Directive Effects in Benzylic Hydrogen Atom Abstraction. Part V.[1] Halogenation of Benzyl Chlorides and α-Substituted Toluenes

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The relative rates of halogenation of $XC_6H_4CH_2Cl$ with *N*-bromosuccinimide in CCl_4 at 80° and with sulphuryl chloride in benzene at 40° are correlated by the Hammett equation to give ρ^+ $-1{\cdot}30$ (r 0·993) and ρ $-0{\cdot}63$ (r 0·997), respectively. These results are consistent with the different nature of the transition states of atomic bromine and the benzene-complexed chlorine atom with the substrates $XC_6H_4CH_2Y$ previously observed. Benzylic halogenation of $PhCH_2Y$ with the two reagents has also been examined. The effect of Y on the reactivity shows that $CH_3 \sim Ph > H > CH_2Cl > CH_2F > CH_2CN > Cl > CN$ towards the benzene-complexed chlorine atom, and the reactivity values correlated by the Hammett equation for σ_p^+ and σ_p gave ρ $-1{\cdot}90$ and ρ $-2{\cdot}44$ (r 0·94 for both).

PREVIOUS studies[1,2] of benzylic chlorination of the series $XC_6H_4CH_2Y$, where $Y = CH_2Cl$, H, Ph, and Me, with sulphuryl chloride in benzene have indicated that the nuclear substituent effects are well correlated by σ constants in the Hammett equation. On the other hand the bromination results from *N*-bromosuccinimide (NBS) are generally[1,3] better correlated by the σ^+ constants. In order to gain further evidence for these general observations we have extended the investigation of polar effects on the series where $Y = Cl$ with the two halogenating agents. The relative reactivities of the benzylic hydrogen atoms in α-substituted toluenes ($PhCH_2Y$) towards atomic bromine[4]

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[2] K. H. Lee and T. O. Teo, *J.C.S. Perkin II*, 1973, 689.

[3] T. P. Low and K. H. Lee, *J. Chem. Soc.* (*B*), 1970, 535.

[4] S. S. Friedrich, E. C. Friedrich, L. J. Andrews, and R. M. Keefer, *J. Org. Chem.*, 1969, **34**, 900.

and the t-butylperoxyl radical[5] show fair correlation with σ_p^+ values for Y. Such a study is now reported for the benzene-complexed chlorine atom.

EXPERIMENTAL

Materials.—The following benzyl chlorides, $XC_6H_4CH_2Cl$, were prepared by standard procedures[1] and the pure (g.l.c.) chlorides have the following constants, X, b.p. at mmHg, (m.p.) and n_D^{25}: *p*-Me, 106—107° at 35, 1·5320 (lit.,[6] 48—50° at 1, n_D^{17} 1·5360); *p*-Bu^t, 65—66° at 0·5, 1·5190 (lit.,[7] 88—89° at 3, n_D^{24} 1·5194); and *p*-Ph (69·5—70°) (lit.,[8] 68·4—68·8°). *p*-Chloromethylbenzyl chloride, m.p. 97—98° (lit.,[9] m.p. 95—97°), was obtained by chlorination of *p*-methylbenzyl chloride with SO_2Cl_2 in refluxing benzene catalysed by benzoyl peroxide. *p*-Methylbenzyl cyanide, b.p. 85—86° at 1 mmHg, n_D^{25} 1·5164 (lit.,[10] 83—84° at 1·5 mmHg, n_D^{25} 1·5153), and β-phenylpropionitrile, b.p. 80—81° at 1·5 mmHg, n_D^{25} 1·5200 (lit.,[11] 74—76° at 1 mmHg, n_D^{22} 1·5220), were synthesised by refluxing *p*-methylbenzyl chloride and phenethyl bromide, respectively, with sodium cyanide in ethanol. Phenethyl fluoride, b.p. 72—73° at 35 mmHg, n_D^{25} 1·4895 (lit.,[12] 55—56° at 12 mmHg) was prepared as reported.[12] All other materials used were purified from commercially available samples.

Competitive Reactions.—The reactivity of $XC_6H_4CH_2Cl$ towards NBS and sulphuryl chloride was measured against benzyl chloride in the usual manner.[1,2] In the NBS brominations the competing substrates were 0·4M each in CCl_4, and in the chlorination reactions all the reactants were 0·67M each in benzene. The 300 W sunlamp used as light source was placed 10 cm from the centre of the Pyrex reaction flask, and in the SO_2Cl_2 reactions the irradiation times were 2·5—3·5 h to allow 25—30% consumption of the substrates. The unconsumed benzyl chlorides were estimated by the g.l.c. method[1,2] which showed the presence of two products one of these being (retention time) $PhCHCl_2$ or PhCHBrCl. The n.m.r. spectrum of the reaction solutions showed a singlet at δ *ca.* 6·6. The reactivity of *p*-$Bu^tC_6H_4CH_2Cl$ towards SO_2Cl_2 was measured against *m*-$FC_6H_4CH_2CH_2Cl$ (see Table 2). Chlorination at the *p*-Bu^t substituent was *ca.* 3% as estimated by n.m.r. at δ 3·5 and corrected for in the relative reactivity value. Competitive bromination and chlorination of other substrates with the two halogenating agents were similarly determined using g.l.c. analyses for unconsumed substrates, and the results are presented in Tables 2 and 3. In the bromination reactions the total substrates consumed were usually 96—102% of the NBS used. All g.l.c. estimations[1,2] of the unconsumed substrates are reproducible to ⩽±2% by careful choice of standard(s), instrumental conditions, and multiple integration of peak areas for reaction solutions and standard mixtures.

RESULTS AND DISCUSSION

Benzyl Chloride System.—The results of competitive bromination and chlorination of $XC_6H_4CH_2Cl$ *vs.* $PhCH_2Cl$ with NBS in CCl_4 at 80° and with sulphuryl chloride in benzene at 40° are in Table 1. Correlation of the results with the Hammett equation by standard statistical methods[13] shows ρ^+ —1·30 (*r* 0·993) and ρ —0·63 (*r* 0·997) for atomic bromine and the benzene-complexed chlorine atom,[1,2] respectively. The excellent correlation with σ^+ constants for the bromination results is in agreement with previous reports on the series $XC_6H_4CH_2Y$ where Y = H,[14] CH_3,[3] CH_2Cl,[1] $CH{=}CH_2$,[3,15] and Bu^t.[16] The magnitude of the ρ^+ value is comparable with that for the toluene system (—1·38)[14a] and this is not unexpected as the benzylic hydrogen atom in benzyl chloride is only 0·57 times as reactive as that in toluene (Table 4).

TABLE 1 *

Halogenation [a] of $XC_6H_4CH_2Cl$

	k/k_0	
Substituent X	NBS (80°, CCl_4)	SO_2Cl_2 (40°, C_6H_6)
p-Bu^t	2·20 ± 0·04	1·39 ± 0·04 [b]
p-Ph	1·78 ± 0·01	1·03 ± 0·01
p-CH_2Cl	1·03 ± 0·01 [c]	0·77 ± 0·01 [c,d]
H	1·00	1·00
p-F	0·99 ± 0·01	0·91 ± 0·01
p-Cl	0·72 ± 0·01	0·75 ± 0·03
m-F	0·34 ± 0·01	0·64 ± 0·01
m-Cl	0·30 ± 0·01	0·54 ± 0·02
ρ	—1·53 ± 0·10	—0·63 ± 0·01
r	0·963	0·997
ρ^+	—1·30 ± 0·04	—0·50 ± 0·04
r	0·993	0·959

[a] Average of three experiments. [b] From Table 2, *p*-$Bu^tC_6H_4CH_2Cl$ *vs.* *m*-$FC_6H_4CH_2CH_2Cl$, and *m*-$FC_6H_4CH_2CH_2Cl$ *vs.* $PhCH_2CH_2Cl$. [c] Statistically corrected. [d] Not included in the correlation by the Hammett equation.

* All results in Tables 1—3 were calculated by the logarithmic equation used in refs. 1 and 2.

The ρ value of —0·63 for the chlorination reaction in benzene is comparable to recently reported ρ values in the series, $XC_6H_4CH_2Y$ where Y = H (—0·83),[2] Me (—0·67),[2] Ph (—0·65),[2] and CH_2Cl (—0·76)[1] which were all well correlated by σ constants. From Table 4 it is seen that the benzylic hydrogen atom in toluene is 5 times as reactive as that in benzyl chloride whereas those in ethylbenzene and diphenylmethane are at least 22 times as reactive. In contrast to the inverse relationship between the magnitude of the ρ values and the relative reactivity values for $PhCH_2Y$ previously noted[15] for atomic bromine the above results for the benzene complexed chlorine atom show no consistent trend and appear rather random. However, this is not unexpected as Russell[17] suggested that if electron

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density of the benzylic C–H bond determines reactivity then the transition state resembles the reactants, and that the polar effects of nuclear substituents are best correlated by σ constants.

Halogenation of $PhCH_2Y$.—The selectivity of the benzene-complexed chlorine atom has been well documented from studies of polar effects[1,2] and from solvent effects,[18-21] but relative reactivity values for $PhCH_2Y$ have not been previously compiled. These substrates have been chlorinated in competitive reactions with SO_2Cl_2 in benzene at 40° and the results are in Table 2, while the relative reactivity values are in Table 4. The effect of Y on the reactivity shows that Me ∼ Ph > H > CH_2Cl > CH_2F > CH_2CN > Cl > CN, fairly closely following the trend in σ_p or σ_p^+ constants given in Table 4. For the CH_2CN substituent the σ_p value 0·18 is from Exner,[22] and the σ_p^+ value of 0·07 is calculated from ρ −1·38 [14a] and log *k* (*p*-$NCCH_2C_6H_4Me$/PhMe) in Table 3. The σ_p value of 0·168 for CH_2Cl is from ref. 2. For CH_2F the σ_p value of 0·11 is based on $\sigma_p = \sigma_I + \sigma_R^0$ from ^{19}F n.m.r. chemical shifts[23] for *m*- and *p*-$FC_6H_4CH_2F$, but unfortunately no σ_p^+ value has been reported. In correlating the log *k* ($PhCH_2Y$/PhMe) values with σ_p or σ_p^+ it appears appropriate to omit the Y = Ph value since this substrate has an additional six π-electron system which the other Y substituents do not possess. The results show ρ −2·44 (*r* 0·943) and ρ+ −1·90 (*r* 0·943). The magnitude of the ρ value is greater than the effect of ring substituents in $XC_6H_4CH_2Y$ (ρ −0·63 to −0·83).

TABLE 2

Benzylic chlorination [a] with sulphuryl chloride in benzene at 40°

Substrate A	Substrate B	k_A/k_B
$PhCH_2CH_3$	PhMe	3·08 ± 0·08
m-ClC_6H_4Me	PhMe	0·50 ± 0·01 [b]
p-$MeC_6H_4CH_2CN$ [c]	PhMe	0·97 ± 0·01
$PhCH_2CH_3$	Ph_2CH_2	0·94 ± 0·01 [b]
$PhCH_2CH_2Cl$	*m*-ClC_6H_4Me	0·96 ± 0·01 [d]
$PhCH_2CH_2F$	$PhCH_2CH_2Cl$	0·75 ± 0·01
$PhCH_2CH_2CN$	$PhCH_2CH_2Cl$	0·50 ± 0·01
m-$FC_6H_4CH_2CH_2Cl$	$PhCH_2CH_2Cl$	0·56 ± 0·01 [d]
m-$FC_6H_4CH_2CH_2Cl$	$PhCH_2Cl$	1·94 ± 0·01
$PhCH_2CN$	*m*-$FC_6H_4CH_2Cl$	0·50 ± 0·01
p-$Bu^tC_6H_4CH_2Cl$	*m*-$FC_6H_4CH_2CH_2Cl$	0·72 ± 0·05 [e]

[a] Average of three experiments. [b] From ref. 2. [c] N.m.r. spectrum of reaction solution showed no chlorination at CH_2. [d] From ref. 1. [e] Corrected for chlorination at *p*-Bu^t group.

TABLE 3

Benzylic bromination [a] with *N*-bromosuccinimide in carbon tetrachloride at 80°

Substrate A	Substrate B	k_A/k_B
p-ClC_6H_4Me	PhMe	0·74 ± 0·01
p-$NCCH_2C_6H_4Me$ [b]	PhMe	0·80 ± 0·01
$PhCH_2CH_2Cl$	PhMe	0·96 ± 0·01 [c]
$PhCH_2CH_2Cl$	*p*-ClC_6H_4Me	1·30 ± 0·01 [c]
$PhCH_2CH_2F$	*p*-ClC_6H_4Me	0·62 ± 0·01
$PhCH_2CH_2Cl$	$PhCH_2Cl$	2·52 ± 0·01
$PhCH_2CN$	$PhCH_2Cl$	0·44 ± 0·01
$PhCH_2Cl$	$PhCH_2CH_2F$	0·82 ± 0·01
$PhCH_2CH_2CN$	$PhCH_2CH_2Cl$	0·31 ± 0·01
p-PhC_6H_4Me	PhMe	3·13 ± 0·01
p-BrC_6H_4Me	PhMe	0·64 ± 0·02
p-$Bu^tC_6H_4Me$	PhMe	2·07 ± 0·05
p-$ClCH_2C_6H_4Me$	*p*-$Bu^tC_6H_4Me$	0·73 ± 0·01
$PhCH_2Br$	$PhCH_2Cl$	0·33 ± 0·01

[a] Average of three experiments. [b] N.m.r. spectrum of reaction solution showed no bromination at CH_2. [c] From ref. 1.

TABLE 4

Relative reactivity values (per hydrogen atom) of $PhCH_2Y$

Substituent Y	Y		*k* ($PhCH_2Y$)	
	σ_p	σ_p^+	NBS (80°, CCl_4)	SO_2Cl_2 (40°, C_6H_6)
MeO	−0·268	−0·778	54 [a]	
Me	−0·170	−0·311	23 [a]	4·62
Ph [b]	−0·01	−0·179	18 [a]	4·92
CH_2Cl	+0·168	−0·01	1·44	0·72
H	0·00	0·00	1·00	1·00
CH_2F	+0·11		0·69	0·54
CH_2CN	+0·18	+0·07	0·45	0·35
Cl	+0·227	+0·114	0·57	0·21
CN	+0·660	+0·659	0·25	0·06
Br	+0·232	+0·150	0·19	
		ρ	−2·67	−2·44
		r	0·84	0·943
		ρ+	−1·97	−1·90
		r	0·89	0·943

[a] From ref. 3. [b] Not included in the correlation by the Hammett equation.

TABLE 5

Relative reactivity values of *p*-XC_6H_4Me towards *N*-bromosuccinimide in CCl_4 at 80°

X	*k* [a]
MeO	(11·7 ± 0·7)
Ph	3·13 ± 0·01
Me	(2·56 ± 0·17)
Bu^t	2·07 ± 0·05 [b]
CH_2Cl	1·51 ± 0·01
H	1·00
CH_2CN	0·80 ± 0·01
Cl	0·74 ± 0·01
Br	0·64 ± 0·02
CN	(0·14)
ρ	−1·70 ± 0·05
r	0·914
ρ+	−1·35 ± 0·01
r	0·984

[a] From Table 3 with values in parentheses from ref. **14***a*. [b] From *p*-$ClCH_2C_6H_4Me$ *vs*. *p*-$Bu^tC_6H_4Me$.

Previous reports[4,14a,24] on the reactivity of atomic bromine (NBS) with $PhCH_2Y$ have shown a fair amount of variation in the reactivity values, and we have measured competitive brominations with NBS in CCl_4 at 80° given in Table 3. Good material balance between g.l.c. analyses of unconsumed substrates and the amount of NBS used was observed. The relative reactivity values and those previously reported[3] from this laboratory are compiled in Table 4. Correlating the log *k*

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(PhCH$_2$Y/PhMe) values with σ_p or σ_p^+ gave ρ −2·67 (r 0·84) and ρ^+ −1·97 (r 0·89) compared to ρ^+ −2·46 (r 0·95) previously reported.[4] Our results, where $r < 0·9$, can be considered to be in the region of non-correlation.[25]

In order to obtain a direct correlation between log k (PhCH$_2$Y/PhMe) *vs.* log k (p-XC$_6$H$_4$Me/PhMe) for NBS brominations the relative reactivities of p-XC$_6$H$_4$Me were measured, and the results in Table 5 show good correlation with σ^+ constants with ρ^+ −1·35 (r 0·984). This result is consistent with previous reports[14] where better correlation with σ^+ constants was observed. Least square treatment of log k (PhCH$_2$Y/PhMe) *vs.* log k(p-XC$_6$H$_4$Me/PhMe) gave a slope of 1·54 (r 0·89), again falling in the region of non-correlation. In conclusion it appears that linear free energy relationships are not very useful in predicting free radical reactivity of PhCH$_2$Y towards atomic bromine or the benzene-complexed chlorine atom.

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