Directive Effects in Benzylic Hydrogen Atom Abstraction. Part III.[1] Chlorination of Nuclear-substituted Toluenes, Diphenylmethanes, and Ethylbenzenes

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The relative reactivities of nuclear-substituted toluenes, diphenylmethanes, and ethylbenzenes towards the benzene–chlorine atom π complex at 40° have been determined using sulphuryl chloride and t-butyl hypochlorite in benzene as reagents. The results show ρ values of −0·83, −0·65, and −0·67 for the former reagent and −0·81, −0·66, and −0·65 for the latter, all well correlated by the Hammett equation. Similar deuterium isotope effects k_H/k_D of 2·4 for [α,α-$^2H_2$]toluene, and of 1·8 for [α,α-$^2H_2$]diphenylmethane for the two reagents also provide strong evidence that the benzene–chlorine atom π complex is the principal hydrogen-abstracting species for benzylic chlorination with these reagents in benzene solution.

SULPHURYL CHLORIDE is a versatile chlorinating agent which has been shown[1-6] to vary in its selectivity in chlorination depending on the nature of the solvent. Walling and Miller[7] reported the same deuterium isotope effect when [α-^{2}H]toluene is photochlorinated or chlorinated with SO_2Cl_2 at 70° in the absence of a solvent. This result has been attributed[5] to hydrogen abstraction by the toluene–chlorine atom π complex. More recent evidence for π complexing of atomic chlorine by alkylbenzenes has been presented by Bruylants *et al.*[8] Although earlier studies on benzylic chlorination with t-butyl hypochlorite have implied that hydrogen abstraction is principally by the t-butoxyl radical, recent work by Sakurai and Hosomi[9] and by Walling and McGuiness[10] indicates convincingly the implication of chlorine-atom chains to a large extent with this reagent.

In extending our investigation on benzylic halogenation,[1,11] we have studied the substituent effects in the chlorination of toluenes, diphenylmethanes, and ethylbenzenes with sulphuryl chloride and with t-butyl hypochlorite in benzene in view of the fact that discrepancies have been found by various workers[9,10,12-14] who treated toluene with Bu^tOCl and $Bu^tO\cdot$ radicals. Previous investigations[11,15] on the *N*-bromosuccinimide bromination of $XC_6H_4CH_2Ph$ using different analytical methods both gave a better Hammett correlation with σ than with σ^+ constants. This bromination has now been reinvestigated under homogeneous conditions using a different approach.

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RESULTS AND DISCUSSION

Toluene System.—The reactivity of *p*-xylene relative to cyclohexane towards SO_2Cl_2 in benzene has been shown[6] to be independent of its concentration up to 2·4M. Thus in the competitive chlorination of XC_6H_4Me *vs*. PhMe with SO_2Cl_2 and Bu^tOCl the total concentration of the hydrocarbons used was kept at 0·8M. The results are in Table 1, where the reactivity of *p*-Bu^t-C_6H_4Me was measured against *p*-xylene. Application of the Hammett equation gave a ρ value of $-0·83 \pm 0·02$ (r 0·994) for SO_2Cl_2 and $-0·81 \pm 0·02$ (r 0·995) for Bu^tOCl, both well correlated by the σ constants of McDaniel and Brown.[16] The ρ values are more negative than the value of $-0·56$ previously reported[1] for SO_2Cl_2 in CCl_4 also at 40°.

TABLE 1

Chlorination[a] of XC_6H_4Me in benzene at 40°

	k/k_0	
X	SO_2Cl_2	Bu^tOCl
p-Me	$1·51 \pm 0·04$ [b]	$1·51 \pm 0·01$ [b]
p-Bu^t	$1·39 \pm 0·01$ [c]	$1·39 \pm 0·01$ [c]
m-Me	$1·14 \pm 0·01$ [b]	$1·14 \pm 0·04$ [b]
H	1·00	1·00
p-F	$0·94 \pm 0·01$	$0·94 \pm 0·01$
m-CH_2Cl	$0·84 \pm 0·01$ [d]	$0·86 \pm 0·02$ [d]
p-CH_2Cl	$0·72 \pm 0·01$ [d]	$0·73 \pm 0·01$ [d]
p-Cl	$0·69 \pm 0·01$	$0·69 \pm 0·01$
m-F	$0·51 \pm 0·01$	$0·53 \pm 0·01$
m-Cl	$0·50 \pm 0·01$	$0·51 \pm 0·01$
$\log (k/k_0)$	$-0·83\sigma \pm 0·02$	$-0·81\sigma \pm 0·02$
r	0·994	0·995
$\log (k/k_0)$	$-0·70\sigma^+ \pm 0·09$	$-0·69\sigma^+ \pm 0·08$
r	0·984	0·983
k_H/k_D ($PhCHD_2$)	2·3	2·3

[a] Average of 3 experiments. [b] Statistically corrected. [c] From values measured against *p*-xylene. [d] Not included in the correlation by the Hammett equation.

The implication of chlorine-atom chains in benzylic chlorination with Bu^tOCl was first pointed out by Sakurai and Hosomi[9] who reported a ρ value of $-0·41$ (Freon-113) at 45° for t-butoxyl radicals from di-t-butyl peroxalate where competing chlorine atoms were absent. This is significantly different from the ρ values of $-0·82$ and $-0·76$ (PhH) at 40° obtained by Walling and Jacknow[12] and by Gilliom and Howles,[13d] respectively, with Bu^tOCl. Subsequently, Walling and McGuiness[10] demonstrated the serious implication of chlorine-atom chains in benzylic chlorination with Bu^tOCl.

The kinetic isotope effect, k_H/k_D, for [α,α-$^2H_2$]toluene is 2·3 for SO_2Cl_2 and 2·5 for Bu^tOCl in benzene at 40°. These values are in good agreement with the value[7] of 2·1 at 70° for photochlorination as well as sulphuryl chloride chlorination of [α-^2H]toluene in the absence of a solvent, and with the value of 2·4 at 40° for the chlorination of $C_6H_5CD_3$ with t-butyl hypochlorite.[14] Russell[5] has interpreted the identical kinetic isotope effect reported by Walling and Miller[7] to be due primarily to hydrogen abstraction by the toluene–chlorine atom π complex. In contrast the kinetic isotope effect reported[10] for the $Bu^tO\cdot$ radical with $C_6H_5CD_3$ and C_6H_5Me at 40° is substantially larger, 5·0—5·5, determined from the t-butyl alcohol : acetone ratios.

The photochlorination of substituted toluenes[17] shows that in benzene the ρ value is significantly more negative than that found for the uncomplexed chlorine atom determined in CCl_4. Studies[18] on hydrogen abstraction from aliphatic compounds indicate that the uncomplexed chlorine atom (ρ^* $-0·85$) is more selective than the t-butoxyl radical (ρ^* $-0·69$) at 40°. The ρ value of $-0·81$ for treatment of the toluene system with Bu^tOCl is in good agreement with the values previously reported[10,13] and also with the value of $-0·76$ at 70° found for photochlorination[7] in the absence of a solvent. In view of the above discussion, the previous conclusions[12-14] that the t-butoxyl radical is the principal hydrogen-abstracting species in the chlorination of the toluene system with Bu^tOCl must now be subject to serious reservations.

Diphenylmethane System.—The relative reactivity of $XC_6H_4CH_2Ph$ towards SO_2Cl_2 and Bu^tOCl in benzene at 40° was measured against *p*-xylene. The results are in Tables 2 and 3. The competitive chlorination of diphenylmethane and *p*-xylene with SO_2Cl_2 in benzene has been shown[19] to yield a constant relative reactivity ratio when the concentrations of the hydrocarbon

TABLE 2

Chlorination of $XC_6H_4CH_2Ph$ with sulphuryl chloride

Subst. X	[$XC_6H_4CH_2Ph$]/ mmol initial/final	[*p*-Xylene]/ mmol initial/final	[Total α-Cl]/ mmol	Material balance (%)	k/k_{xylene}
p-Bu^t	6·03/4·83(4·85) [a]	6·05/4·88	2·15	98	1·03
p-Bu^t	6·00/4·65(4·71)	6·00/4·64			0·99
p-Bu^t	6·01/4·98(5·05)	6·03/5·00	2·10	100	1·00
p-Ph	6·02/(4·72)	6·00/4·36	2·86	99	0·76
p-Ph	6·02/(4·77)	6·00/4·53	2·80	101	0·82
p-Ph	6·02/(4·90)	6·03/4·64	2·55	100	0·78
H	10·01/7·50(7·40)	10·00/6·80	5·30	98	0·74
H	10·00/7·28(7·35)	10·02/6·54	5·58	97	0·74
H	10·00/7·28	10·02/6·54			0·74
p-F	6·03/4·32	5·97/3·77			0·72
p-F	6·02/4·36	6·02/3·82	3·22	95	0·71
p-F	6·04/4·41	6·01/3·82			0·68
p-Cl	6·04/4·66	5·98/3·67			0·53
p-Cl	6·00/4·55	6·05/3·69			0·56
p-Cl	6·00/4·85	6·02/4·15			0·57
m-F	6·02/5·43	5·98/4·75			0·45
m-F	6·03/4·73	6·00/3·56	3·66	99	0·47
m-F	6·00/4·59	6·05/3·42	3·80	98	0·47
m-Cl	6·02/4·48	6·02/3·06			0·43
m-Cl	6·03/4·86	6·05/3·65			0·43
m-Cl	6·05/4·96	6·00/3·78			0·43
	Ph_2CD_2	*p*-Xylene			
	6·00/4·74	5·98/3·34	3·67	98	0·403
	6·00/4·67	5·98/3·20	3·61	96	0·400
	5·98/4·82	5·97/3·52	3·50	99	0·415

[a] All values in parentheses were determined by the n.m.r. method.

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[19] T. O. Teo, unpublished results.

substrates were varied from 0·4 to 2·4M. For the *p*-phenyl substituent the unconsumed diphenylmethane was estimated by the n.m.r. method as the hydrocarbon is too high boiling for the g.l.c. columns used. In the case of X = *p*-Bu^t the analysis for the unconsumed diphenylmethane by g.l.c. was checked by the n.m.r. method where the integrated peak area of CH_2 (δ *ca.* 3·8) was measured against the CH_2 peak area (δ *ca.* 4·93) of benzyl acetate. The excellent agreement showed that attack on the t-butyl group to be negligible. The estimation of total benzyl chloride by titrimetry for representative experiments indicates a good material balance of 95—101%.

TABLE 3

Chlorination of $XC_6H_4CH_2Ph$ with t-butyl hypochlorite

Subst. X	$[XC_6H_4CH_2Ph]$/ mmol initial/final	[*p*-Xylene]/ mmol initial/final	[Total α-Cl]/ mmol	Material balance (%)	k/k_{xylene}
p-Bu^t	6·01/4·57(4·70)[a]	5·98/4·58	2·70	99	1·02
p-Bu^t	6·04/4·65(4·60)	6·00/4·62	2·37	96	1·00
p-Bu^t	6·00/4·50(4·51)	5·98/4·51	2·58	97	1·02
p-Ph	6·01/(4·90)	5·99/4·59	2·63	101	0·77
p-Ph	6·05/(4·83)	6·00/4·60	2·49	99	0·80
p-Ph	6·03/(4·85)	6·01/4·62	2·22	97	0·82
H	10·00/8·09(8·15)	9·99/7·57	4·05	99	0·76
H	10·01/7·90(7·81)	10·07/7·35	4·21	97	0·74
H	10·00/7·96	10·00/7·40	4·04	97	0·76
p-F	6·04/4·38	6·00/3·75	3·32	95	0·69
p-F	6·02/4·41	5·99/3·84	3·16	95	0·70
p-F	6·01/4·41	6·00/3·78			0·67
p-Cl	6·04/4·90	6·00/4·07			0·54
p-Cl	6·00/4·89	5·97/4·11			0·55
p-Cl	6·05/4·88	6·02/4·15			0·58
m-F	10·01/8·47	10·03/6·87			0·44
m-F	10·02/8·77	9·95/7·92			0·43
m-F	6·02/5·04	6·00/4·10	2·52	97	0·47
m-Cl	6·00/5·17(5·10)	5·97/4·19			0·42
m-Cl	6·01/5·13(5·20)	6·03/4·18	2·59	98	0·43
m-Cl	6·00/5·11(5·05)	5·96/4·15	2·34	97	0·44
	Ph_2CD_2	*p*-Xylene			
	6·00/4·94	6·02/3·64	3·10	97	0·39
	6·02/4·84	6·01/3·52	3·11	95	0·41
	6·00/5·00	6·03/3·77	2·75	96	0·39

[a] All values in parentheses were determined by the n.m.r. method.

The results of the substituent effects are presented in Table 4, in which the data for homogeneous *N*-bromosuccinimide (NBS) bromination in CH_2Cl_2 are included. The ρ values are −0·65, −0·66, and −1·06 for SO_2Cl_2, Bu^{t}OCl, and NBS, respectively, all well correlated by the σ constants, while the corresponding deuterium isotope effects are 1·84, 1·88, and 3·20. The practically identical ρ values and k_H/k_D effects for the two chlorinating agents provide further supporting evidence for the benzene-chlorine atom complex as the principal hydrogen-abstracting species in the toluene system. The better correlation with σ than with the σ$^+$ constants of Brown and Okamoto[20] for the NBS bromination of $XC_6H_4CH_2Ph$ confirms the previous reports[11,15] where different methods of analysis were used.

TABLE 4

Substituent effects on halogenation of $XC_6H_4CH_2Ph$ at 40° and k_H/k_D values[a]

		k/k_0	
X	SO_2Cl_2 in C_6H_6	Bu^{t}OCl in C_6H_6	NBS in CH_2Cl_2
p-PhO			2·44 ± 0·10[b]
p-Bu^t	1·36 ± 0·02	1·35 ± 0·01	1·64 ± 0·02
p-Ph	1·06 ± 0·03	1·06 ± 0·02	
H	1·00	1·00	1·00
p-F	0·95 ± 0·02	0·91 ± 0·02	0·77 ± 0·01
p-Cl	0·73 ± 0·03	0·74 ± 0·02	0·66 ± 0·01
p-Br			0·64 ± 0·02
m-F	0·62 ± 0·01	0·60 ± 0·02	0·45 ± 0·01
m-Cl	0·58 ± 0·01	0·57 ± 0·01	0·40 ± 0·01
m-Br			0·40 ± 0·01
ρ	−0·65 ± 0·02	−0·66 ± 0·03	−1·06 ± 0·02
r	0·999	0·998	0·992
ρ$^+$	−0·52 ± 0·04	−0·53 ± 0·04	−0·83 ± 0·07
r	0·972	0·972	0·981
k_H/k_D	1·84 ± 0·02	1·88 ± 0·04	3·20 ± 0·02[c]

[a] Corrected for traces of Ph_2CHD. [b] The reactivities of the *p*-PhO and the *p*-F compounds were measured against the *p*-Bu^t and the *m*-Cl compounds, respectively. [c] Measured from Ph_2CD_2 against *m*-$ClC_6H_4{\cdot}CH_2Ph$.

TABLE 5

Chlorination[a] of XC_6H_4Et at 40° in benzene

	SO_2Cl_2		Bu^{t}OCl	
X	$k_\alpha/k_{C_6H_{12}}$	k/k_0	$k_\alpha/k_{Ph_2CH_2}$	k/k_0
p-Bu^t	0·45 ± 0·02	1·47	1·36 ± 0·04	1·45
p-Et	0·86 ± 0·03	1·37[b]	2·57 ± 0·02	1·37[b]
m-Et	0·66 ± 0·01	1·06[b]	1·98 ± 0·02	1·05[b]
H	0·31 ± 0·01	1·00	0·94 ± 0·01	1·00
p-F	0·27 ± 0·01	0·87	0·82 ± 0·01	0·87
p-CH_2Cl	*c*	0·78[b]	0·74 ± 0·01	0·79[b]
p-Cl	0·24 ± 0·01	0·77	0·73 ± 0·01	0·78
m-Cl	0·17 ± 0·01	0·57	0·53 ± 0·01	0·56
log (k/k_0)	−0·67σ ± 0·03		+0·65σ ± 0·03	
r	0·983		0·986	
log (k/k_0)	−0·58σ$^+$ ± 0·04		+0·59σ$^+$ ± 0·04	
r	0·960		0·965	

[a] Average of 3 experiments. [b] Statistically corrected. [c] Measured against Ph_2CH_2, $k_\alpha/k_{Ph_2CH_2}$ = 0·73 ± 0·01. [d] Not included in the correlation by the Hammett equation.

Ethylbenzene System.—The relative rates of benzylic chlorination of XC_6H_4Et with SO_2Cl_2 and with Bu^{t}OCl in benzene at 40° were measured by means of competitive reactions using cyclohexane[1] and diphenylmethane, respectively, as standard substrates. In the SO_2Cl_2 system, for X = *p*-CH_2Cl the reactivity of this compound was measured against diphenylmethane which in turn has a reactivity value $k_{PhEt}/k_{Ph_2CH_2}$ of 0·94 identical to the value found for Bu^{t}OCl. The results given in Table 5 show good correlation by the Hammett equation using σ constants with ρ values of −0·67 ± 0·03 (*r* 0·983) for SO_2Cl_2 and −0·65 ± 0·03 (*r* 0·986) for Bu^{t}OCl. The former value is more negative than the value of −0·49 previously reported[1] in CCl_4 at 40°. The Hammett ρσ treatment of substituent effects in benzylic[21,22] and allylic[23] brominations has been successfully used in ascertaining the chain-carrying species. The toluene–Cl

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[22] K. H. Lee, *Tetrahedron*, 1969, **25**, 4357.

[23] J. H. Incremona and J. C. Martin, *J. Amer. Chem. Soc.*, 1970, **92**, 627.

atom π complex has been established[5] as the chain-carrying species from the measurements of deuterium isotope effects in the chlorination of [α-^{2}H]toluene with molecular chlorine and with sulphuryl chloride in the absence of a solvent. The near identity of the selectivities in benzylic chlorination with sulphuryl chloride and t-butyl hypochlorite in benzene together with the practically identical deuterium isotope effects provides strong evidence that the mechanism in these two chlorinating agents is one involving the benzene–Cl atom π complex as the chain-carrying species.

It appears that the σ_m and σ_p constants for the CH_2Cl group have not been previously evaluated. In view of the excellent correlation with σ constants found in the chlorination reactions these have been calculated and reported in Table 6; the average values being $\sigma_m = 0{\cdot}08_6$ and $\sigma_p = 0{\cdot}168 \pm 0{\cdot}007$.

TABLE 6

σ Constants for the chloromethyl group [a]

	SO_2Cl_2 in PhH		Bu^tOCl in PhH	
System	σ_m	σ_p	σ_m	σ_p
XC_6H_4Me	0·091	0·172	0·081	0·169
XC_6H_4Et		0·162		0·159
$XC_6H_4CH_2Cl$ [b]		0·181		

Average values $\sigma_m = 0{\cdot}086$ $\sigma_p = 0{\cdot}168 \pm 0{\cdot}007$

[a] Calculated from the equation $\log (k/k_0) = \rho\sigma$. [b] Based on unpublished data[19] where $\log (k/k_0) = -0{\cdot}63\sigma \pm 0{\cdot}01$ (r 0·997).

EXPERIMENTAL

N.m.r. spectra were recorded with a Hitachi–Perkin-Elmer R20-B instrument using tetramethylsilane as internal standard. G.l.c. analyses were performed on an Aerograph 1520 instrument equipped with a hot wire detector and a disc integrator using 20% SE-30 (5 ft × $\frac{1}{4}$ in), 20% FFAP (5 ft × $\frac{1}{8}$ in), 20% QF-1 (5 ft × $\frac{1}{8}$ in), and 10% QF-1 (5 ft × $\frac{1}{4}$ in) columns packed with Chromosorb W.

Materials.—The substituted diphenylmethanes were prepared as previously described[11] and the physical constants agreed with the reported values. [α,α-$^2H_2$]Diphenylmethane, b.p. 93° at 1 mmHg, n_D^{23} 1·5750, was synthesised in 84% yield by the reduction of benzophenone with lithium tetradeuterioaluminate (deuterium content >99%) and aluminium chloride. Mass spectrometric analyses gave a composition of 96·5% Ph_2CD_2 and 3·5% Ph_2CHD. [α,α-$^2H_2$]Benzyl bromide was prepared[24] from the alcohol obtained by reducing methyl benzoate with $LiAlD_4$. Reduction of the bromide with $LiAlH_4$ gave [α,α-$^2H_2$]toluene. A sample of [α,α-$^2H_2$]benzyl chloride, n_D^{20} 1·5355, prepared from the above alcohol gave an n.m.r. spectrum with the absence of the triplet at δ 4·1 characteristic of [α-^{2}H]benzyl chloride. *m*- and *p*-Methylbenzyl chlorides and *p*-ethylbenzyl chlorides were synthesised from the corresponding alcohols. Substituted ethylbenzenes were obtained as previously described.[25] t-Butyl hypochlorite, b.p. 78° at 760 mmHg, was prepared from the alcohol and sodium hypochlorite. All g.l.c. standards and other materials were purified in the usual manner.[1,11,25] All hydrocarbon substrates used in the competitive reactions were at least 99% pure by g.l.c.

Competitive Chlorination of XC_6H_4Me.—(*a*) *With* SO_2Cl_2 *at* 40°. Reactions were performed in benzene solution with XC_6H_4Me, PhMe, and SO_2Cl_2 (each 0·4M) under nitrogen in the usual way[1] irradiating with a 300 W Phillips sunlamp for 30—50 min to allow 20—25% consumption of the hydrocarbons. After adding the appropriate standard(s) and washing with saturated aqueous Na_2CO_3 the unconsumed hydrocarbons were analysed by g.l.c. which showed no other materials except the two benzyl chlorides. The reactivity of *p*-t-butyltoluene was measured against *p*-xylene, and under these conditions attack on the t-butyl group was negligible.

(*b*) *With* Bu^tOCl *at* 40°. These reactions were run in benzene using the toluenes (each 0·4M) and Bu^tOCl (0·24M) by irradiation with the sunlamp for 1—2 h. The solutions were treated as above and analysed for unconsumed hydrocarbons by g.l.c. which also showed the presence of the two benzyl chlorides. Analyses of the chlorides by g.l.c. in selected experiments indicated good material balance based on the hydrocarbons. The reactivity of *p*-t-butyltoluene was estimated as above.

Chlorination of [α,α-$^2H_2$]*Toluene at* 40°.—A known weight of a solution of the deuteriated toluene (1·6M) in benzene was allowed to react with SO_2Cl_2 (40 mol %) in the usual way. The initial and final amount of benzylic C–H in the [$^2H_2$]-toluene was estimated by the n.m.r. method using the set of peaks centred at δ 2·1 relative to known weights of added Ph_2CH_2 (δ 3·75). The reaction of [$^2H_2$]toluene (7·85 mmol) with SO_2Cl_2 (3·2 mmol) gave [α-^{2}H]benzyl chloride (1·49 mmol) and unchanged [$^2H_2$]toluene (4·64 mmol). Known weights of the solution were concentrated at 20° and 50 mmHg to remove gaseous products and then refluxed with aniline in CCl_4 for 1·5 h. The aqueous extract gave a total of 3·12 mmol of benzyl chlorides by the Volhard method.[1] The total consumption of benzylic proton was 3·21 mmol. Thus the amount of [α,α-$^2H_2$]benzyl chloride formed was 1·72 mmol, giving a k_H/k_D value of 2·3.

The reaction of [$^2H_2$]toluene (8·65 mmol) with Bu^tOCl (3·5 mmol) in benzene (concentrations as above) for 1·75 h gave [α-^{2}H]benzyl chloride (0·97 mmol) (by n.m.r.), and unconsumed [$^2H_2$]toluene (6·40 mmol) by g.l.c. as the acetone formed interfered in the n.m.r. method. The total benzyl chlorides estimated as above was 2·19 mmol. Thus the amount of [α,α-$^2H_2$]benzyl chloride formed was 1·22 mmol, giving a k_H/k_D value of 2·5. The estimated error is <10% in the k_H/k_D values.

Competitive Chlorination of $XC_6H_4CH_2Ph$.—(*a*) *With* SO_2Cl_2 *at* 40°. These reactions were carried out in benzene solution with the diphenylmethane, *p*-xylene, and sulphuryl chloride (each 0·4M) by irradiating for 30—50 min to allow 20—30% consumption of the hydrocarbons. Unconsumed hydrocarbons were analysed by g.l.c. after adding the appropriate standard(s) to aliquot portions of the reaction solution and treating with sodium carbonate as above. In representative experiments benzyl acetate was added to portions of the reaction solution, which was then concentrated at 40° and 50 mmHg, and diluted with a small volume of CCl_4. The unconsumed diphenylmethanes were estimated by multiple integration of the singlet at δ *ca.* 3·8 relative to the singlet at δ 4·93 for benzyl acetate. The average deviation for the area ratio on 5 integrations is usually ±2%. The total benzyl chlorides were estimated by concentrating portions of the reaction solution at 30°

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[24] R. T. Letsinger and D. F. Pollart, *J. Amer. Chem. Soc.*, 1956, **78**, 6079.

[25] E. P. Chang, R. L. Huang, and K. H. Lee, *J. Chem. Soc.* (*B*), 1969, 878.

and 50 mmHg and then refluxing for 2·5 h with 80% aqueous ethanol before titrating for the chloride by the Volhard method.[1]

(*b*) *With* Bu^tOCl *at* 40°. These reactions were run in benzene solution with *p*-xylene and the diphenylmethane (each 0·4M) and Bu^tOCl (0·24M) under nitrogen as above for 1—1·75 h. G.l.c. analyses were run as above. The minimum t-butanol–acetone ratio of 30 : 1 was estimated in selected experiments. Determination of the unconsumed diphenylmethanes by the n.m.r. method were carried out as described and showed good agreement with the g.l.c. values. Estimation of total benzyl chlorides carried out on selected experiments indicated good material balance.

Competitive Reactions of $XC_6H_4CH_2Ph$ *with* NBS *at* 40°.—These experiments were run in methylene chloride solution with Ph_2CH_2 and $XC_6H_4CH_2Ph$ (each 0·25M) and NBS (0·20M) in the usual way.[11] Unconsumed hydrocarbons were analysed by g.l.c. after adding a weighed amount of reference compound. Based on the NBS used, good material balance ($\geqslant$95%) was found in all cases. The results of triplicate experiments are given in Table 4. The reactivity values for the *p*-PhO and *p*-F compounds were measured against *p*-Bu^t and *m*-Cl compounds, respectively.

Competitive Chlorination of XC_6H_4Et.—(*a*) *With* SO_2Cl_2 *at* 40°. Reactions were carried out as above in benzene solution with XC_6H_4Et, cyclohexane, and SO_2Cl_2 (each 0·4M) by irradiating for 30—45 min to allow 20—24% consumption of the hydrocarbons. Cyclohexyl chloride was estimated by g.l.c. The benzyl chlorides were hydrolysed in 80% aqueous ethanol at room temperature and estimated by the Volhard method. For X = *p*-CH_2Cl, the substrate reactivity was estimated against Ph_2CH_2 as described below.

(*b*) *With* Bu^tOCl *at* 40°. These reactions were performed in the usual manner in benzene solution with XC_6H_4Et and Ph_2CH_2 (each 0·65M) and Bu^tOCl (0·32M) by irradiating for 1—2 h to allow 20—25% consumption of the hydrocarbons. Unconsumed hydrocarbons were analysed by g.l.c. Except for the reactions where X = *p*-CH_2Cl the total benzyl chlorides were estimated as above giving material balance of 99—101% in all cases based on the initial hydrocarbons. For X = *p*-Bu^t, the *ca.* 3% *p*-$EtC_6H_4C(Me_2)CH_2Cl$ formed was estimated by the n.m.r. method using the singlet at δ *ca.* 3·5, and the appropriate correction was made for the relative reactivity value.

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