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POLAR EFFECTS IN HYDROGEN ABSTRACTION FROM BENZALDEHYDES—II

RADICAL CHLORINATION BY CCl_3SO_2Cl

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Abstract— The relative rates of chlorination of substituted benzaldehydes with CCl_3SO_2Cl (I) have been determined in dilute CCl_4 solution at 80° by means of competitive reactions using *p*-diethylbenzene as reference standard. A polar effect ($\rho = -0.54$) correlated by the Hammett equation with the σ constant was found to differ from the value (-0.74) previously reported for $BrCCl_3$. Different selectivity values were obtained for I and $BrCCl_3$ toward benzaldehyde, ethylbenzene, benzyl methyl ether, benzhydryl methyl ether, and benzyl benzhydryl ether. These results indicate that the CCl_3SO_2 radical is mainly responsible for benzylic hydrogen-abstraction.

TRICHLOROMETHANE sulphonyl chloride (I) has been found to be a specific and effective free-radical chlorinating agent[1, 2] for n-alkanes and alkylbenzenes. Mechanistic studies indicate that chloroform, sulphur dioxide and alkyl chlorides were formed by the following free-radical chain sequence:-

$$R\cdot + CCl_3SO_2Cl \rightarrow RCl + CCl_3SO_2\cdot \qquad (1)$$

$$CCl_3SO_2\cdot + RH \rightarrow R\cdot + CCl_3SO_2H \qquad (2)$$

$$CCl_3SO_2H \rightarrow CHCl_3 + SO_2 \qquad (3)$$

The light-induced chlorination of n-hexane[1b] with I showed that only secondary chlorides were formed as monochlorinated products, whereas chlorination of n-hexane with chlorine and sulphuryl chloride gave monochlorinated products containing 22 and 17% l-chlorohexane, respectively. n-Decane[2] was chlorinated by I induced by benzoyl peroxide to the extent of only 1·5% at the primary position whereas chlorination with chlorine and sulphuryl chloride gave monochlorinated products containing 15 and 10% l-chlorodecane, respectively.

In contrast to the reported[3] occurrence of substitution of aromatically bonded bromide by chlorine in benzylic chlorinations of *p*-bromotoluene with both chlorine and sulphuryl chloride, the alkyl side-chain of this compound was chlorinated[1b] with I without any halogen substitution. Chlorination of ethylbenzene[1b] with I gave only α-chloroethylbenzene compared to the significant amounts of β-chloroethylbenzene found in the monochlorinated products when chlorine and sulphuryl chloride were used to chlorinate ethylbenzene under comparable conditions.

It was found[1d] that the relative reactivity of cyclohexane and toluene towards I is significantly different from that found for bromotrichloromethane. Furthermore, it is of interest to note that carbon tetrachloride has never been found as a product in the reactions of Cl_3CSO_2Cl with hydrocarbons. The polar effects in hydrogen abstraction from substituted benzaldehydes by the trichloromethyl radical generated from $BrCCl_3$ have been reported[4] to be correlated by the Hammett equation. The investigation of such effects has now been extended to the chlorination of benzaldehydes with I. Relative reactivity values for benzaldehyde, ethylbenzene, benzyl methyl ether, benzhydryl methyl ether, and benzyl benzhydryl ether toward I have been measured and compared with those found for bromotrichloromethane.

RESULTS AND DISCUSSION

The reactivity of substituted benzaldehydes towards Cl_3CSO_2Cl (I) relative to *p*-diethylbenzene have been measured in dilute CCl_4 soln at 80°. Some representative results are given in Table 1 where the reactivity values were calculated by the usual relative rate equation[4] based on the amount of aroyl chlorides formed and the unconsumed *p*-diethylbenzene. The unconsumed aldehydes were also estimated and the material balance for initial aldehyde was good in every case. The *p*-diethylbenzene was assumed to have been chlorinated only in the α-position as reported in the case of ethylbenzene.[1b] No suitable method could be developed for the estimation of α-chloro-*p*-diethylbenzene in the presence of aroyl chlorides and unconsumed (I). The GLC analysis for unconsumed *p*-diethylbenzene against two standards was found to be accurate to ±2%. The material balance for (I) based on unconsumed *p*-diethylbenzene and (I), and the XC_6H_4COCl formed was usually 88 to 96%.

TABLE 1. SOME REPRESENTATIVE RESULTS OF COMPETITIVE REACTIONS[a] OF XC_6H_4CHO AND p-EtC_6H_4Et WITH Cl_3CSO_2Cl AT 80°

	ArCHO			p-EtC_6H_4Et		Cl_3CSO_2Cl		
Aldehyde	Initial mmole	Final mmole	ArCOCl mmole	Initial mmole	Final mmole	Initial mmole	Final mmole	Rel. Reactivity[b] $k_{ArCHO}/k_{p-EtC_6H_4Et}$
C_6H_5CHO	10·10	8·01	2·38	10·00	6·85	9·47	3·10	0·70
C_6H_5CHO	10·00	7·81	2·36	9·87	6·88	9·46	3·50	0·71
C_6H_5CHO	9·90	7·15	2·55	9·85	6·55	9·85	3·51	0·73
p-$Bu^tC_6H_4CHO$	9·99	7·60	2·52	10·05	7·30	9·49	3·88	0·91
p-$Bu^tC_6H_4CHO$	9·98	7·08	2·88	10·00	6·81	9·48	3·12	0·90
p-$Bu^tC_6H_4CHO$	10·00	7·10	3·02	9·95	6·74	9·47	3·00	0·92
m-FC_6H_4CHO	9·99	8·56	1·39	9·85	7·27	9·43	4·86	0·49
m-FC_6H_4CHO	10·00	8·45	1·42	9·83	7·02	9·47	4·72	0·46
m-FC_6H_4CHO	9·99	7·93	2·10	10·10	6·02	9·46	2·79	0·45

[a] Carried out in CCl_4 (25 ml) under irradiation with a Sunlamp for 2 to 4½ hrs.

[b] Calculate by the usual relative rate equation[4] based on ArCOCl and unconsumed p-EtC_6H_4Et.

The results given in Table 2 indicate that the chlorination of benzaldehydes is subject to polar influences as in the case of bromination by bromotrichloromethane.[4] Application of the Hammett equation by standard statistical methods[8] shows that the substituent effects are better correlated by the σ constants of McDaniel and Brown[9] with $\rho = -0{\cdot}54 \pm 0{\cdot}04$ ($r = 0{\cdot}999$) than by the σ^+ constants of Brown and Okamato[10] with $\rho = -0{\cdot}46 \pm 0{\cdot}03$ ($r = 0{\cdot}979$).

In order to ascertain the hydrogen-abstracting species involved the halogenation of $PhCH_2OCHPh_2$ (II) and the competitive halogenation of a number of substrates was carried out with $BrCCl_3$ and Cl_3CSO_2Cl. The reaction of $BrCCl_3$ with (II) gave the corresponding bromo-ethers (cf. $ArCHBrOMe$[11, 12] and $PhCHBrOCH_2Ph$[12]) which partially decompose thermally to benzaldehyde and benzophenone. The remaining bromo-ethers were quantitatively converted to these carbonyl products by treatment with sat. Na_2CO_3 aq. The ratio of $PhCHO:Ph_2CO$ measured by IR was 1·30 ± 0·04 and this is taken as the intramolecular reactivity k_s/k_t of (II) towards the $\cdot CCl_3$ radical. The reaction of Cl_3CSO_2Cl with (II) gave PhCHO (0·52 mmole) and PhCOCl (0·57 mmole) estimated by IR, and $PhCH_2Cl$ (1·40 mmoles) measured by GLC. After treatment with Na_2CO_3 aq the total PhCHO measured was 2·48 mmoles and Ph_2CO 1·39 mmoles. The ratio of (PhCHO + PhCOCl):Ph_2CO found was 2·05 ± 0·04, and, taking the amount of PhCOCl to be equivalent to a similar quantity of PhCHO initially formed, this ratio gives the k_s/k_t value of (II) towards Cl_3CSO_2Cl, significantly different from the value observed for $BrCCl_3$.

TABLE 2. RELATIVE REACTIVITY OF XC_6H_4CHO TOWARD Cl_3CSO_2Cl AT 80°

Substituent	p-Bu^t	p-Me	m-Me	H	p-Cl	m-F	m-Cl
$k_{XC_6H_4CHO}/k_{p\text{-}EtC_6H_4Et}$	0·91 ± 0·01	0·87 ± 0·01	0·77 ± 0·02	0·71 ± 0·01	0·54 ± 0·01	0·47 ± 0·02	0·44 ± 0·01
k/k_0	1·28	1·23	1·08	1·00	0·76	0·66	0·62

log $(k/k_0 = -0{\cdot}54\sigma \pm 0{\cdot}04$ (corr. coeff. = 0·999)
log $(k/k_0) = -0{\cdot}46\sigma^+ \pm 0{\cdot}03$ (corr. coeff. = 0·979)

The reaction of benzyl methyl ether with (I) gave benzaldehyde (0·46), no benzoyl chloride and $PhCHClOMe$[13] quantitatively converted by Na_2CO_3 aq treatment to a total of 4·50 mmoles PhCHO. The unconsumed $PhCH_2OMe$ (5·41 mmoles) measured by GLC shows that the material balance for initial ether was 99 %, and the unreacted I and PhCHO accounted for 95 % of the initial Cl_3CSO_2Cl. Chlorination of benzyl methyl ether with (I) is thus highly specific in contrast to the results with molecular chlorine[14] which gave mono-chlorinated products containing 68 % PhCHClOMe and 32 % $PhCH_2OCH_2Cl$. The present results also indicate that the implication of atomic chlorine is insignificant.

The completely different selectivity values given in Table 3 for halogenation by $BrCCl_3$ and by Cl_3CSO_2Cl tend to support previous reports[1] that the $Cl_3CSO_2\cdot$ radical is mainly responsible for hydrogen-abstraction in chlorination with (I). Atomic chlorine may be implicated in chlorinations with (I) as was found to be the case of t-butyl hypochlorite chlorination of substituted toluenes studied by Walling and McGiness.[15] The competitive chlorination of benzaldehyde and ethylbenzene with (I) was also carried out in triplicate in presence of 2 mole % $CHClCCl_2$ (relative to I) which has been found to be an effective chlorine trap.[15] The k_{PhCHO}/k_{PhEt} value of 2·12 ± 0·05 found was quite identical to the value of 2·07 ± 0·06 measured in the absence of the chlorine trap. Thus the implication of atomic Cl appears to be negligible or that atomic Cl gives similar selectivity values to those found for the $Cl_3CSO_2\cdot$ radical contrary to previous findings.[1, 2]

The ρ-value of $-0{\cdot}54$ found for substituted benzaldehydes towards (I) appears reasonable, and the better correlation with σ constants by the Hammett equation in the present study is consistent with the explanation offered previously[4] in the case of $BrCCl_3$.

EXPERIMENTAL

Materials. Trichloromethanesulphonyl chloride (Eastman Kodak) was recrystallized from aq EtOH until constant apparent molar ε (740 at 1408 cm^{-1} in CCl_4). All the aldehydes used were purified as previously described.[4] The aroyl chlorides required for IR calibration were from commercial sources or prepared from the corresponding pure acid and $SOCl_2$, and purified by standard procedures. All other chemicals employed were purified in the usual manner.[4, 5, 6]

IR analysis[4] *and GLC analysis.*[7] These were carried out as previously reported. Quantitative analyses by GLC for ethylbenzene, benzyl chloride and benzyl methyl ether were based on integrated peak areas relative to that of bromobenzene, and for *p*-diethylbenzene two standards were used, bromobenzene and *p*-bromotoluene. The GLC results given in Tables 1 and 3 are the average of at least 5 integrated peak area ratios.

TABLE 3. COMPARISON OF REACTIVITY VALUES[a] FOR $BrCCl_3$ and Cl_3CSO_2Cl IN CCl_4 AT 80°

Substrates		KA/KB	
A	B	$BrCCl_3$	Cl_3CSO_2Cl
PhCHO	PhEt	1·20 ± 0·01[b]	2·07 ± 0·05 (2·12 ± 0·05)[c]
$PhCH_2OMe$	PhEt	5·95 ± 0·16	2·80 ± 0·03
$PhCH_2OMe$	Ph_2CHOMe	1·67 ± 0·03	2·05 ± 0·17
PhCHO	Ph_2CHOMe	0·45 ± 0·04	1·38 ± 0·02

[a] Average of triplicate experiments.
[b] from Ref. 4.
[c] 2 mole % $CHClCCl_2$ added as a chlorine trap in these experiments.

Reaction of Cl_3CSO_2Cl *with* (*a*) $PhCH_2OCH_3$. A soln of the ether (1·221 g; 10·0 mmoles) and I (2·18 g; 10·0 mmoles) in CCl_4 (25 ml) was irradiated for 3 hr at 80° under N_2 with a 275-W GE Sunlamp. IR analysis of the soln gave PhCHO (0·46 mmoles), no PhCOCl and unconsumed I (5·01 mmoles). When an aliquot of the reaction soln was diluted and treated with sat. Na_2CO_3 aq and dried ($CaCl_2$) the total PhCHO found was 4·50 mmoles. A weighed amount of PhBr was added to an aliquot of the reaction soln and then treated with sat. Na_2CO_3 aq and dried ($CaCl_2$). Gas chromatographic estimation at 95° showed 5·41 mmoles of unconsumed $PhCH_2OMe$.

Reaction of Cl_3CSO_2Cl *with* (*b*) Ph_2CHOCH_2Ph(II). A soln of the ether (2·742 g; 10·0 mmoles) and I (2·18 g; 10·0 mmoles) in CCl_4 (25 ml) was irradiated for 2 hr at 80° as described above. Temp programmed GLC analysis gave the following compounds in order of retention time: Cl_3CSO_2Cl, $PhCH_2Cl$, PhCHO, PhCOCl, Ph_2CHOCH_2Ph and Ph_2CO. The benzyl chloride estimated at 85° by GLC was 1·40 mmoles. After treatment of the reaction soln with sat Na_2CO_3 aq benzhydrol was found in the gas chromatogram indicating that chlorodiphenylmethane was present in the reaction soln. IR analysis of the reaction soln gave PhCOCl (0·57 mmole) PhCHO (0·52 mmole) and, after suitable dilution, I (4·06 mmoles). IR estimation of a diluted aliquot of the reaction mixture, after Na_2CO_3 treatment as above, gave PhCHO (2·48 mmoles) and Ph_2CO (1·39 mmoles).

Competitive chlorination with Cl_3CSO_2Cl. A soln of CCl_4 (25 ml) containing the two substrates (10 mmoles each) and I (10 mmoles) was irradiated at 80° with the Sunlamp as described above for 2 to 4½ hr during which time 20 to 35% of the substrates had reacted. Aliquots of the reaction soln were suitably diluted for IR estimation of unconsumed aldehydes, Cl_3CSO_2Cl, benzophenone and aroyl chlorides. Reaction solns that contain an ether as one of the competing substrates were also treated with Na_2CO_3 aq as above prior to IR measurement. Unconsumed hydrocarbons and benzyl methyl ether were determined by GLC using aliquots of the reaction soln added to a known weight of standard(s). All competitive experiments were carried out in triplicate and the results are given in Tables 1 and 3.

Competitive bromination with $BrCCl_3$. These were carried out at 80° in CCl_4 soln in the usual manner.[4, 6] Bnezoyl bromide was estimated by titration,[4] benzophenone and unconsumed benzaldehyde were analysed by the IR method. Reaction solns containing an ether substrate were also treated with Na_2CO_3 aq in the usual way before IR measurement. Unconsumed ethylbenzene and benzyl methyl ether were estimated by GLC with bromobenzene as standard. All the results reported in Table 3 are the average of triplicate experiments.

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