[26,27] It is presumed that the phenomenon of ion pair return in the present context is related to return of an intimate ion pair to starting material. This kind of return should be most characteristic of the *p*-methylbenzyl halides and least so of the *m*-fluoro derivatives, inasmuch as solvent involvement as a nucleophile must occur early along the reaction coordinate in solvolyses of the latter.[28] The lower sensitivity of the k_{RBr}/k_{RCl} ratios for the *m*-fluoro-

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[23] In this connection it is of interest to note that as an outgrowth of studies of the rates and products of solvolyses of a series of 2-adamantyl arenesulfonates, it appears that an appropriate means for making such diagnoses may be developed. The slope of the so called sensitivity–stability plot may be indicative of the kind of ion pair, intimate or solvent separated, which is the product precursor. See J. M. Harris, J. F. Fagan, F. A. Walden, and D. C. Clark, *Tetrahedron Lett.*, 3023 (1972).

[24] A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, 79, 1608 (1957).

[25] Ratios of k_{RBr}/k_{RCl}, unlike those of k_{ROTs}/k_{RBr}, do not vary as widely nor do they range from relatively low to relatively high values as substrates are changed from primary to secondary to tertiary. These differences in responses of the ratios to the structural changes in question have been ascribed, among other causes, to the preference of chlorine over bromine to engage in hydrogen bonding. See H. M. R. Hoffmann, *J. Chem. Soc.*, 6753 (1965); R. C. Bingham and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 3189 (1971).

[26] A. H. Fainberg and S. Winstein, *ibid.*, 79, 1602 (1957).

[27] For other evidence of internal return in trifluoroethanolysis see: (a) J. R. Hazen, *Tetrahedron Lett.*, 1897 (1969); (b) D. D. Roberts *J. Org. Chem.*, 37, 1510 (1972).

[28] *Cf.* ref 14 and ref 17, p 110.

benzyl halides to changes in medium, as compared with that for the *p*-methylbenzyl halides, is regarded as an indication that activation in the reactions of the former occurs without much stretching of the carbon–halogen bonds and with correspondingly close coordination of the solvent as a nucleophile.[29]

[29] J. J. Frisone and E. R. Thornton, *J. Amer. Chem. Soc.*, 90, 1211 (1968).

Studies of Solvent Effects on the Nature of Ion Pair Interaction in 9-(2-Hexyl)fluorenyllithium[1a]

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Abstract: The hydrocarbon solubility of 9-(2-hexyl)fluorenyllithium (**1**) permits evaluation of its aggregation and spectral behavior in nonpolar solvents, which is compared with that in polar solvents. Ebulliometry shows **1** to be a dimer in cyclohexane at 25° over the concentration range of 0.01 to 0.1 *m*. A finite equilibrium between monomeric and dimeric ion pairs over the concentration range 0.002 to 0.04 *m* is indicated in THF at 25°. Lithium-7 and proton nmr spectra recorded in polar and nonpolar solvents reveal a regular trend of increasing cation–anion interaction with decreasing solvent polarity. The ^{7}Li chemical shifts cover the largest range and those in hydrocarbon solution are found to be the farthest upfield of ^{7}Li resonances reported to date. The electronic spectrum of **1** in ether solvents has previously been reported and found consistent with the description of contact and solvent-separated ion pairs. An apparently striking departure from the predictions of this description is observed in the electronic spectrum of **1** in hydrocarbon solvents. The band associated with the contact ion pair of **1** occurs in diethyl ether at 358 nm and that associated with the solvent-separated ion pair occurs in tetrahydrofuran at 387 nm. In hydrocarbon solvents, however, this absorption band occurs at 368 nm. Possibilities for this discrepancy are considered. Of note is that **1** is a nonalternant π system; the irregular spectral behavior of perturbed nonalternants is a significant factor for consideration. As an alternative, a sandwich structure for **1** is considered reasonable in those solvents where it is found as a contact ion pair.

Continuing studies of carbon–lithium bonding[2–4] required an organolithium compound which is appreciably soluble in hydrocarbons and whose carbanion is geometrically constrained to planar sp^2 hybridization. Fluorenyllithium,[5,6] although geometrically suitable, does not have the required solubility in hydrocarbons. Examination of the recently investigated[7] 9-(2-hexyl)fluorenyllithium (**1**) showed it to meet the hydrocarbon solubility requirement.[8] This paper deals with information obtained through studies of electronic spectra and lithium-7 and proton magnetic resonance of **1** in hydrocarbon, ether, and mixed hydrocarbon–ether solutions and of colligative properties of **1** in tetrahydrofuran (THF) and cyclohexane.

Intensive investigation of fluorenyl carbanions in ether solvents[5,7] has established contact and solvent-separated ion pair type species. The intent here is to reveal the nature of the ion pair species in hydrocarbon and hydrocarbon–ether mixed solutions. Such data for species that have not contacted ether are lacking. Of note is that **1** is a nonalternant molecule.[9] Other examined systems are odd alternants.[3,4] Although the electronic spectra of the latter type molecules behave in a regular way to steric strain[10] and inductive effects[11] (*i.e.*, local charge density changes), the former do not.[12]

Experimental Section

Glassware and syringes were oven dried at 110° overnight and allowed to cool either under vacuum or under inert gas. Solution transfers were made with gas-tight syringes. All chemical reactions were carried out on a vacuum line under positive argon pressure.[13] Precautions were taken to shield reactions from direct exposure to light. Melting points, obtained on a Thomas Hoover capillary melting point apparatus, are uncorrected.

Materials. 9-Ethylidenefluorene (Aldrich Chemical Co.) was recrystallized from absolute ethanol and freed of residual solvent under vacuum. The recrystallized solid was stored under argon in the dark in a sealed container at −10° until use: mp 102–104° [lit. 102–104,[14a] 104–105° [14b]]; uv max (abs C_2H_5OH) sh 224 (ϵ 39,400), 230 (46,300), sh 236 (30,700), 247 (31,700), 256 (46,300), 272 (13,400), 280 (14,400), 297 (10,400), sh 307 (8,200), 312 (9,700), sh 350 nm ($\sim$25) [lit.[15] 229.5 (ϵ 50,000), 247.0 (33,100), 256.0 (46,800), 270.0 (14,500), 280.0 (15,500), 297.0 (11,800), 311.0 nm

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[1] (a) Presented in part at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 1971, Abstract ORGN-184; (b) Midland Macromolecular Institute, Midland, Mich. 48640.

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[8] Analogously, the alkyl substituent in 1,1-diphenylhexyllithium (**2**) induces hydrocarbon solubility, contrasted with the relatively hydrocarbon-insoluble diphenylmethyllithium.[4]

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