270. *Polar Effects of Alkyl Groups in the Absence of Vicinal Steric Effects.*

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In replacement reactions of benzyl, phenyl and some related compounds the effect of a *p*-t-butyl group is similar to, but less than, that of a *p*-methyl group whether supply or removal of electrons is required. A large differentiation between the effects of these two groups on changing from bimolecular to unimolecular transition states is demonstrated and confirms the importance of the polarisability of alkyl groups.

A tentative explanation is given for exceptional behaviour of 4-alkylbenzyl fluorides in reaction with ethoxide ion.

WE report a further study of the polar effects of methyl and t-butyl groups in nucleophilic replacement reactions where vicinal steric factors are absent.

Reaction rates and conditions are summarised in Table 1. Reactions (1)—(8) are of the type $ArCabX + \colon Y \longrightarrow ArCabY + \colon X$ (where the dots represent electrons). Reactions (1)—(7) are of the second order, as has been shown for the analogous reactions

TABLE 1. *Reaction rates showing polar effects of* 4-*alkyl groups* (k_2 *in sec.*$^{-1}$ *mole*$^{-1}$ *l.*; k_1 *in sec.*$^{-1}$).

No.	Reaction	Solvent	Temp. (° c)	Rates for various *p*-substituents		
				H	Me	Bu^t
1	R·C$_6$H$_4$·CH$_2$Br + I$^-$	Me$_2$CO	0·0	10^2k_2 = 2·89	4·23	3·92
2	R·C$_6$H$_4$·CH$_2$Br + Bu^{t}O$^-$	Bu^{t}OH	60·0	10^3k_2 = 3·75	5·03	4·46
3	R·C$_6$H$_4$·CH$_2$Br + EtO$^-$	EtOH	25·1	10^3k_2 = 1·84	2·73	2·54
4	R·C$_6$H$_4$·CH$_2$Cl + EtO$^-$	EtOH	25·1	10^5k_2 = 3·72	5·85	5·45
5	R·C$_6$H$_4$·CH$_2$F + EtO$^-$	EtOH	118·0	10^4k_2 = 5·38	5·49	7·02
6	R·C$_6$H$_4$·CH$_2$·N$^+$C$_5$H$_5$ + EtO$^-$	EtOH	20·0	10^4k_2 = 4·01	2·02	2·77
7	R·C$_6$H$_4$·CO$_2$Et + OH$^-$	85% w/w EtOH–H$_2$O	25·1	10^4k_2 = 7·18	3·13	4·42
8	R·C$_6$H$_4$·COCl + EtOH	EtOH	0·0	10^5k_1 = 7·89	4·49	5·26
9	R·C$_6$H$_2$(NO$_2$)$_2$Cl * + EtO$^-$	EtOH	50·0	10^3k_2 = 14·7	2·59	4·55
10	R·C$_6$H$_4$·CH$_2$Br + H$_2$O	H·CO$_2$H	25·1	10^7k_1 = 3·68	213	103

* 1-Chloro-2,6-dinitro.

of 4-alkylbenzyl bromides with pyridine in acetone [1] and of benzyl chloride with hydroxide ion in aqueous ethanol,[2] and for hydrolysis of ethyl *p*-alkylbenzoates.[3] In the solvolytic process (8), ethanol is in large excess and the reaction is of the first order. It is probable, however, that, as pointed out by Hughes,[4] this change is also substantially bimolecular. Reaction (10) is a first-order replacement at a saturated carbon atom under conditions especially conducive to a unimolecular mechanism.[5] It was included to compare the effects of the two main substitution mechanisms, S_N2 and S_N1. Reaction (9) is a second-order nucleophilic replacement at an aromatic carbon atom.

Since the preliminary communication of these results by Bevan, Hughes, and Ingold,[6] a number of reasons have been suggested for the varying order of effects of alkyl groups. Good summaries are provided by Schubert and Sweeney [7] and by Berliner and Chen.[8]

Reactions (1)—(4) are facilitated by electron-release; 4-methyl substituents in the benzyl group increase the reaction rate; *p*-t-butyl substituents also increase it but to a smaller extent (see Table 1).

In reactions (7)—(9) the rate is generally enhanced by electron-withdrawal; a *p*-methyl group retards reaction; a *p*-t-butyl group also does this, but not to the same extent.

Reaction (10), compared with, say, reaction (3), shows clearly the considerable polarisability of alkyl groups when called upon to supply electrons to a strongly electron-demanding reaction in which the transition state is, or approximates to, a carbonium ion. Here again, what a *p*-t-butyl group does a *p*-methyl group does better.

Reaction (6) was shown, at least for the first 30% of change, to be of the first order with respect to each of the reagents (see Tables 2 and 3).

TABLE 2. *Determination of k_2 (l. sec.$^{-1}$ mole^{-1}) for reactions of benzylpyridinium bromide and ethoxide ion in absolute ethanol.*

Initially, [bromide] = 0·0277M, [EtO$^-$] = 0·0554M. Temp. 20·04°. Concns. in ml. of 0·01388N-NaOH per 4·98 ml. sample.

Time (min.)	0	127·5	140·5	161	175·5	186·5	203·0	312·5	339·5
[NaOH]	19·68	18·31	18·17	18·01	17·81	17·78	17·57	16·76	16·60
[Bromide]	9·74	8·37	8·23	8·07	7·87	7·84	7·63	6·82	6·66
10^4k_2	—	3·75	3·79	3·71	3·88	3·73	3·87	3·68	3·72

Over 18—36% of reaction, average $k_2 = 3·77 \times 10^{-4}$ l. mole^{-1} sec.$^{-1}$.
k_2 at 20·0° = $3·77 \times 10^{-4}$ l. sec.$^{-1}$ mole^{-1}.
k_2 at 35·0° = $1·108 \times 10^{-3}$ l. sec.$^{-1}$ mole^{-1}.
$E = 12·8$ kcal. mole^{-1}; $\log_{10} B = 6·2$.

TABLE 3. *Independence of k_2 (l. sec.$^{-1}$ mole^{-1}) for reactions of benzylpyridinium bromide and ethoxide ion in absolute ethanol of the concentration of the reagents.*

[Bromide] (M)	[NaOEt] (M)	10^4k_2 at 20·04°
0·0400	0·0400	3·92
0·0277	0·0554	3·77
0·0554	0·0277	3·78

No method could be evolved for a satisfactory estimation of pyridine under the conditions of the reaction, so that the production or otherwise of benzyl ethyl ether was used as a criterion of whether reaction (6) involved replacement of —$^+NC_5H_5$ by OEt, in a manner analogous to (1)—(5), or attack by ethoxide ion on the pyridine ring.

After 25% reaction no benzyl ethyl ether was detected, by a method capable of estimating this compound in the reaction medium.

An alternative possibility involves attack on the pyridine ring (cf. Bergstrom [9] and

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[1] Baker and Nathan, *J.*, 1935, 1844.

[2] Olivier and Weber, *Rec. Trav. chim.*, 1934, **53**, 869.

[3] Various authors; reported by Day and Ingold, *Trans. Faraday Soc.*, 1941, **37**, 686.

[4] Hughes, *Trans. Faraday Soc.*, 1941, **37**, 603.

[5] Bateman and Hughes, *J.*, 1940, 945.

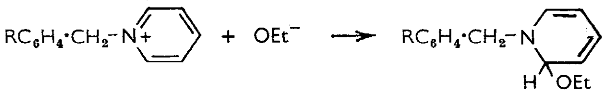
[6] Bevan, Hughes, and Ingold, *Nature*, 1953, **171**, 301.

[7] Schubert and Sweeney, *J. Org. Chem.*, 1956, **21**, 119.

[8] Berliner and Chen, *J. Amer. Chem. Soc.*, 1958, **80**, 343.

[9] Bergstrom, *Chem. Rev.*, 1944, **35**, 77.

Elderfield [10]). Electron release from R will inhibit the formation of structure (II), and the effects of alkyl groups on the rate of ring fission involving this as an intermediate are consistent with the usual order of electron release, *viz.*, *p*-methyl > *p*-t-butyl > H.



(II)

This observation removes the apparent exception noted by Streitwieser [11] to the general picture of the accelerating effect of *p*-methyl groups on S_N2 reactions at a benzyl carbon atom.

One further point concerns reaction (5), in which the usual order of electron release Me > Bu^t > H has changed to Bu^t > Me ~ H, with Me exerting only a very small effect (cf. Miller and Bernstein [12]). Further work is required before this result can properly be assessed, but it may be connected with entropy effects resulting from the relatively large solvation energy of the fluoride ion and the fact that the reaction was studied some hundred degrees above that for the analogous bromides and chlorides. Under these conditions it is possible that solvent effects would not be sufficient to reverse the inductive order of electron-release from alkyl groups by steric hindrance of solvation of the transition state.

EXPERIMENTAL

Materials.—All solids used in the kinetic measurements were recrystallised to constant m. p. from the appropriate solvent; liquids were purified by repeated distillation at reduced pressure.

Benzyl bromide. A commercial sample was dried (Na_2CO_3) and fractionated. The fraction boiling at 192° (uncorr.) was distilled at reduced pressure and stored in glass ampoules (b. p. 84°/13 mm.) (Found: Br, 46·5. Calc. for C_7H_7Br: Br, 46·8%).

4-*Methylbenzyl bromide.* *p*-Xylene was brominated by Atkinson and Thorpe's method.[13] The fraction of the product of b. p. 210—220° had m. p. 35·3° (from ethanol) (Found: Br, 43·1. Calc. for C_8H_9Br: Br, 43·2%).

4-*t-Butylbenzyl bromide.* *p*-t-Butyltoluene, obtained by Verley's method, was brominated and the named compound isolated as described by Baker and Nathan;[1] it had m. p. 15·2° (from ethanol) (Found: Br, 35·2. Calc. for $C_{11}H_{15}Br$: Br, 35·3%).

Benzyl chloride. A commercial sample, dried (Na_2CO_3) and fractionated, had b. p. 69°/15 mm. (Found: Cl, 28·3. Calc. for C_7H_7Cl: Cl, 28·1%).

4-*Methylbenzyl chloride.* *p*-Xylene (100 g.), sulphuryl chloride (90 g.), and benzoyl peroxide (0·5 g.) in carbon tetrachloride (100 g.) were refluxed on a water-bath for 2 hr., the carbon tetrachloride and excess of hydrocarbon were distilled off, and the residue was fractionated; the chloride had b. p. 92°/20 mm. (Found: Cl, 24·8. Calc. for C_8H_9Cl: Cl, 25·3%).

4-*t-Butylbenzyl chloride.* t-Butylbenzene was chlorinated by Sommelet's method.[14] The product was fractionated, boiling at 114·5°/10 mm. (Found: C, 72·3; H, 8·8; Cl, 19·6. Calc. for $C_{11}H_{15}Cl$: C, 72·3; H, 8·22; Cl, 19·5%).

Ethyl benzoate. A commercial sample, shaken with 15% aqueous potassium carbonate and fractionated, had b. p. 98°/19 mm., n_D^{25} 1·5043.

Ethyl p-*toluate.* Prepared from *p*-toluic acid by a method analogous to the above, the ester had b. p. 122°/18 mm., n_D^{25} 1·5060.

Ethyl p-*t-butylbenzoate.* *p*-t-Butylbenzoic acid, prepared by oxidation of *p*-t-butyltoluene with chromic acid,[15] was treated as for ethyl *p*-toluate. It gave the ester, b. p. 145°/7 mm., n_D^{25} 1·4996.

Benzoyl chloride. A commercial specimen (50 g.), refluxed with thionyl chloride (50 g.) for

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[10] Elderfield, " Heterocyclic Compounds," Wiley, New York, 1950, Vol. I, p. 421.
[11] Streitwieser, *Chem. Rev.*, 1956, **56**, 571.
[12] Miller and Bernstein, *J. Amer. Chem. Soc.*, 1948, **70**, 3600.
[13] Atkinson and Thorpe, *J.*, 1907, **91**, 1695.
[14] Sommelet, *Compt. rend.*, 1913, **157**, 1445.
[15] Hickinbottom, " Reactions of Organic Compounds," Longmans, 1936, p. 34.

2 hr. and twice fractionated, had b. p. 51·5°/2 mm. (Found: Cl, 25·2. Calc. for C_7H_5OCl: Cl, 25·3%).

p-*Toluoyl chloride.* This had b. p. 82°/5 mm. (Found: Cl, 22·8. Calc. for C_8H_7OCl: Cl, 22·9%).

p-*t-Butylbenzoyl chloride.* *p*-t-Butylbenzoic acid, treated as for benzoyl chloride, gave the chloride, b. p. 114°/5 mm. (Found: Cl, 18·1. Calc. for $C_{11}H_{13}OCl$: Cl, 18·0%).

1-*Benzylpyridinium bromide.* Equimolar proportions of purified pyridine and benzyl bromide were refluxed in absolute acetone. The precipitated crystals were filtered at the pump, washed repeatedly with acetone, and dried under vacuum (Found: Br, 31·8. Calc. for $C_{12}H_{12}NBr$: Br, 32·0%).

1-4′-*Methylbenzylpyridinium bromide.* This was prepared analogously (Found: Br, 30·2. Calc. for $C_{13}H_{14}NBr$: Br, 30·1%).

1-4′-*t-Butylbenzylpyridinium bromide* was prepared similarly from *p*-t-butylbenzyl bromide (Found: Br, 26·0. $C_{16}H_{20}Br$ requires Br, 26·1%).

1-*Chloro*-2,6-*dinitrobenzene.* *o*-Nitrophenol was nitrated by Kulikow and Panowa's method [16] and the 2,6-dinitrophenol was chlorinated by Kubota's method; [17] the *product* had m. p. 88·5° (from absolute ethanol) (Found: C, 36·4; H, 1·6; Cl, 17·2; N, 13·4. $C_6H_3O_4N_2Cl$ requires C, 36·4; H, 1·5; Cl, 17·5; N, 13·8%).

1-*Chloro*-4-*methyl*-2,6-*dinitrobenzene.* Acet-*p*-toluidide was nitrated by the method of Brady *et al.*,[18] and the resulting 2,6-dinitro-*p*-toluidine was converted into the *chloro-compound* by Welch's method; [19] this had m. p. 114° (from absolute ethanol) (Found: C, 39·1; H, 2·5; Cl, 16·6; N, 12·8. $C_7H_5O_4N_2Cl$ requires C, 38·8; H, 2·3; Cl, 16·4; N, 12·9%).

1-*Chloro*-2,6-*dinitro*-4-*t-butylbenzene.* Friedel–Crafts reaction between phenol and t-butyl chloride gave *p*-t-butylphenol which was nitrated by Studer's method,[20] and chlorinated as in the case of 2,6-dinitrophenol; the *product* had m. p. 116·5° (from absolute ethanol) (Found: C, 46·6; H, 4·5; Cl, 13·7; N, 10·7. $C_{10}H_{11}O_4N_2Cl$ requires C, 46·2; H, 4·6; Cl, 13·7; N, 10·8%).

4-*Alkylbenzyl fluorides.* These compounds were prepared by the method of Ingold and Ingold.[21] Contrary to the findings of Bernstein, Roth, and Miller,[22] yields of 60% were obtained if before decomposition the quaternary fluoride was thoroughly anhydrous as indicated to be necessary by the former authors.

Benzyl fluoride, prepared from benzyl bromide by the above method, had b. p. 39°/13 mm., n_D^{20} 1·4890 (Ingold and Ingold [21] give n_D^{20} 1·4892) (Found: C, 76·9; H, 6·5; F, 16·9. Calc. for C_7H_7F: C, 76·4; H, 6·4; F, 17·2%).

4-Methylbenzyl fluoride, prepared analogously, had b. p. 60°/14 mm., n_D^{20} 1·4920 (Bernstein *et al.*[22] give n_D^{20} 1·4918) (Found: C, 76·9; H, 7·8; F, 15·1. Calc. for C_8H_9F: C, 77·4; H, 7·3; F, 15·3%).

4-*t-Butylbenzyl fluoride*, prepared analogously, had b. p. 90°/12 mm. (Found: C, 79·5; H, 9·1; F, 11·4. $C_{11}H_{15}F$ requires C, 79·5; H, 9·0; F, 11·4%).

Acetone. "AnalaR" acetone was purified by Conant and Kirner's method.[23]

Ethyl alcohol. Commercial absolute ethyl alcohol was dried by Manske's method.[24]

t-Butyl alcohol. Crystalline commercial t-butyl alcohol (2 l.) was warmed on a water-bath until about 0·5 l. was molten. This volume was rejected and the remainder was refluxed with sodium (5 g.) and distilled through an all-glass apparatus protected from moisture. An initial fraction of 150 ml. was rejected and the remainder, leaving an end-fraction of 150 ml., boiled at 82·8°/760 mm.

Kinetic Measurements.—(a) *Exchange reaction of* 4-*alkylbenzyl bromides with iodide ion.* Sodium iodide, dried at 130° under a vacuum, was used. Solutions of the organic and inorganic halides were made up in pure acetone under anhydrous conditions. Aliquot parts were mixed at −80°, sealed, and immersed in a thermostat for definite periods. The reaction was stopped

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[16] Kulikow and Panowa, *Biochem. Z.*, 1932, **87**, 246.

[17] Kubota, *J. Chem. Soc. Japan*, 1932, **53**, 404.

[18] Brady, Day, and Rolt, *J.*, 1922, **121**, 528.

[19] Welch, *J. Amer. Chem. Soc.*, 1941, **63**, 3276.

[20] Studer, *Ber.*, 1881, **14**, 1474.

[21] Ingold and Ingold, *J.*, 1928, 2249.

[22] Bernstein, Roth, and Miller, *J. Amer. Chem. Soc.*, 1948, **70**, 2310.

[23] Conant and Kirner, *J. Amer. Chem. Soc.*, 1924, **46**, 245.

[24] Manske, *J. Amer. Chem. Soc.*, 1931, **53**, 1106.

by cooling to −80° and the decrease in concentration of iodide ion was measured by Lang's method.[25]

(b) *Reaction of* 4-*alkylbenzyl bromides and chlorides with sodium ethoxide.* Solutions of known concentration in halide and sodium ethoxide were allowed to react in stoppered flasks immersed in a thermostat. Aliquot parts, withdrawn from time to time in a calibrated fast-delivery pipette, were run into 50 ml. of ice-cold acetone. This solution was titrated with standard hydrochloric acid (lacmoid).

(c) *Alkaline hydrolysis of ethyl* 4-*alkylbenzoates.* The method was analogous to the above except that aliquot parts were run into a known excess of standard hydrochloric acid and titrated with standard carbonate-free sodium hydroxide in 85% ethanol to Bromothymol Blue. The solvent was 85% aqueous ethyl alcohol.

(d) *Alcoholysis of* 4-*alkylbenzoyl chlorides in absolute ethyl alcohol.* Solutions of the organic chlorides of known strength in absolute ethanol were made up in stoppered flasks at thermostat temperature. Aliquot parts of the reaction mixture were run into 70 ml. of acetone at −80°, and titrated with carbonate-free sodium hydroxide (lacmoid). Constants were evaluated graphically.

(e) *Solvolysis of* 4-*alkylbenzyl bromides in* (*Kahlbaum*) *formic acid.* Solutions of the organic bromides of known strength in formic acid were made up in stoppered flasks at thermostat temperature. Aliquot parts of the reaction mixture were run into 50 ml. of carbon tetrachloride, which was twice extracted with distilled water. Bromide ion in the aqueous extract was estimated by Volhard's method.

(f) *Reaction of* 4-*alkylbenzyl bromides with sodium t-butoxide in absolute alcohol.* Constant-delivery pipettes kept in heating jackets at 35° were used to deliver solutions of the bromides and of sodium t-butoxide into tubes cooled to −80°. These were then sealed and the reaction rate measured in the usual way. Aliquot parts were analysed potentiometrically for bromide ion.

(g) *Decomposition of* 1-4′-*alkylbenzylpyridinium ethoxide in absolute ethyl alcohol.* Solutions of the bromides and sodium ethoxide were found, on mixing, to develop a red colour which deepened considerably with time. The reaction was followed by determination of the decrease in concentration of the ethoxide ion. Appropriate volumes of standard bromide and sodium ethoxide solution were mixed in stoppered flasks immersed in the thermostat. Aliquot parts were withdrawn at intervals, run into a known excess of hydrochloric acid and titrated in a glass-electrode half-cell with carbonate-free sodium ethoxide solution. Maximum change of pH with added volume of ethoxide was determined as the end-point. Good second-order rate constants were obtained in the range 5—20% of reaction (cf. Table 2).

(h) *Reaction of* 4-*alkyl*-1-*chloro*-2,6-*dinitrobenzenes with sodium ethoxide in absolute ethanol.* A method analogous to (e) was used.

(i) *Reaction of* 4-*alkylbenzyl fluorides with sodium ethoxide in absolute ethanol.* Sealed tubes were used. Aliquot parts were titrated with hydrochloric acid, to a mixture of Cresol Red and Thymol Blue.

Product Analysis for Reaction (6).—Benzyl ethyl ether[26] (2·94 g.) was dissolved in ethanol (1 l.), water (9 l.) was added, and the mixture continuously extracted with cyclohexane (1 l.) for 72 hr. The extract was fractionated from a Claisen flask through a vacuum-jacketed column, with pure diethyl phthalate as a chaser. This gave fractions (1) b. p. 90°, (2) b. p. 184—188° (2·36 g.), and (3) b. p. 188—288°. Repetition with 2·79 g. of benzyl ethyl ether gave a recovery of 2·43 g. (b. p. 185—190°).

To a 0·0527N-solution of benzylpyridinium bromide (500 ml.) was added 0·0727N-sodium ethoxide (500 ml.), both being at 20·0°, and the mixture was kept at 20° for 194 min., corresponding to 25% reaction (*i.e.*, 1·8 g. of benzyl ethyl ether if it is a product). The reaction was stopped by the addition of a slight excess of hydrobromic acid. Water was added (9 l.) and continuous extraction with cyclohexane (1 l.) was carried out for 72 hr. Fractionation as above gave fractions (1) b. p. 90° and (2) b. p. 282—288°, but no benzyl ethyl ether.

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[25] Lang, *Z. anorg. Chem.*, 1922, **122**, 332; 1925, **142**, 229, 279.
[26] Braun, *Ber.*, 1910, **43**, 1351.