Polar Effects in Hydrogen Abstraction from Benzaldehydes. Part IV.[1] Solvent Effect on Chlorination by Sulphuryl Chloride

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Enhancement of the reactivity of benzaldehyde relative to cyclohexane towards sulphuryl chloride at 40° in CCl_4 was demonstrated by modifying the reactivity of the hydrogen-abstractor radical in the rate-determining step with added benzene and t-butylbenzene which are able to complex with atomic chlorine. Relative rates of chlorination of substituted benzaldehydes with SO_2Cl_2 have been determined in benzene, and in 2M-$PhBu^t$ in CCl_4 at 40°. The Hammett correlations with σ constants (ρ −0·68 and −0·86, respectively) are attributed to the selective benzene and t-butylbenzene π-complexed chlorine atom.

In Part III[1] the radical chlorination of *meta*- and *para*-substituted benzaldehydes with SO_2Cl_2 in CCl_4 was found to obey the Hammett, $\rho\sigma$ relationship. It was also established[2] that $k(PhCHO)/k(C_6H_{12})$ values towards SO_2Cl_2 in CCl_4 at 40° were independent of the concentration of the aldehyde up to 2·4M, even in the presence of 2% trichloroethylene which is known to be an efficient chlorine-atom trap.[3] However, at a fixed concentration of benzaldehyde the reactivity values were reported to be significantly increased by added t-butylbenzene. The investigation of such a solvent effect has now been extended to the chlorination of substituted benzaldehydes in benzene and also in 2M-$PhBu^t$ in CCl_4.

EXPERIMENTAL

I.r. analysis[4] for ArCHO and ArCOCl, and g.l.c. analysis[5,6] for cyclohexyl chloride were performed as previously reported.

Materials.—Benzene and t-butylbenzene (AnalaR grade) were distilled from P_2O_5 and stored over molecular seive (3 A). All the aldehydes and other chemicals employed were purified in the usual manner.[1,4,5]

Competitive Reactions at 40°.—These were carried out as previously described[1] using an aldehyde : C_6H_{12} : SO_2Cl_2 ratio of 1 : 1 : 1·5 in the appropriate solvent. For experiments on substituent effects the concentration of the aldehyde was 0·6M. Irradiation times with a 275 W sunlamp were 0·5—2 h to allow 26—33% consumption of the organic substrates. For g.l.c. estimation of $C_6H_{11}Cl$ a portion of the reaction solution was added to a known weight of *p*-xylene or PhBr and treated[1] with saturated aqueous Na_2CO_3. Polychlorination of cyclohexane was found (g.l.c.) to be negligible. Aroyl chlorides and unconsumed aldehydes were estimated by i.r. spectrophotometry.[4,5] Determination of the aroyl chlorides was also carried out by titri-

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[1] Part III, K. H. Lee, *Tetrahedron*, 1970, **26**, 2041.

[2] K. H. Lee and T. O. Teo, *Chem. Comm.*, 1970, 860.

[3] C. Walling and J. A. McGuiness, *J. Amer. Chem. Soc.*, 1969, **91**, 2053.

[4] K. H. Lee, *Tetrahedron*, 1968, **24**, 4793.

[5] K. H. Lee, *Tetrahedron* (*a*) 1969, **25**, 4363; (*b*) 1970, **26**, 1503.

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

metry [5a] after reaction with $PhNH_2$ at room temperature. Cyclohexyl and neophyl chlorides were not implicated in this method of estimation of ArCOCl which gave good agreement with the i.r. method. A check with known solutions of ArCOCl shows that the two methods gave results agreeing within ±2%. The results, calculated by the usual relative rate equation [4] and presented in Tables 1 and 2, are the average of triplicate experiments.

RESULTS AND DISCUSSION

The competitive chlorination of benzaldehyde and cyclohexane with SO_2Cl_2 at 40° was performed in CCl_4 with added benzene and also in pure benzene as solvent. Estimation of benzoyl chloride and unconsumed benzaldehyde by i.r. spectrometry gave an excellent material balance for the initial aldehyde used. The reactivity values, $k/k_{C_6H_{12}}$ (per molecule) together with those previously reported [2] for reactions in CCl_4 containing added t-butylbenzene are given in Table 1. The reactivity values are enhanced by 2·20 in changing the solvent composition from pure CCl_4 to pure benzene and by 2·39 from pure CCl_4 to 2M-PhBu^t in CCl_4. Neophyl chloride formation became significant when the concentration of t-butylbenzene was increased beyond 2M where estimation of benzoyl chloride and cyclohexyl chloride gave less reliable data.

TABLE 1

Effects of added aromatic hydrocarbons on reactivity [a] of benzaldehyde toward SO_2Cl_2 at 40° in CCl_4

Diluent	[Hydrocarbon]/M	0·0	0·4	0·8	1·2	1·6	2·0	2·4	11·2
C_6H_6	$k/k_{C_6H_{12}}$ for 0·8M-PhCHO	0·66	0·90	1·02	1·09	1·16		1·28	1·46
PhBu^t	$k/k_{C_6H_{12}}$ for 1·6M-PhCHO	0·72	1·20	1·42	1·56	1·64	1·72		

[a] Per molecule relative to cyclohexane based on the average of triplicate experiments with average deviation of < ±3%.

TABLE 2

Relative reactivity [a] of substituted benzaldehydes toward SO_2Cl_2 at 40°

	C_6H_6		2M-PhBu^t in CCl_4	
Substituent	k/kC_6H_{12}	k/k_0	k/kC_6H_{12}	k/k_0
p-Bu^t	2·05 ± 0·02	1·40	3·03 ± 0·04	1·53
p-Me	1·89 ± 0·03	1·30	2·80 ± 0·04	1·42
m-Me	1·61 ± 0·05	1·10	2·23 ± 0·04	1·13
None	1·46 ± 0·02	1·00	1·98 ± 0·03	1·00
p-Cl	1·02 ± 0·02	0·70	1·25 ± 0·02	0·63
m-F	0·85 ± 0·01	0·58	1·02 ± 0·02	0·50
m-Cl	0·83 ± 0·02	0·57	1·00 ± 0·02	0·50
	ρ −0·68 ± 0·01 (r 0·999)		ρ −0·86 ± 0·01 (r 0·999)	

[a] Per molecule relative to cyclohexane.

Having established the enhanced reactivity in aromatic solvents, the reactivity of substituted benzaldehydes relative to cyclohexane towards SO_2Cl_2 at 40° has been measured in benzene, and in 2M-PhBu^t in CCl_4. For the *m*- and *p*-methyl-, and the *p*-t-butylbenzaldehydes chlorination at these substituents was found by g.l.c. to be significantly low compared with the other products (ArCOCl and $C_6H_{11}Cl$). However, such side-products were not implicated in the analytical procedures adopted. Application of the Hammett equation to the results in Table 2, by standard statistical methods,[7] shows that in both solvent systems the results are well correlated by the σ constants of McDaniel and Brown,[8] with ρ −0·68 ± 0·01 (r 0·999) for benzene, and −0·86 ± 0·01 (r 0·999) for 2M-PhBu^t in CCl_4, respectively. This finding is in agreement with correlations using σ constants previously reported [1,4,5b] for substituted benzaldehydes with SO_2Cl_2, Cl_3CSO_2Cl, and $BrCCl_3$ in CCl_4 solution. A recent study of hydrogen abstraction from benzaldehydes by nitrogen dioxide [9] yielded results which are also better correlated with σ rather than with σ^+ constants, giving ρ −1·10 ± 0·03 (r 0·998) at 40°.

Photochemical chlorination and chlorination with SO_2Cl_2 yielded different reactivity values in the chlorination of branched-chain hydrocarbons.[10] However, in aromatic hydrocarbons little difference was noted in the results from both methods of chlorination. From studies of solvent effects in the photochlorination of aralkyl hydrocarbons,[11] substituted toluenes,[12] and alkyl acetates [13] it is well established that aromatic hydrocarbons, which are good π-electron donors to atomic chlorine, greatly enhance selectivity. More recently it was established [6] from measurements of polar and deuterium-isotope effects that the benzene-complexed chlorine atom is the principal hydrogen-abstracting species in the chlorination of nuclear-substituted toluenes, ethylbenzenes, and diphenylmethanes in benzene with SO_2Cl_2 and with t-butyl hypochlorite. The highly selective benzene-complexed chlorine atom has also been attributed as the abstracting radical in chlorination of 2-arylethyl chlorides,[14] benzyl chlorides and α-substituted toluenes,[15] and 2-arylethyl fluorides [16] with SO_2Cl_2 in benzene. The present ρ value, −0·68, for chlorination of benzaldehydes in benzene compared with −0·53 [1] in CCl_4 shows consistent trends for substituted toluenes (−0·83 [15] and −0·56 [5a]) and for ethylbenzenes (−0·67 [15] and −0·49 [5a]) in the two solvent systems. The larger magnitude of −0·86 for the ρ value found for chlorination of the benzaldehydes in 2M-PhBu^t in CCl_4 solution is consistent with the electron-donating t-butyl group which makes PhBu^t a better complexing agent for chlorine atoms than benzene.

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