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POLAR EFFECTS IN HYDROGEN ABSTRACTION FROM BENZALDEHYDES—I

ABSTRACTION BY THE TRICHLOROMETHYL RADICAL

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Abstract—The relative rates of hydrogen abstraction by the trichloromethyl radical have been determined for nine *m*- and *p*-substituted benzaldehydes by means of competitive reactions using ethylbenzene as reference standard. A polar effect ($\rho = 0{\cdot}74$) was shown to be correlated by the Hammett equation with the σ constants, and the anomalous behaviour of the *p*-MeO and *p*-PhO substituents is discussed. The deuterium isotope effect K_H/K_D was found to be 2·4 at 80°.

THE abstraction of benzylic H atoms from alkylbenzenes,[1,2] allylbenzenes,[3] benzyl ethers[1,4] benzaldehyde dimethyl acetals[4,5] and phenolic H atoms[6] by a variety of radicals has been investigated extensively in recent years. The rates of formation of benzylic and PhO radicals resulting from such homolytic dehydrogenation have been found to obey the Hammett $\rho\sigma$ relationship for *m*- and *p*-substituents in the ring. In contrast very limited data are available on the relative rates of hydrogen abstraction from substituted benzaldehydes. Walling and McElhill[7] compared the relative reactivities of a limited number of substituted benzaldehydes towards the perbenzoate and the *p*-chloroperbenzoate radicals and found a fair correlation by the Hammett equation, the polar effect being rather sensitive to the structure of the abstracting radical. More recently, Arai[8] investigated the substituent effects in the radical chlorination of benzaldehyde by sulphuryl chloride and obtained a ρ-value of $-0{\cdot}48$. The present investigation of the relative reactivity of nine *m*- and *p*-substituted benzaldehydes, measured against ethylbenzene as standard, towards the trichloromethyl radical generated from bromotrichloromethane represents the first extensive and fruitful study of polar effects in the homolytic hydrogen abstraction from the benzaldehyde system.

RESULTS AND DISCUSSION

It was observed[9] that aromatic aldehydes do not react with carbon tetrachloride and bromotrichloromethane at the b.ps of the polyhalomethanes. However, high yields (83–94%) of aroyl chlorides and bromides and of chloroform were obtained from benzaldehyde and the *p*-chloro and *p*-methoxy derivatives when the reaction was carried out at 180–205° using a polyhalomethane to aldehyde ratio of 2 to 5·1. In this work the aldehyde (0·4 molar) and bromotrichloromethane (0·8 molar) in carbon tetrachloride were irradiated at 80° with light of wavelength > ca. 320 mμ. Only the bromides were formed, and characterized in the case of benzoyl bromide by ν_{max} at 1780, 1194, 1172 and 853 cm^{-1} (lit.[10] 1792, 861 cm^{-1}), and of *p*-chlorobenzoyl bromide by ν_{max} at 1774, 1194, 1170 and 854 cm^{-1}, and by the absence of the aroyl chloride peaks at 875 and 878 cm^{-1}, respectively. In the absence of bromotrichloromethane, irradiation of the carbon tetrachloride solution a much slower rate of formation of benzoyl chloride, ν_{max} 1778, 1737, 1203, 1175 and 875 cm^{-1} (lit.[11] 1782, 1740, 875 cm^{-1}) and of *p*-chlorobenzoyl chloride, ν_{max} 1780, 1740, 1172, and 878 cm^{-1} (lit.[11] 1783, 1742 cm^{-1}) from the corresponding aldehydes was observed.

The results of the product studies are given in Table 1. The unreacted aldehydes were estimated by IR spectrophotometry and the acyl halides were determined by (a) titration with sodium methoxide, and (b) reacted with excess aniline and the aqueous extract of anilinium halide estimated by Volhard's method. Excellent agreement on the determinations by the two methods was achieved. In experiments Nos 1 and 2 the benzoyl bromide was shaken with anhydrous methanol and estimation of the methyl benzoate by IR gave values of 97 to 98% of that found by the other two methods. However, the methyl benzoate method is not generally applicable to the other substituted benzoyl bromides as the hydrogen bromide released rapidly catalysed the conversion of the excess benzaldehydes to the di-methyl acetals with the consequent formation of water which partly hydrolysed the bromides to the acids. In experiment No. 3 when the benzoyl bromide was titrated in presence of added α-bromoethylbenzene with sodium methoxide no significant implication of the added bromide was noted. In all the experiments of Table 1 the material balance based on the two titrimetric methods and the unreacted aldehydes was in the range of 97·4 to 100·6%.

The results shown in Table 1, in the case of bromotrichloromethane as the halogenating agent, can be interpreted by the following reaction scheme:

$$\mathrm{BrCCl_3} \rightarrow \mathrm{Br^{\bullet}} + {}^{\bullet}\mathrm{CCl_3}$$

$$\cdot\mathrm{CCl_3} + \mathrm{PhCHO} \xrightarrow{k_1} \mathrm{CHCl_3} + \mathrm{Ph\dot{C}O} \tag{1}$$

$$\mathrm{Ph\dot{C}O} + \mathrm{BrCCl_3} \xrightarrow{k_2} \mathrm{PhCOBr} + \cdot\mathrm{CCl_3} \tag{2}$$

$$\mathrm{Ph\dot{C}O} + \mathrm{PhCHO} \xrightarrow{k_3} \mathrm{Ph\dot{C}HOCOPh} \tag{3}$$

$$2\,\mathrm{Ph\dot{C}HOCOPh} \xrightarrow{k_4} (\mathrm{PhCHOCOPh})_2 \tag{4}$$

$$\mathrm{PhCO} \xrightarrow{k_5} \mathrm{Ph}\cdot + \mathrm{CO} \tag{5}$$

The rate constant K_2 would be expected to be faster than K_1 and this is indeed the case as the deuterium isotope effect K_H/K_D found at 80° was 2·41 (see below). Since K_1 is rate determining the relative rates of hydrogen abstraction from *meta* and *para* substituted benzaldehydes by the trichloromethyl radical would be expected to show a polar effect by application of the Hammett equation.

The absence of peaks in the 1260–1280 and 1725–1735 cm^{-1} region in the spectra of the reaction mixtures shows the absence of the ester $(\mathrm{Ph\overset{|}{C}HOCOPh})_2$[12] and the excellent material balance (PhCHO + PhCOBr) suggests that reactions (3) and (4) to be unimportant when bromotrichloromethane is present in excess.

Although the decarbonylation of benzoyl radicals has been previously noted,[12] recent recombination studies[13] of the orange-red benzoyl radical, which is stable

TABLE 1. PRODUCT STUDIES OF REACTION OF BENZALDEHYDES WITH BROMOTRICHLOROMETHANE[a]

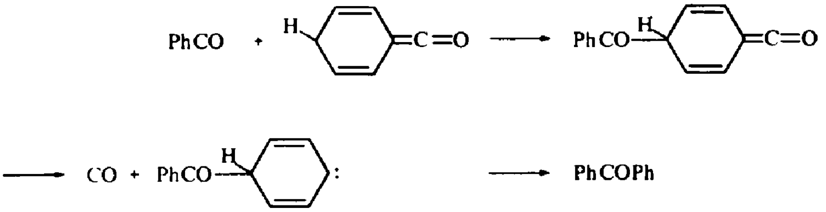
Expt. No.	Aldehyde mmole	Br CCl$_3$ mmole	Irradiation time, min	Unreacted ArCHO by IR mmole	Method of aroyl halide analysis	
					NaOMe mmole	Volhard mmole
1	C_6H_5CHO, 10·0	20·2	60	2·96	Br, 7·10 (6·97)[b]	Br, 7·00
2	C_6H_5CHO, 20·2	40·4	30	14·6	Br, 5·01 (4·88)[b]	Br, 5·05
3	C_6H_5CHO, 20·0	40·4	30	13·8	Br, 6·23 (6·25)[c]	Br, 6·25
4	C_6H_5CHO, 10·0	none	90	6·30	—	Cl, 3·94
5	*p*-$MeOC_6H_4CHO$, 10·0	20·2	60	6·39	Br, 3·40	Br, 3·45
6	*p*-ClC_6H_4CHO, 10·0	20·2	60	3·90	Br, 5·84	Br, 5·94
7	*p*-ClC_6H_4CHO, 20·0	none	90	15·3	—	Cl, 4·21

[a] Carried out in ca. 25 ml CCl_4 under N_2.

[b] Estimated as methyl benzoate by IR.

[c] Estimation in presence of added α-bromoethylbenzene.

at 70°K, indicated that when they are present in high concentration carbon monoxide and benzophenone are formed in the following manner:



Recent estimates[14] for D(Ph—CO) and D(Me—CO) of 30 and 19 kcal/mole, respectively, also support the stability of the benzoyl radical at low temperature. The results of Table 1 suggest that reaction (5) is also unimportant in the presence of bromotrichloromethane, and consequently the bromination of aromatic aldehydes is governed only be reactions (1) and (2).

It was shown by Huyser[15] that bromotrichloromethane reacts with ethylbenzene to give a quantitative yield of α-bromoethylbenzene which has been found[16] to react quantitatively when heated with excess aniline to give aniline hydrobromide. In view of its close reactivity value with that of benzaldehyde, ethylbenzene was chosen as a standard substrate for measuring the relative reactivity of all the benzaldehydes towards the trichloromethyl radical as α-bromoethylbenzene was found not to be implicated in the titration of benzoyl bromides with sodium methoxide in methanol/benzene. Furthermore, when a 5 ml aliquot of 0·20 molar solution of α-bromoethylbenzene in carbon tetrachloride was shaken with 0·5 ml anhydrous methanol for up to $2\frac{1}{2}$ hr the free hydrogen bromide formed amounted to less than 1 % of the alkyl bromide. Thus the benzoyl bromides in reaction mixtures containing unreacted substrates and α-bromoethylbenzene are readily estimated by the sodium methoxide method. The total bromide ($ArCOBr + PhCHBrCH_3$) was converted to aniline hydrobromide by heating with excess aniline under nitrogen and then estimated by the Volhard method. Bromotrichloromethane and chloroform are not implicated in both determinations. The difference of the two determinations yields the amount of α-bromoethylbenzene. Typical results are given in Table 2. The short irradiation times (30–90 min) resulted in 25 to 35 % reaction of the substrates. The amount of unreacted benzaldehydes was estimated by infrared and the material balance shown in Table 2 for the initial aldehydes was in the range of 97 to 103 %. The relative reactivity values were calculated both from the ratio $ArCOBr/PhCHBrCH_3$ as well as from the expression used by Huyser,[17] the amount of an unreacted substrate being the initial amount less the quantity of product.

The reactivities of nine *m*- and *p*-substituted benzaldehydes and the parent compound relative to ethylbenzene towards the trichloromethyl radical have been measured in this manner and are given in Table 3. For the *m*- and *p*-methylbenzaldehydes minor corrections were applied to take account of abstraction from the Me group. This was achieved by reacting these two compounds separately with bromotrichloromethane; the ratio of the reactivity of the aldehydic C—H to that of the Me C—H being 22·7 ± 1·3 and 18·8 ± 1·3 per molecule for the *m*- and *p*-isomers, respectively. When these aldehydes were used with ethylbenzene in competitive experiments it is not unreasonable to assume that such values could be used to correct

TABLE 2. TYPICAL RESULTS OF COMPETITIVE REACTION OF X-C_6H_4CHO AND $PhCH_2CH_3$ WITH $BrCCl_3$[a]

Aldehyde	Unreacted ArCHO, mmole	ArCOBr mmole	Mole % Initial ArCHO Accounted	ArCOBr + PhCHBrCH$_3$ mmole	PhCHBrCH$_3$ mmole	Rel. Reactivity[b] $K_{ArCHO}/K_{PhCH_2CH_3}$
C_6H_5CHO	7·39	2·91 (2·92)[c]	103	5·42	2·51	1·19
C_6H_5CHO	7·05	3·05 (3·03)[c]	101	5·67	2·62	1·20
C_6H_5CHO	6·42	3·60	100	6·67	3·07	1·22
p-$MeOC_6H_4CHO$	6·83	2·91	97	4·92	2·03	1·49
p-$MeOC_6H_4CHO$	6·62	3·18	98	5·40	2·22	1·43
p-$MeOC_6H_4CHO$	6·40	3·39	98	5·67	2·28	1·60
p-ClC_6H_4CHO	7·62	2·43	101	5·46	3·03	0·77
p-ClC_6H_4CHO	7·70	2·26	100	5·08	2·82	0·77
p-ClC_6H_4CHO	7·81	2·21	100	4·91	2·70	0·79

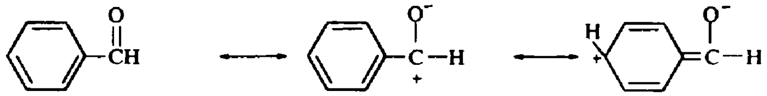
[a] $ArCHO:PhCH_2CH_3:BrCCl_3 = 10:10:20{\cdot}2$ mmole in ca. 25 ml CCl_4.

[b] Determined by expression $\log\left(\frac{ArCHO_0}{ArCHO_0 - ArCOBr}\right) \quad \log\left(\frac{PhCH_2CH_{3\,0}}{PhCH_2CH_{3\,0} - PhCHBrCH_3}\right)$

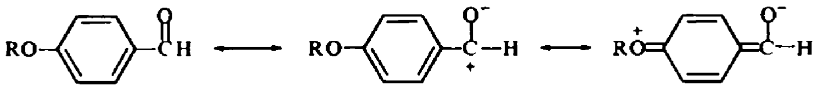
[c] Estimated as methyl benzoate by IR.

for the abstraction from the Me hydrogen atoms. For benzaldehyde the ratio of the products $PhCOBr/PhCHBrCH_3$ found was 1·16 and the calculated[17] relative reactivity $K_{PhCHO}/K_{PhCH_2CH_3}$ value being 1·20. The relative reactivity values K/Ko of the substituted benzaldehydes were calculated by dividing the measured values against ethylbenzene by these standard values. It is seen from Table 3 that electron-releasing groups enhance the reactivity while electron-withdrawing groups retard the reactivity. Application of the Hammett equation, by standard statistical methods,[18] shows that the results (omitting the *p*-MeO and *p*-PhO values, see below) are well correlated by the σ constants of McDaniel and Brown,[19] with $\rho = -0{\cdot}74 \pm 0{\cdot}07$ (corr. coeff = 0·994), whereas the correlation with the σ^+ constants of Brown and Okamoto[20] was poor ($\rho = -0{\cdot}67 \pm 0{\cdot}22$, $r = 0{\cdot}951$). The magnitude of the ρ-value is slightly lower ($\rho = -0{\cdot}64 \pm 0{\cdot}06$, $r = 0{\cdot}994$) when the ratios of the products $ArCOBr/PhCHBrCH_3$ were used in the correlation.

The result of the correlation is in contrast to the recent findings that abstraction of benzylic hydrogen atoms by the trichloromethyl radical from substituted toluenes[17] ($\rho = -1{\cdot}46$), ethylbenzenes[21] ($\rho = -0{\cdot}45$) and benzyl methyl ethers[4] ($\rho = -0{\cdot}36$) is best correlated by the σ^+ constants. Resonance stabilization of the benzoyl radical formed appears to be unimportant. This seems to be the case as low temperature studies[13] show that the stability of the benzoyl radical is not enhanced by a methoxy group or Cl atom in the *para* position. It was suggested by Russell[22] that when the polar effects are correlated by σ constants the attacking radical seeks centres of high electron density and that the transition state resembles the reactants $R{:}HX^{\bullet}$ with little bond breaking. A contrasting feature of the benzaldehyde series is the high degree of polarization of the CO double bond that is possible in structures II and III which reduce the electron availability on the aldehydic H atom. This would be expected to be enhanced by the *p*-MeO and *p*-PhO groups. The lower reactivity of these two substituted benzaldehydes than expected from the $\rho\sigma$ correlation (calculated from these and benzaldehyde alone gave ρ-values of $-0{\cdot}37$ and $-0{\cdot}17$, respectively) has a significant effect on the reactivity different from other benzaldehydes. That is structures V and VI become very important and thus increasing the activation energy involved in forming the transition state. In contrast no anomalous behaviour was found for the *m*-MeO result as the resonance structure equivalent to VI is not possible for this aldehyde. Arai[8] also noted the rather low reactivity of *p*-methoxybenzaldehyde in the radical chlorination by sulphuryl chloride which fits in with the explanation given above, although chlorination of the MeO group could not be ruled out.



I II III



IV V VI

Since the trichloromethyl radical is known[16] to be more selective than the t-butoxy radical,[23] the reactivity ratio of $K_{PhCHO}/K_{PhCH_2CH_3} = 1{\cdot}20$ towards the former radical

TABLE 3. RELATIVE REACTIVITY OF SUBSTITUTED BENZALDEHYDES TOWARDS THE TRICHLOROMETHYL RADICAL

Substituent	*p*-PhO	*p*-MeO	*p*-Bu^t	*p*-Me	*m*-Me	none	*m*-MeO	*p*-Cl	*m*-Cl	*m*-Br
$K_{X\cdot C_6H_4CHO}/K_{PhEt}$	1·36 ± 0·02	1·51 ± 0·06	1·73 ± 0·06	1·65 ± 0·01	1·39 ± 0·01	1·20 ± 0·01	0·95 ± 0·01	0·78 ± 0·01	0·65 ± 0·01	0·62 ± 0·01
K/K_0	1·13	1·26	1·44	1·38	1·16	1·00	0·79	0·65	0·54	0·52

Hammett rho, $\rho = -0{\cdot}74\sigma \pm 0{\cdot}07$ ($r = 0{\cdot}994$); $\rho = -0{\cdot}67\sigma^+ \pm 0{\cdot}22$ ($r = 0{\cdot}951$)

Substituent	*p*-PhO	*p*-MeO	*p*-Bu^t	*p*-Me	*m*-Me	none	*m*-MeO	*p*-Cl	*m*-Cl	*m*-Br
$X\cdot C_6H_4COBr/PhCHBrCH_3$	1·30 ± 0·01	1·45 ± 0·03	1·60 ± 0·02	1·54 ± 0·01	1·33 ± 0·01	1·16 ± 0·01	0·96 ± 0·01	0·81 ± 0·01	0·68 ± 0·01	0·62 ± 0·01
$X\cdot C_6H_4COBr/PhCOBr$	1·12	1·25	1·38	1·33	1·15	1·00	0·83	0·70	0·59	0·54

Hammett rho, $\rho = -0{\cdot}64\sigma \pm 0{\cdot}06$ ($r = 0{\cdot}994$)

TABLE 4. DEUTERIUM ISOTOPE EFFECT

Expt No.	Mmole	PhCHO	Mmole	PhCDO	PhCOBr mmole	% Material balance	K_H/K_D
	Initial	Final	Initial	Final			
1	15·70	9·89	9·03	7·42	6·33	95·7	2·34
2	11·00	6·75	9·03	7·31	6·10	100·6	2·31
3	14·10	8·92	9·03	7·57	6·22	98·2	2·58
4	16·95	10·30	11·00	8·95	7·95	97·3	2·40

Ave. 2·41 ± 0·09.

is in the correct order of magnitude compared to that of 0·91 per molecule found for the latter. On the other hand the selectivity of the peroxy radical[2,24] is somewhat intermediate in value compared with the other two radicals. The data of Walling and McElhill[7] on the relative reactivity of substituted benzaldehydes towards the perbenzoate radical, as calculated by Jaffe[18] gave a ρ-value of $-0·49$ at 30°. The ρ-value of $-0·74$ at 80° from the present result is compatible with the perbenzoate value and also with that of $-0·48$ at 80° towards sulphuryl chloride obtained by Arai[8] as chlorination of aromatic hydrocarbons with this reagent[25] has been shown to be somewhat less selective.

The kinetic isotope effect K_H/K_D towards the trichloromethyl radical was measured by IR technique utilizing both the two C—H and C—D stretching bonds for the unreacted aldehydes. The results are given in Table 4 and the K_H/K_D value found was $2·41 \pm 0·09$. Benzoyl bromide was estimated by Volhard's method and the material balance was 95·7 to 100·6%. The only data with which the present results can be compared on hydrogen abstraction from benzaldehydes where both the deuterium isotope effect and the substituent effects (where ρ is negative) have been investigated are those of Wiberg and Lepse.[26] They found that the oxidation of benzaldehyde by chromyl acetate in acetic anhydride at 25° proceeds in two stages, the first giving chromium (V) and the second giving chromium (IV); the K_H/K_D found for the two steps being 2·3 and 3·3, respectively. The effects of substituents showed a fair correlation with σ^+ constants with ρ-value for step one being $-0·2$ and ρ-value for step two being $-0·9$, although the limited number of substituents investigated precluded a clear distinction in the use of σ or σ^+ constants to correlate the results.

EXPERIMENTAL

Materials. Carbon tetrachloride, bromotrichloromethane and ethylbenzene were purified as previously described.[5] Reagent grade aniline was redistilled under N_2. *p*-Phenoxybromobenzene, b.p. 142–144°/1 mm, was prepared[27] in 60% yield.

p-Phenoxybenzaldehyde, b.p. 130–131°/1·5 mm, n_D^{24} 1·6094, was obtained in 60% yield by reacting the Grignard compound from *p*-phenoxybromobenzene with tri-ethyl orthoformate (lit.[28] b.p. 157–160°/6 mm). *p*-t-Butyl-benzaldehyde, b.p. 55–56°/0·2 mm, n_D^{24} 1·5226, was prepared in 68% yield from *p*-t-butylbenzyl bromide by the 2-nitropropane method.[29] *p*-Chlorobenzaldehyde was washed with Na_2CO_3aq and then recrystallized from light petroleum. The other liquid aldehydes used were fractionated twice under N_2.

Benzaldehyde α-D, was prepared by the method of Cohen and Song.[30] Phenyglyoxalic acid (32 g) in dry benzene (250 ml) was azeotropically distilled with 3 × 5 ml of D_2O (99·7%). To the residual liquid was added recrystallized benzoic anhydride (100 g), dry benzene (150 ml) and anhyd pyridine (18 ml) and the mixture refluxed under N_2 for 3½ hr during which time the theoretical amount of CO_2 was evolved. After distilling off the benzene and pyridine, the fraction having b.p. 78–85°/35 mm was collected. Redistillation of this fraction gave the required product, b.p. 82·0–82·5°/35 mm, 10·5 g (46%). The extent of α-deuteration was found to be 90% by IR spectropheotometry using variable path-length cells.

IR analysis. All the spectra were recorded in CCl_4 soln on a Hilger–Watts Infrascan Spectrophotometer calibrated against polystyrene. Beer–Lambert's law is obeyed on all analytical peaks used and apparent molar ε were determined using a set of variable path-length cells. A set of matched path length cells was used for quantitative analysis and the NaCl windows were maintained in optimum condition by regular polishing and checking for optical flatness. Under optimum instrumental conditions the accuracy of the analysis was ±2%.

Product studies. The aldehyde and bromotrichloromethane in a ratio of 1:2 in CCl_4 (ca. 25 ml) in a pyrex flask with a N_2 inlet, coil condenser and drying tube were heated at 80 ± 1° with magnetic stirring after replacing the atmosphere with N_2. The soln was maintained under a slow stream of the gas and irradiated with a 275-Watt G.E. sunlamp for 30–90 min after which the N_2 flow rate was increased moderately and maintained for 15 min to remove traces of HBr. An aliquot of the soln was suitably diluted for IR determination of the unreacted aldehyde. Two aliquots were added to 0·5 ml anhyd MeOH containing a crystal of thymol blue in two stoppered flasks under N_2 and the liberated HBr was titrated with standard 0·05N NaOMe in MeOH-benzene to the yellow end-point. Two aliquots (5 ml) were added to aniline (5 ml) in two stoppered flask under N_2 and after thorough mixing for 5 min the aniline hydrobromide formed was extracted 3 times with water. The combined extracts and washings were estimated for bromide by Volhard's method using standard 0·1N $AgNO_3$ and 0·1N KCNS with ferric alum indicator. In experiments where the benzoyl bromide was estimated as methyl benzoate, an aliquot of the soln was shaken for 20 min with 0·5 ml anhyd MeOH in a stoppered flask under N_2. After suitable dilution with CCl_4 the soln was washed with sat Na_2CO_3 aq, dried over $CaCl_2$ and the ester measured by IR spectrophotometry using the 1275 cm^{-1} peak. The volume of the remaining reaction mixture was measured and from the known total volume of soln after reaction the quantities of unreacted aldehydes and the benzoyl bromide were calculated. The results are summarized in Table 1.

Correction factors for abstraction from CH_3 *groups in* m- *and* p-*methylbenzaldehydes.* The individual aldehydes and bromotrichloromethane in a ratio of 1:2 in CCl_4 were irradiated at 80° until ca. 25 to 35% of the aldehyde had reacted. The MeC_6H_4COBr was estimated by the NaOMe method and the total bromides ($MeC_6H_4COBr + BrCH_2C_6H_4CHO$) by the Volhard method after heating with excess aniline at 80° for 3 min. The difference of the two results gave an estimate of the amount of $BrCH_2C_6H_4CHO$. Thus the ratio of $MeC_6H_4COBr/BrCH_2C_6H_4CHO$ represents the relative reactivity of the aldehydic C—H to the methyl C—H; the values found for four experiments were 18·8 ± 1·3 and 22·7 ± 1·3 per molecule for the *p*- and *m*-isomers, respectively.

Competitive reactions of substituted benzaldehydes and ethylbenzene with bromotrichloromethane. A soln of the aldehyde, ethylbenzene and bromotrichloromethane in the ratio of 10:10:20·2 mmole in CCl_4 (ca. 25 ml) was irradiated at 80° for 30–90 min as described above. The unreacted aldehyde and the two bromides were analysed as described above; the total bromide ($ArCOBr + PhCHBrCH_3$) being the determination by the Volhard method after heating with excess aniline at 80° for 3 min under N_2. The difference of the two titrimetric analyses yields the amount of α-bromoethylbenzene, except for the results from the *m*- and *p*-methyl isomers where the total alkyl bromides were corrected by the above correction factors for the amount of $BrCH_2C_6H_4CHO$ that should be formed based on the amount of MeC_6H_4COBr found. α-Bromoethylbenzene is not implicated in the determination of aroyl bromide by the NaOMe method as can be seen in experiment No. 3 of Table 1 in which benzoyl bromide was estimated in presence of added α-bromoethylbenzene. Furthermore, when a 5 ml aliquot of 0·20 molar solution of pure α-bromoethylbenzene in CCl_4 was shaken with 0·5 ml anhyd MeOH for up to 2½ hr the extent of solvolysis found by titration with NaOMe was less than 1%. A pure sample of α-bromoethylbenzene, n_D^{25} 1·5592, analysed by the Volhard method and by the method previously used[16] gave values of 100·3 and 100·2%, respectively. All competitive experiments are in triplicate and all the titrimetric analyses done in duplicate. Some typical results are presented in Table 2 and these are summarised in Table 3. The material balance for initial aldehyde, apart from *m*- and *p*-methylbenzaldehydes, was better than 96% in all cases. The data for relative reactivity values were calculated by two methods, (i) from the ratio of $X \cdot C_6H_4COBr/PhCHBrCH_3$ and (ii) by the usual expression employed[17] with the unconsumed substrate equals initial amount minus the amount of product.

Deuterium isotope effect. A weighed quantity of α-deutero-benzaldehyde, purified by double fractionation at two pressures under N_2 and of known α-deuterium content (90% by IR), and of benzaldehyde were irradiated with bromotrichloromethane (5 ml) in CCl_4 (ca. 20 ml) at 80° for 60 min. Benzoyl bromide was estimated by the Volhard method. IR analysis of the two aldehydes was carried out using both the 2815 and 2732 cm^{-1} peaks for the unlabeled material and both the 2103 and 2050 cm^{-1} peaks for the deuterated compound. The results are summarized in Table 4 and the material balance were found to be in the range of 95·7 to 100·6%. The deuterium isotope effect calculated by the usual expression[17] was 2·41 ± 0·09.

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