Directive Effects in Benzylic Hydrogen Atom Abstraction. Part IV.[1] Halogenation of 2-Arylethyl Chlorides

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The relative rates of benzylic hydrogen abstraction from $XC_6H_4CH_2CH_2Cl$ by atomic bromine, the trichloromethyl radical, and by the benzene-complexed chlorine atom have been measured by means of competitive reactions with N-bromosuccinimide, with bromotrichloromethane in carbon tetrachloride at 80°, and with sulphuryl chloride in benzene at 40°. The results, correlated by the Hammett equation, gave ρ values of −1·10, −0·93, and −0·76, respectively by use of σ+ constants for atomic bromine and σ constants in the other two cases.

THE preceding paper interpreted the benzylic chlorination of $XC_6H_4CH_2Y$ by both sulphuryl chloride and t-butyl hypochlorite in benzene, where Y = H, Ph, or Me, in terms of hydrogen abstraction principally by the benzene-complexed chlorine atom. This report extends the investigation of polar effects on the series where Y = CH_2Cl with three halogenating agents, sulphuryl chloride, N-bromosuccinimide (NBS), and bromotrichloromethane.

EXPERIMENTAL

Materials.—Substituted phenethyl alcohols were prepared by reduction of methyl arylacetates or reacting aryl-magnesium bromides with ethylene oxide, and have physical constants agreeing with reported values. The chlorides, $XC_6H_4CH_2CH_2Cl$, were prepared in 75—85% yield from the alcohols by dropwise addition of thionyl chloride in refluxing benzene–pyridine. The pure (g.l.c.) chlorides have the following constants, X, b.p. at mmHg, n_D^{25}, p-Me, 117—

118° at 35, 1·5232 (lit.,[2] 67° at 4 mmHg); p-Bu^t, 89—90° at 1, 1·5140 (Found: C, 73·3; H, 8·65, Cl, 18·0. $C_{12}H_{17}Cl$ requires C, 73·2, H, 8·7, Cl, 18·1%); p-F, 108—109° at 35, 1·5040 (lit.,[3] 80° at 30 mmHg); m-F, 103—104° at 35, 1·5040 (Found: C, 61·1; H, 5·0. C_8H_8ClF requires C, 60·6; H, 5·05%); p-Cl, 138—139° at 35, 1·5442 (lit.,[3] 135° at 35 mmHg); m-Cl, 137—138° at 35, 1·5440 (lit.,[4] 111—113° at 13 mmHg, n_D^{22} 1·5474); p-Br, 80—81° at 1, 1·5690 (lit.,[4] 137° at 35 mmHg). β-Chloroethylbenzene (Eastman–Kodak) was redistilled before use. α-Bromo-β-chloroethylbenzene,[5] m.p. 29—30°, was obtained from NBS bromination of the β-chloroethylbenzene. All competing substrates and g.l.c. and n.m.r. standards used were pure by g.l.c. analyses. Other materials used were purified in the usual manner.[1,6,7]

Reaction of β-Chloroethylbenzene with SO_2Cl_2.—The chloride (25·0 mmol) and sulphuryl chloride (10 mmol) in benzene (25 ml) were irradiated [1] at 40° for 1·5 h under N_2. After removal of the volatile gaseous products by flushing with N_2, a portion of the reaction solution was analysed for unconsumed β-chloride (16·8 mmol) by g.l.c. which showed

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only a single product. The n.m.r. estimation[1] for unconsumed β-chloride [δ 2·7—3·1 (ArCH$_2$^{2})] and PhCHCl-CH$_2$Cl [δ 4·7 (q, CHCl)] using triphenylmethane (δ 5·44) as standard gave 17·0 and 8·3 mmol, respectively.

(40 mol %). The concentration of the substrates were 0·7M each in the brominations with bromotrichloromethane (3M) in CCl$_4$ and the irradiation times were 4—6 h to allow 20—37% consumption of the substrates. For chlorination

TABLE 1

Bromination of XC$_6$H$_4$CH$_2$CH$_2$Cl with N-bromosuccinimide in CCl$_4$ at 80°

Subst. X	[XC$_6$H$_4$CH$_2$CH$_2$Cl]/mmol initial/final	[PhMe]/mmol initial/final	[PhCH$_2$Br]/mmol	[XC$_6$H$_4$CHBrCH$_2$Cl]/mmol	k_α/k_{PhMe}
p-Me	5·00/(3·06) a,b	5·22/4·02	1·01	(1·82) a	1·89
p-Me	5·00/(3·08) b	5·04/3·91	1·07	(1·93)	1·91
p-Me	4·99/(3·09) b	5·01/3·92	1·02	(2·01)	1·94
H	5·00/(3·11)	5·05/(3·12) a	(2·00) a		0·98
H	4·98/(3·16)	4·98/(3·06)	(1·97)	(1·75)	0·94
H	4·90/(3·04)	5·13/(3·10)	(1·92)	(1·92)	0·95

Subst. X		p-ClC$_6$H$_4$Me e	p-ClC$_6$H$_4$CH$_2$Br		$k_\alpha/k_{p\text{-}ClC_6H_4Me}$
p-Bu^t	4·85/2·11(2·20)	5·08/3·70			2·62
p-Bu^t	4·94/2·11(2·18)	5·04/3·73			2·82
p-Bu^t	4·83/2·09	5·15/3·79			2·66
H	10·03/5·73	10·24/6·65			1·29
H	10·07/5·68	10·00/6·45	3·31	4·36	1·31
H	10·00/5·63	10·00/6·43	3·38	4·32	1·30
p-F	3·00/1·71	3·02/1·86			1·16
p-F	3·00/1·62	3·04/1·82			1·18
p-F	3·00/1·65	3·03/1·84			1·19
p-Cl	2·98/1·74(1·77)	3·03/1·73(1·87)	(1·22)		0·96
p-Cl	2·98/1·78(1·83)	3·00/1·73(1·80)	(1·13)		0·94
p-Cl	3·00/1·76	3·02/1·71			0·94
p-Br	5·02/3·06	4·99/2·87	(2·06)		0·89
p-Br	5·02/3·10(3·19)	5·03/2·94(3·08)	(1·90)		0·89
p-Br	5·00/3·08(3·16)	5·00/2·88(2·95)	(1·90)		0·88
m-F	5·00/3·60	5·07/2·54			0·48
m-F	5·02/3·56	5·00/2·47			0·49
m-F	5·00/3·58	5·00/2·42			0·46
m-Cl	2·96/(2·17)	3·00/1·45	(1·48)		0·43
m-Cl	2·97/(2·12)	3·04/1·43(1·47)	(1·41)		0·45
m-Cl	5·00/3·58	5·02/2·44			0·46

a Figures in parentheses were estimated by the n.m.r. method. b Includes p-BrCH$_2$C$_6$H$_4$CH$_2$CH$_2$Cl. e $k_{p\text{-}ClC_6H_4Me}/k_{PhMe}$ = 0·74 ± 0·01 with NBS.

TABLE 2

Chlorination of XC$_6$H$_4$CH$_2$CH$_2$Cl with SO$_2$Cl$_2$ in benzene at 40°

Subst. X	[XC$_6$H$_4$CH$_2$CH$_2$Cl]/mmol initial/final	[m-ClC$_6$H$_4$Me]/mmol initial/final	[m-ClC$_6$H$_4$CH$_2$Cl]/mmol	[XC$_6$H$_4$CHClCH$_2$Cl]/mmol	$k_\alpha/k_{m\text{-}ClC_6H_4Xo}$
p-Bu^t	5·92/(4·00) a,b	6·00/4·70	(1·47) a	(1·90) a	1·39
p-Bu^t	5·93/(4·13) b	6·12/4·73	(1·25)		1·40
p-Bu^t	5·93/(4·12) b	6·05/4·68	(1·41)		1·42
H	10·00/6·40	9·98/6·26(6·20) a	(3·87)	(3·65)	0·96
H	10·02/6·40	9·97/6·36	(3·46)	(3·36)	0·96
H	10·00/7·10	10·02/7·00	(3·05)	(2·82)	0·95
p-F	5·99/4·14(4·22)	6·00/3·90	(2·15)		0·86
p-F	6·00/4·09	6·03/3·92	(1·76)	(1·80)	0·89
p-F	6·03/3·76	6·00/3·51			0·88
p-Cl	5·95/4·52(4·55)	6·00/4·02	(1·82)		0·69
p-Cl	5·95/4·48(4·53)	6·05/4·10	(1·99)		0·73
p-Cl	5·97/4·56	6·00/4·07			0·69
m-F	6·00/4·60(4·82)	6·00/3·70	(2·44)		0·55
m-F	6·00/4·72(4·81)	6·00/3·82	(1·91)		0·53
m-F	6·02/4·57(4·51)	6·32/3·83	(2·36)		0·55
m-Cl	3·92/3·01(3·15)	4·00/2·34	(1·40)		0·49
m-Cl	3·92/3·09(3·11)	4·00/2·56(2·57)	(1·46)		0·50
m-Cl	6·02/4·62(4·55)	6·00/3·58(3·65)			0·51

Subst. X		PhMe	PhCH$_2$Cl		$k_{\alpha\text{-}CH_3}/k_{PhMe}$
p-Me	6·01/(4·74) c	5·98/4·20	1·60	(1·51)	0·67
p-Me	6·03/(4·85) c	5·98/4·28	1·52	(1·33)	0·66
p-Me	6·01/(4·97) c	5·98/4·50	1·36	(1·20)	0·67

a Figures in parentheses were estimated by the n.m.r. method. b Includes p-ClCH$_2$C(Me$_2$)C$_6$H$_4$CH$_2$CH$_2$Cl. c Includes p-ClCH$_2$C$_6$H$_4$CH$_2$CH$_2$Cl.

Competitive Reactions.—These were carried out as previously described.[1,6,7] In the NBS brominations the competing substrates were 0·2M each in CCl$_4$ with NBS

with SO$_2$Cl$_2$ all reactants were 0·4M in benzene and irradiation times were 0·4—1·5 h to allow 27—37% consumption of the competing substrates. A 300 W sunlamp was used

as light source for all reactions. Analyses by g.l.c. and n.m.r. were performed in the usual way [1] and the results are given in Tables 1—3.

RESULTS AND DISCUSSION

Bromination with N-Bromosuccinimide.—Bromination of β-chloroethylbenzene with NBS gave only a single product, α-bromo-β-chloroethylbenzene [5] whose n.m.r. spectrum has the characteristic ABX pattern of α β-di-bromoethylbenzene [8] and is well resolved from the

k_{PhMe} value of 0·96 shows that the CH_2Cl group is a powerful deactivating group on the reactivity of the benzylic C–H and the magnitude of the ρ value is of the expected order compared to that for XC_6H_4Me (−1·38).[10]

Chlorination with Sulphuryl Chloride.—Chlorination of β-chloroethylbenzene with sulphuryl chloride in benzene gave only the expected αβ-dichloride. The relative reactivity of $XC_6H_4CH_2CH_2Cl$ towards SO_2Cl_2 in benzene at 40° was measured against *m*-chlorotoluene while that for p-$MeC_6H_4CH_2CH_2Cl$ was determined against toluene.

TABLE 3

Bromination of $XC_6H_4CH_2CH_2Cl$ with bromotrichloromethane in CCl_4 at 80°

Subst. X	[XC₆H₄CH₂CH₂Cl]/mmol initial/final	[p-ClC₆H₄Me]/mmol initial/final	[p-ClC₆H₄CH₂Br]/ mmol	[XC₆H₄CHBrCH₂Cl]/ mmol	$k_\alpha/k_{p\text{-ClC}_6\text{H}_4\text{Me}}$
p-Bu^t	6·95/4·98(5·25) *ᵃ*	6·99/5·98(6·10) *ᵃ*	(1·01) *ᵃ*	(1·80) *ᵃ*	2·13
p-Bu^t	7·03/5·18(5·32)	7·03/6·11(6·15)	(1·01)	(1·79)	2·18
p-Bu^t	7·01/5·40(5·35)	7·03/6·20(6·15)			2·06
p-Me	6·98/(5·10) *ᵇ*	7·00/6·05			2·12
p-Me	6·97/(5·05) *ᵇ*	6·98/6·02		(2·02)	2·19
p-Me	7·00/(4·57) *ᵇ*	7·00/5·76		(2·50)	2·18
H	7·00/4·74(4·97)	7·00/5·31(5·39)	(1·49)	(2·15)	1·42
H	7·02/5·10(5·15)	6·97/5·54(5·67)	(1·46)	(1·95)	1·39
H	7·03/5·13(5·25)	6·95/5·60(5·70)	(1·42)	(1·85)	1·46
p-Cl	7·02/(4·74)	6·97/4·62	(2·33)	(2·20)	0·96
p-Cl	7·05/(5·60)	7·00/5·45(5·50)	(1·38)	(1·31)	0·92
p-Cl	7·03/(4·85)	6·98/4·75(4·70)	(2·20)	(2·12)	0·98
p-Br	7·35/5·35(5·40)	7·02/4·85	1·98	(2·06)	0·86
p-Br	7·04/4·68(4·68)	7·00/4·50(4·52)	2·45	(2·48)	0·92
p-Br	7·00/4·56	7·00/4·35			0·90

		$C_6H_4CH_2CH_2Cl$			k/k_0
m-F	7·01/5·30	7·01/3·84			0·47
m-F	7·07/5·40	7·03/4·02			0·48
m-F	7·00/5·15	7·01/3·58			0·46
m-Cl	7·01/5·25	7·00/3·73			0·45
m-Cl	7·04/5·27	7·02/3·60			0·43
m-Cl	7·01/5·59	7·22/4·40			0·46

ᵃ Figures in parentheses were estimated by the n.m.r. method. *ᵇ* Includes p-$BrCH_2C_6H_4CH_2CH_2Cl$.

methylene protons of the monochloride. In the competitive bromination of $XC_6H_4CH_2CH_2Cl$ with NBS, toluene and *p*-chlorotoluene were chosen as standard substrates in order that the products and the unconsumed substrates could be analysed by the n.m.r. method as well as by g.l.c. Except for X = *p*-Me, only two products were formed in all cases, and good material balance was observed in representative experiments. For X = *p*-Me the total amount of p-$BrCH_2C_6H_4CH_2$-CH_2Cl and unconsumed p-$MeC_6H_4CH_2CH_2Cl$ estimated by n.m.r. integration of the triplet at δ 2·8 and that of p-$MeC_6H_4CHBrCH_2Cl$ by estimation at δ 3·8—4·1, gave good material balance. All brominations were done at 80° to facilitate comparison with the substituent effects previously investigated.[6] Correlation of the relative reactivity data given in Table 4 for atomic bromine by the Hammett equation shows that $\rho^+ = -1·10 \pm 0·05$ (r 0·987) and $\rho = -1·29 \pm 0·06$ (r 0·977). The better correlation with σ^+ constant of Brown and Okamoto [9] is consistent with data for other substrates towards atomic bromine.[6,10–12] From Table 1 the $k_{\alpha\text{-PhCH}_2\text{CH}_2\text{Cl}}/$

For the *p*-Me and *p*-Bu^t group, the reactivity values of the benzylic hydrogens relative to those of the methyl

TABLE 4

Substituent effects in the halogenation of $XC_6H_4CH_2CH_2Cl$

Subst. X	NBS (80°, CCl₄)	SO₂Cl₂ (40°, PhH)	BrCCl₃ (80°, CCl₄)
p-Bu^t	2·08 ± 0·06	1·46 *±0·01	1·50 ± 0·03
p-Me	1·99 *± 0·02	1·38 *± 0·01	1·52 *± 0·02
H	1·00	1·00	1·00
p-F	0·91 ± 0·01	0·92 ± 0·01	
p-Cl	0·73 ± 0·01	0·73 ± 0·02	0·67 ± 0·02
p-Br	0·68 ± 0·01		0·63 ± 0·01
m-F	0·37 ± 0·01	0·56 ± 0·01	0·47 ± 0·01
m-Cl	0·34 ± 0·01	0·52 ± 0·01	0·45 ± 0·01

* Corrected for halogenation at the substituent.

$\rho = -1·29 \pm 0·06;$ $\rho = -0·76 \pm 0·01;$ $\rho = -0·93 \pm 0·02$
$r = 0·977;$ $r = 0·996;$ $r = 0·996$

$\rho^+ = -1·10 \pm 0·05;$ $\rho^+ = 0·63 \pm 0·04;$ $\rho^+ = -0·80 \pm 0·03$
$r = 0·987;$ $r = 0·983;$ $r = 0·990$

group of toluene were evaluated by n.m.r. integration of the triplet at δ *ca.* 2·8. Good material balances were

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found by n.m.r. analyses for the $ArCHClCH_2Cl$ products. Table 2 shows good material balance for unconsumed toluene and m-chlorotoluene (g.l.c.) and the corresponding benzyl chlorides (n.m.r.). From the previously determined value[1] of 0·50 for $k_{m\text{-}ClC_6H_4Me}/k_{PhMe}$ the effects of substituents on the chlorination of $XC_6H_4CH_2$-CH_2Cl are compiled in Table 4. The polar effects show that $\rho = -0·76 \pm 0·01$ (r 0·996) and $\rho^+ = -0·63 \pm 0·04$ (r 0·983); the better correlation with the σ constants of McDaniel and Brown[13] is consistent with the report[1] for the sulphuryl chloride chlorination in benzene of $XC_6H_4CH_2Y$, where $Y = H$, Ph, and Me. Compared to the toluene series, the magnitude of the polar effect for the phenethyl chlorides is not unexpected since the relative reactivity $k_{\alpha\text{-}PhCH_2CH_2Cl}/k_{PhMe}$ calculated from Table 2 and previous results[1] is 0·48.

Bromination with Bromotrichloromethane.—The relative reactivities of the substituted phenethyl chlorides toward the trichloromethyl radical at 80° are presented in Table 3. The chain length for photoinitiated bromination of toluene with $BrCCl_3$ was found[14] to be *ca.* 20. Since these substrates are of similar reactivity as p-chlorotoluene the overall chain length for the trichloromethyl radical in the competitive reaction would not be expected to be less than the value found for toluene. The main product arising from $BrCCl_3$ was chloroform (g.l.c.); the amount of hexachloroethane so detected

was <5% of the overall reaction. Thus the contribution of the bromine atom chain in the present study is not likely to be significant. For p-$MeC_6H_4CH_2CH_2Cl$, bromination at the p-Me position was corrected for in the estimation of the reactivity of the benzylic hydrogens as indicated above. Correlation of the substituent effects gave $\rho = -0·93 \pm 0·02$ (r 0·996) and $\rho^+ = 0·80 \pm 0·03$ (r 0·990); σ constants appear to give a slightly better correlation. Similar results have previously been reported for bromination with bromotrichloromethane of substituted isopropylbenzenes[15] and benzaldehydes.[16] On the other hand, for substituted toluenes[17] and ethylbenzenes[7] σ^+ constants were found to be more appropriate. Although factors governing the use of σ or σ^+ constants in the Hammett equation have previously been discussed,[15,16] further work on the series XC_6H_4-CH_2Y appears appropriate before a more meaningful conclusion can be drawn.

A recent paper by Kieboom[18] has cautioned against the application of the modified Hammett equation in free-radical reactions, such as the type suggested by Yamamoto[19] where resonance and inductive effects are separated. This and the preceding paper[1] have demonstrated that either σ or σ^+ constants can be adequately used in correlating data in benzylic hydrogen atom abstraction by radicals.

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