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DIRECTIVE EFFECTS IN BENZYLIC HYDROGEN ATOM ABSTRACTION—II

RADICAL CHLORINATION BY SULPHURYL CHLORIDE

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Abstract—Relative reactivity values for benzaldehyde, deoxybenzoin, alkylbenzenes and cyclohexane toward sulphuryl chloride have been measured at 40° in carbon tetrachloride. The values (per α-H atom) for ethylbenzene, cumene and diphenylmethane, and that for cyclohexane relative to toluene are found to be significantly different from those reported for photochlorination under similar conditions. α-Chlorination of substituted toluenes relative to cyclohexane and of substituted ethylbenzenes relative to *m*-chlorobenzaldehyde by sulphuryl chloride in dilute CCl_4 solution at 40° has been measured and the results show a polar effect with ρ-values of -0.56 and -0.49, respectively, correlated by σ constants. Although the relative reactivity data for alkylbenzenes can probably be interpreted as evidence for H abstraction mainly by the chlorosulphinyl radical the reaction constant ρ found for the toluene system cannot be utilised to identify the principal H-abstracting species. Nevertheless, abstraction by the "π-complexed" Cl atom has been ruled out under the condition studied.

The light induced chlorination of substituted benzaldehydes[1] by sulphuryl chloride has been measured against *p*-diethylbenzene as standard substrate. It was shown that the total labile chloride ($ArCOCl + p\text{-}EtC_6H_4CHClCH_3$) amounted to 90 ± 2 mole% of the sulphuryl chloride used. This competitive technique has now been applied to evaluate the relative reactivities of some alkylbenzenes, cyclohexane, benzaldehyde and deoxybenzoin measured at low concentration of the substrates in carbon tetrachloride. The substituent effects in α-chlorination of nuclear-substituted toluenes and ethylbenzenes have also been studied.

The most probable course in the radical chlorination of hydrocarbons in non-complexing solvents by sulphuryl chloride can be represented by Eqs (1) and (2):

$$RH + \cdot SO_2Cl \rightarrow R\cdot + HCl + SO_2 \tag{1}$$

$$R\cdot + SO_2Cl_2 \rightarrow RCl + \cdot SO_2Cl \tag{2}$$

$$\cdot SO_2Cl \rightleftharpoons SO_2 + Cl\cdot \tag{3}$$

$$Ar + \cdot SO_2Cl \rightleftharpoons SO_2 + Ar \rightarrow Cl\cdot \tag{4}$$

The evidence for the existence of the $\cdot SO_2Cl$ radical has been provided by Kharasch and Zavist.[2] In presence of excess alkylbenzene solvents little difference was noted by Russell[3] between the products of photochlorination and sulphuryl chloride chlorination, possible because in both types of chlorination most of the Cl atoms are complexed with the solvent. Since it is now known that in presence of aromatic hydrocarbons

Cl atoms are mainly complexed,[4] it was suggested[3] that in presence of large excess of aromatic hydrocarbons equilibrium 3 is replaced by equilibrium 4.

In the absence of aromatic hydrocarbons photochemical chlorination and sulphuryl chloride chlorination gave different products in the chlorination of branched chain hydrocarbons. Thus photochlorination of 2,3-dimethylbutane at 55° gave a relative k_t/k_p ratio of 3·7 while sulphuryl chloride chlorination is much more selective, the k_t/k_p ratio being 10. The ratio of reactivity of secondary to primary H atoms, k_s/k_p, in n-alkanes[5] is 2·1 for photochlorination (20°) and 3·5 for sulphuryl chloride (85°) which would be expected to be larger at the lower temperature.

In competitive chlorination of toluene and t-butylbenzene[3] no difference in reactivity, as measured by the amounts of benzyl chloride and neophyl chloride formed, was noted when sulphuryl chloride or chlorine was used as the chlorinating agent. Walling and Miller[6] reported the same deuterium-isotope effect when α-d$_1$-toluene is photochlorinated or chlorinated with sulphuryl chloride in the absence of a solvent other than the hydrocarbon itself. This deuterium-isotope effect ($k_H/k_D = 2·1$ at 70°) is due primarily to the reactivity of the toluene-Cl atom π-complex. The chlorination of α-d$_1$-toluene in an aliphatic solvent gave lower deuterium-isotope effects with both reagents.[7] A larger deuterium-isotope effect was observed in sulphuryl chloride chlorination in carbon tetrachloride solution than for photochlorination performed in this solvent. In the photochlorination of α-d$_1$-toluene at 77° the deuterium-isotope effect, k_H/k_D· is reported to be 1·30 ± 0·01, while sulphuryl chloride chlorination, involving the more selective SO_2Cl radical, gives a value of 1·42 ± 0·02. These findings seem to suggest that, in non-complexing solvents, H-abstraction is mainly by the chlorosulphinyl (·SO_2Cl) radical in chlorination reactions of hydrocarbons by sulphuryl chloride.

RESULTS AND DISCUSSION

The relative reactivity of the benzylic H atoms in *p*-xylene, ethylbenzene, cumene and deoxybenzoin towards sulphuryl chloride has been measured against benzaldehyde as the reference compound and the reactivity of diphenylmethane was measured against *m*-chlorobenzaldehyde by a similar procedure. In order to facilitate comparison with relative reactivity values found for other radicals all competitive experiments were carried out in carbon tetrachloride at 40° and at a total concentration of 0·8 molar in aromatic compounds. Benzoyl chloride and *m*-chlorobenzoyl chloride formed were analysed by IR spectrophotometry.[8] The total labile chlorides (ArCOCl + Ar′CRR′Cl) were estimated by titrimetry as described for bromides.[8] In competitive reactions of *p*-xylene *vs* toluene and *p*-xylene *vs* cyclohexane gas chromatography was used to determine unconsumed aromatic hydrocarbons and cyclohexyl chloride formed. The results are given in Table 1. In experiments of benzaldehyde *vs* *p*-xylene the total chlorides found averaged 94·3 mole% of the total sulphuryl chloride used. The analytical procedure was checked with authentic mixtures of benzoyl chloride and *p*-methylbenzyl chloride and found to be accurate to ±2%. With experiments involving ethylbenzene the total labile chlorides ($PhCOCl + PhCHClCH_3$) found averaged 90·6% of the SO_2Cl_2 used, in agreement with those found for competitive reactions of benzaldehyde and *p*-diethylbenzene. The results are not affected by small amounts of β-chloroethylbenzene added before analysis for total labile chlorides.

In evaluating the reactivity of diphenylmethane a value of 0·64 for *m*-chlorobenzaldehyde relative to benzaldehyde based on the Hammett equation ($\rho = -0{\cdot}52$)[1] was used. The relative reactivity per α-H atom of the aromatic compounds studied and that for cyclohexane toward the $\cdot SO_2Cl$ radical are presented in Table 2 in which the data are compared with those previously reported for atomic Cl,[9] t-butoxy radical[10] and *p*-nitrophenyl[11] radicals. The present data for the hydrocarbons have been obtained under conditions almost identical to those reported for atomic Cl by Russell[9] who extrapolated their results to zero concentration of aromatic hydrocarbons in order to give values for the uncomplexed Cl atom. Russell's study of solvent effects in radical chlorination[9b] indicates that for an approximately one molar concentration of aromatic hydrocarbon the $k/k_{C_6H_{12}}$ values are very close to those extrapolated to zero concentration. The selectivity values for the two halogenating agents are significantly different, and the results tend to support the view[3–5, 7] that H-abstraction in sulphuryl chloride chlorination is primarily by the $\cdot SO_2Cl$ radical in non-complexing solvents.

In assessing radical selectivity it is also pertinent to consider polar effects due to nuclear substituents on the Hammett equation. The polar effects in α-chlorination of substituted toluenes and ethylbenzenes by sulphuryl chloride have been investigated to provide further evidence about the principal H-abstracting species. The substituted toluenes (0·8 molar) were allowed to react with SO_2Cl_2 in presence of an equimolar amount of cyclohexane. Since cyclohexane is more reactive than the toluenes the irradiation times were adjusted to allow 25 to 30% consumption of total substrates in order that a significant consumption of some of the substituted toluenes could be measured. The results given in Table 3 are based on gas chromatographic analysis of unconsumed toluenes and the cyclohexyl chloride formed. Application of the Hammett equation to the $k/k_{C_6H_{12}}$ values, by standard statistical methods,[12] show a polar effect with $\rho = -0{\cdot}56 \pm 0{\cdot}02$ (corr. coeff. 0·98) correlated by the σ constants[13] whereas correlation with the σ^+ constants[14] was poor ($\rho = -0{\cdot}47 \pm 0{\cdot}09$; $r = 0{\cdot}81$).

Each of the substituted ethylbenzenes was allowed to react with sulphuryl chloride at 40° in CCl_4 in presence of the standard substrate, *m*-chlorobenzaldehyde. The *m*-chlorobenzoyl chloride and the total labile chlorides (*m*-ClC_6H_4COCl + $ArCHClCH_3$) were determined as outlined above. The results are given in Table 4 in which the k/k_0 value of 1·14 for the *p*-ethyl substituent is in good agreement with the value of 1·12 calculated from the results in Table 1 where benzaldehyde was used as the reference compound. A ρ-value of $-0{\cdot}49 \pm 0{\cdot}02$ (corr. coeff. = 0·98) was found to be correlated by σ constants rather than by σ^+ constants ($\rho = -0{\cdot}40 \pm 0{\cdot}05$; $r = 0{\cdot}89$).

The available data from substituent effects on the toluene system are also given in Table 2. Comparison of the ρ-values for atomic Cl[15] ($\rho = -0{\cdot}48$) and for the *p*-nitrophenyl[11] radical ($\rho = -0{\cdot}59$), both correlated to σ constants at 60° in CCl_4, shows that atomic Cl is less selective. The magnitude of the polar effect for the t-butoxy[16] radical ($\rho = -0{\cdot}76$) at 40°, now established[16] to be better correlated by σ than by σ^+ constants appears to be larger than for atomic Cl,[15] in agreement with its higher selectivity.

Substituent effects in sulphuryl chloride chlorination of toluenes have been investigated recently by Yamamoto[17] at 70° and 80° in the absence of a solvent. The relative rates of formation of $ArCH_2Cl$ were obtained with reference to the formation of neophyl chloride from the standard substrate, t-butylbenzene. In the light of the known effects of aromatic solvents on such chlorinations enumerated in the introduction it is clear that in this particular case the H-abstracting species involved[4,7] is the π-complexed Cl atom. Thus the ρ-value of −0·75 at 70°, reported to be correlated by the modified Hammett equation[18] is due to the π-complexed Cl atom since photochlorination under identical conditions gave a similar ρ-value which is in agreement with a ρ-value of −0·76 at 70° for photochlorination[6] in the absence of a solvent. The photochlorination of substituted toluenes[15] in benzene (60°), chlorobenzene (80°) and benzonitrile (80°) gave ρ-values of −0·997, −0·779 and −0·530, respectively, all correlated with σ constants and these results can also be ascribed to the π-complexed Cl atom.

In contrast the ρ-value of −0·56 now found for the toluene system with sulphuryl chloride is definitely not due to H-abstraction by the π-complexed Cl atom. When compared with the value found for atomic Cl[15] (−0·48) at 60° the two halogenating agent appears to show the same substituent effect on the toluene system. For photochlorination of substituted toluenes at 40° in CCl_4 Russell and Williamson[19] obtained a ρ-value of −0·66 correlated to σ^+ constants in contrast to the σ correlation found by Hradil and Chvalovsky[15] for this solvent as well as for aromatic solvents. Russell and Williamson's study included *m*- and *p*-phenoxy substituents which may have resulted in nuclear chlorination since chlorination of *p*-methoxy toluene by t-butyl hypochlorite[16] resulted in ring chlorination as well. With ρ-values of −1·66 found for atomic Br[15] (PhCl, 80° and −1·46 for the $\cdot CCl_3$ radical[20] (PhCl, 50°) for the toluene system the extent of the polar effect as found by the Hammett equation for a number of radicals can now be arranged in decreasing order of magnitude: $Br\cdot > \cdot CCl_3 \gg Bu^tO\cdot \sim p\text{-}NO_2C_6H_4\cdot > SO_2Cl \sim Cl\cdot > Ph\cdot$. Except the first two radicals which show better correlation by σ^+ constants, the rest are correlated by σ constants for the toluene system, indicating that there is very little bond breaking in the transition state which resembles the reactants[21] for the more reactive and less selective radicals. Since Wiberg and Slaugh[7] found that the deuterium isotope effect, k_H/k_D, for the chlorination of α-d_1-toluene by sulphuryl chloride at 77° in CCl_4 is only 10% higher

TABLE 1. COMPETITIVE REACTIONS OF AROMATIC COMPOUNDS WITH SO_2Cl_2 AT 40° IN CCl_4

Substrates A	Substrates B	$K_A/K_{\alpha\text{-}B}$	mole% product[b]
PhCHO	p-MeC_6H_4Me	5·16 ± 0·16[a]	94·3
PhCHO	PhEt	5·62 ± 0·09	90·6
PhCHO	p-EtC_6H_4Et	2·51 ± 0·02	90·4
PhCHO	$PhCHMe_2$	5·83 ± 0·18	84·7
PhCHO	$PhCH_2COPh$	3·71 ± 0·15	—
m-ClC_6H_4CHO	Ph_2CH_2	3·54 ± 0·09	—
p-MeC_6H_4Me	PhMe	3·05 ± 0·03	—
C_6H_{12}	p-MeC_6H_4Me	1·88 ± 0·02	—

[a] average deviation from the mean of triplicate experiments.

[b] PhCOCl + α-chloride based on the amount of SO_2Cl_2 used.

TABLE 2. RELATIVE REACTIVITIES (PER α-HYDROGEN ATOM) FOR RADICAL REACTIONS

Substrates	·SO_2Cl (40°, CCl_4)	Bu^tO· (40°)[a]	Cl· (40°, CCl_4)[b]	p-$NO_2C_6H_4$· (60°, CCl_4)
$PhCH_3$	1·00	1·00	1·00	1·00
Ph_2CH_2	3·7	4·7	2·0	—
$PhCH_2CH_3$	4·2	3·2	2·5	6·2
$PhCH_2COPh$	6·3	—	—	—
$PhCH(CH_3)_2$	8·1	6·8	5·5	26
PhCHO	47	—	—	—
C_6H_{12}	1·4	1·5	2·0	1·4
Ref. No.	this work	10	9	11
		Toluene system		
ρ-value[c]	−0·56	−0·76	−0·48	−0·59
Solvent (temp)	CCl_4 (40°)	C_6H_6 (40°)	CCl_4 (60°)	CCl_4 (60°)
ref. no.	this work	16	15	11

[a] small amounts of CCl_4 or PhCl used as internal standard.

[b] extrapolated to zero conc. of alkylbenzenes.

[c] all correlated by σ constants.

TABLE 3. RELATIVE REACTIVITY OF SUBSTITUTED TOLUENES TOWARDS SO_2Cl_2 AT 40° IN CCl_4

X in X—$C_6H_4CH_3$	$K/K_{C_6H_{12}}$	K/K_0
p-Me	0·53 ± 0·02	1·26*
m-Me	0·42 ± 0·01	1·00*
H	0·21 ± 0·01	1·00
p-F	0·19 ± 0·01	0·91
p-Cl	0·15 ± 0·01	0·72
m-F	0·14 ± 0·01	0·67
m-Cl	0·12 ± 0·01	0·57

* statistically corrected.

$\log(K/K_0) = -0{\cdot}56\,\sigma \pm 0{\cdot}02$ (corr. coeff. = 0·98)

$\log(K/K_0) = -0{\cdot}47\,\sigma^+ \pm 0{\cdot}09$ (corr. coeff. = 0·81).

than that found for molecular chlorine under similar conditions the activati energy for the H-abstraction step by both atomic Cl and the ·SO_2Cl radical from nuclear substituted toluenes should be almost identical. Thus the reaction constant ρ found for sulphuryl chloride in the toluene system cannot be used to identify the principal H-abstracting species.

In comparison with the results found for atomic Br and the trichloromethyl radical the ρ-value of −0·49 found for the ·SO_2Cl radical at 40° for the ethylbenzene system appears reasonable. For the same system the ρ-values found[22] were −0·86 for atomic Br and −0·53 for the trichloromethyl radical, both at 80°.

TABLE 4. RELATIVE REACTIVITY OF SUBSTITUTED ETHYLBENZENES TOWARDS SO_2Cl_2 AT 40° IN CCl_4

X in X—$C_6H_4CH_2CH_3$	$K_x/K_{m\text{-}ClC_6H_4CHO}$	K/K_0
p-Bu^t	0·40 ± 0·01	1·33
p-Et	0·68 ± 0·02	1·14*
m-Et	0·64 ± 0·01	1·07*
H	0·30 ± 0·01	1·00
p-Cl	0·23 ± 0·02	0·77
m-Cl	0·20 ± 0·01	0·62

* statistically corrected.

$\log(K/K_0) = -0{\cdot}49\,\sigma \pm 0{\cdot}02$ (corr. coeff. = 0·98)

$\log(K/K_0) = -0{\cdot}40\,\sigma^+ \pm 0{\cdot}05$ (corr. coeff. = 0·89).

EXPERIMENTAL

Materials. Toluene, *m*- and *p*-xylenes (all Fluka puriss grade), *m*- and *p*-chlorotoluenes, and *m*- and *p*-fluorotoluenes (all Eastman Kodak white label grade) were dried and fractionated. *p*-Chloroethylbenzene, prepared in 73% yield by the Sandmeyer method from *p*-aminoethylbenzene, had b.p. 88–89°/35 mm, n_D^{23} 1·5156 (lit.[23] b.p. 182°/760 mm, n_D^{20} 1·5175). The other substituted ethylbenzenes except *m*-diethylbenzene (Aldrich, puriss grade) were prepared as previously described.[24] Cumene, diphenylmethane, bromobenzene and cyclohexane (spectrograde) were redistilled under N_2. All the hydrocarbons were passed through silica gel and stored under N_2, *p*-methylbenzyl chloride (Koch–Light puriss grade). α-Chloroethylbenzene, β-chloroethylbenzene and cyclohexyl chloride were redistilled and deoxybenzoin recrystallized before use. Sulphuryl chloride, (Fluka, puriss grade) stored in a dessicator, was used directly. All other materials used were purified as described elsewhere.[8]

Competitive reactions with sulphuryl chloride at 40°. These were carried out in CCl_4 soln containing a total concentration of 0·8 molar in aromatic substrates and 0·4 molar in SO_2Cl_2 in a 100 ml flask with a N_2 inlet, a coiled condenser and a drying tube ($CaCl_2$). After replacing the air with N_2 the flask was thermostated and irradiated with a 275-Watt G.E. sunlamp under a slow stream of N_2. In experiment involving benzaldehyde or *m*-chlorobenzaldehyde as one of the two competing substrates irradiation times were usually 1 to 3 hr during which time the SO_2Cl_2 was completely consumed (checked by IR at 1410 cm^{-1}). The exceptions are experiments which involve deoxybenzoin and diphenylmethane. In these experiments some SO_2Cl_2 remained unconsumed after 3 hr and had to be removed from aliquots of the reaction soln by evacuation at 50 mm press at room temp prior to estimation of total labile chlorides. The reaction soln was flushed with N_2 to remove SO_2 and HCl before estimation of benzoyl and *m*-chlorobenzoyl chlorides by IR spectrophotometry,[8] and for total labile chlorides (ArCOCl + Ar′CRR′Cl) aliquots of the soln were evacuated as above before estimation by titrimetry as previously described[8] for bromides. Optimum times for complete reaction of α-chlorides with aniline in CCl_4 at 80° varied from 10 min for cumyl chloride to 30 min for *p*-methylbenzyl chloride. With authentic mixtures of benzoyl chloride and *p*-methylbenzyl chloride the estimation for total labile chlorides was accurate to ±2%. In reaction of ethylbenzene vs benzaldehyde the estimation of the labile chlorides ($PhCOCl + PhCHClCH_3$) was not affected by small amounts of added β-chloroethylbenzene which by itself did not react with aniline at 80° under the conditions used. All competitive experiments were carried out in triplicate and the results given in Tables 1 and 4 were calculated by the usual relative rate equation.[8] *p*-Methylbenzyl chloride formed in competitive reactions between *p*-xylene and cyclohexane (see below) was determined by IR at 1267 cm^{-1} after evacuating off the more volatile components.

Competitive reactions of substituted toluenes and cyclohexane for SO_2Cl_2. These were carried out at 40° as described above in CCl_4 containing 0·8 molar concentration each of the toluene cyclohexane and SO_2Cl_2. Irradiation times were 6 to 10 hr depending on the substituted toluene to allow a 25 to 30% consumption of the substrates. Without flushing the soln with N_2 a 5 ml aliquot was shaken for 3 min with sat Na_2CO_3 aq, containing a known weight of bromobenzene (Ref standard), to destroy unconsumed SO_2Cl_2 and neutralize acidic products, and the soln dried ($CaCl_2$). Gas chromatographic analyses were carried out with an Aerograph 1520 instrument equipped with a disc integrator and a hot wire detector. A 5 ft × $\frac{1}{8}$ in column containing 20% QF-1 (Fluorosilicone) on Chromosorb W operated at 75° or 85° was used to analyse for the unconsumed toluenes and the cyclohexyl chloride formed, calibrated against bromobenzene. With *p*-xylene vs cyclohexane only cyclohexyl chloride and *p*-methylbenzyl chloride were formed, identified by retention time. The sum of the unconsumed *p*-xylene and the amount of *p*-methylbenzyl chloride found by IR (see above) averaged 103% of the initial *p*-xylene. With the other substituted toluenes, apart from the substituted benzyl chlorides and cyclohexyl chloride no other significant peaks were detected. The results present in Tables 1 and 3 are the average of triplicate experiments.

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