The Reactions of Polyhalogenomethanes with Aldehydes and with 1,3,5-Trinitrobenzene in the Presence of Tin(II) Salts: Evidence for the Formation of Trihalogenomethyl Anions

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The (previously reported) formation of 2,2,2-tribromoethanols by the reaction of aromatic aldehydes with tetrabromomethane in the presence of tin(II) fluoride in dimethyl sulphoxide solution also occurs when tin(II) chloride is used in place of the fluoride. Analogous reactions occur with certain other tetrahalogenomethanes, but not with trihalogenomethanes nor with fluorine-containing tetrahalogenomethanes. When the aldehyde is replaced by 1,3,5-trinitrobenzene, Meisenheimer adducts derived from trihalogenomethyl anions are formed. The trihalogenomethyl anions are thought to be a product of the two-electron reduction of tetrahalogenomethanes by tin(II).

Mukaiyama and his co-workers[1] have reported the preparation of 2,2,2-tribromoethanols by the reaction between aldehydes and tetrabromomethane in the presence of tin(II) fluoride in dimethyl sulphoxide solution at room temperature [equation (1)]. We have recently described[2] the formation of 2,2,2-trihalogenoethanols from aldehydes in dimethyl sulphoxide by an apparently quite different reaction, *viz.* by use of trihalogenoacetic acids (or their salts). The reaction scheme given in equations (2)—(5) (where X = Br or Cl) was deduced as describing the mechanism of the conversion. The intermediate formation of the trihalogenomethyl anions (CX_3^-) during the reaction of trihalogenoacetic acids was demonstrated by trapping these species with 1,3,5-trinitrobenzene (TNB), resulting in formation of a Meisenheimer adduct [equation (6)]. With aromatic aldehydes the reactions (4) and (6) occur at similar rates, and the trapping reaction (6) was shown to be competitive with aldehyde for the same reactive intermediate.

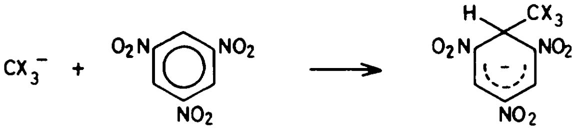
$$\mathrm{RCHO} \xrightarrow[\mathrm{Me_2SO}]{\mathrm{CBr_4,\ SnF_2}} \mathrm{RCH(CBr_3)OH} \qquad (1)$$

$$\mathrm{CX_3CO_2H} \rightleftharpoons \mathrm{CX_3CO_2^-} + \mathrm{H^+_{solv}} \qquad (2)$$

$$\mathrm{CX_3CO_2^-} \longrightarrow \mathrm{CX_3^-} + \mathrm{CO_2} \qquad (3)$$

$$\mathrm{CX_3^-} + \mathrm{RCHO} \longrightarrow \mathrm{RCH(CX_3)O^-} \qquad (4)$$

$$\mathrm{RCH(CX_3)O^-} + \mathrm{H^+_{solv}} \longrightarrow \mathrm{RCH(CX_3)OH} \qquad (5)$$



(6)

The use of the same solvent in Mukaiyama's procedure and the nature of the reagents used suggested to us that reaction (1) might also involve the intermediate formation of trihalogenomethyl anions. Tin(II) salts are known to be two-electron reducing agents and it therefore seemed plausible that the transfer of two electrons to tetrabromomethane might be accompanied by the dissociative formation of two anions [equation (7)].

$$\mathrm{CBr_4} + \mathrm{Sn^{II}} \longrightarrow \mathrm{CBr_3^-} + \mathrm{Br^-} + \mathrm{Sn^{IV}} \qquad (7)$$

The present work was undertaken to test this hypothesis by attempting to effect the trapping process (6) in the reaction of tetrabromomethane [equation (1)]. On this interpretation the use of tin(II) in the form of the fluoride should not necessarily be essential to the success of reaction (1) and we therefore examined the alternative use of the less expensive tin(II) chloride in these preparations. We have also investigated the possible extension of the reaction to some other halogenoalkanes as reagents.

Experimental

The reactions between polyhalogenomethanes and aldehydes were carried out according to two alternative procedures (A and B). The solvent used was Me_2SO, except where stated otherwise, and the reactants were in all cases kept in the molar ratio aldehyde:tin(II) halide:polyhalogenomethane 1:2:3, the proportions reported by Mukaiyama *et al.*[1] to give the highest yield of tribromoethanols with respect to aldehydes. In method A the aldehyde and tin(II) halide were dissolved in Me_2SO and the polyhalogenomethane was added last. In method B, the tin(II) halide was added to a solution of the other two reagents. In general the reactions were conducted at room temperature.

Table 1 gives a summary of the systems investigated, the letters C and F denoting the use of tin(II) chloride or fluoride, respectively. The words 'yes' and 'no' indicate the successful or unsuccessful outcome of the attempted preparations, as deduced from the proton magnetic resonance spectra of the solution after mixing of the reactants, both before and after addition of water [to achieve the conversion of the alkoxide ion into alcohol according to equation (5) (see Table 2)]. The following notes refer to the numbered experiments of Table 1.

Reaction 1. Some trichloroethanol and some trichloromethane are formed. The ^{13}C n.m.r. spectrum of this reaction solution in $(CD_3)_2SO$, after addition of water, showed bands for the trichloroethanol in fair agreement with a spectrum reported by Freidlina *et al.*[3] for a benzene–trichloromethane solvent. The following chemical shifts were observed (corresponding literature values[3] in parentheses): 136.9 (135.2), 129.2 (129.2), 128.7 (127.7), 127.3 (126.5), 82.9 (84.3), 103.7 (103.0).

Reaction 2. No aldehyde remains at the end; not all the tin(II) fluoride dissolves.

Reaction 4. Tetrafluoromethane was bubbled through the solution of the other components. The ^1H n.m.r. spectrum did not indicate formation of trifluoromethane.

Reaction 8. The result is negative even after heating to 80—90 °C for 15 min.

Table 1. Outcome of reactions between aldehydes and halogenoalkanes in Me_2SO containing tin(II) halides

Reaction no.	Aldehyde	Tin halide[a]	Halogenoalkane	Method	Ethanol product
1	Benzaldehyde	C	CCl_4	A	Yes
2	Benzaldehyde	F	CCl_4	A	Yes
3	Benzaldehyde	C	CBr_4	B	Yes
4	Benzaldehyde	C	CF_4	A	No
5	Benzaldehyde	C	$CHCl_3$	A	No
6	Benzaldehyde	C	$CFCl_3$	A	No
7	Benzaldehyde	C	CF_3Cl	B	No
8	Benzaldehyde	C	CF_3CH_2I	A	No
9	Benzaldehyde	F	CF_3CH_2I	A	No
10	Benzaldehyde	C	CF_2Br_2	B	No
11	4-Chlorobenzaldehyde	C	CCl_4	B	Yes
12	4-Chlorobenzaldehyde	C	$CHCl_3$	A	No
13	4-Chlorobenzaldehyde	C	CBr_4	B	Yes
14	4-Chlorobenzaldehyde	C	$CHBr_3$	B	No
15	4-Chlorobenzaldehyde	C	CF_3Br	B	No
16	4-Chlorobenzaldehyde	C	CF_3Cl	B	No
17	2,4-Dichlorobenzaldehyde	C	CCl_4	B	Yes
18	2,4-Dichlorobenzaldehyde	C	$CFCl_3$	B	No
19	2,4-Dichlorobenzaldehyde	C	CF_3Cl	B	No
20	4-Nitrobenzaldehyde	C	CCl_4	A,B	No
21	4-Nitrobenzaldehyde	C	CBr_4	B	Yes
22	4-Nitrobenzaldehyde	C	$CBrCl_3$	B	Yes
23	4-Nitrobenzaldehyde	C	$CHBr_3$	B	No
24	4-Nitrobenzaldehyde	C	$CFCl_3$	B	No
25	Pyridine-4-carbaldehyde	C	CCl_4	B	Yes

[a] C, $SnCl_2$; F, SnF_2.

Table 2. ^1H N.m.r. chemical shift data (relative to Me_4Si) attributable to the trihalogenoethanols

Reaction no.	Product	C*H*OH (*i.e.* after H_2O addition)	C*H*O$^-$ (*i.e.* before H_2O addition)	Ring protons[a]	Remarks
1	2,2,2-Trichloro-1-phenylethanol[b]	5.20 (s)	5.57 (s)	7.20—8.07 (m)	Signal δ *ca.* 8.23 observed.[d] ^{13}C N.m.r. chemical shifts given in text. Product not benzyl alcohol[e]
2	2,2,2-Trichloro-1-phenylethanol[b]	5.20 (s)	5.50 (s, br)	7.30—7.77 (m)	Signal δ *ca.* 8.25 observed[d]
3	2,2,2-Trichloro-1-phenylethanol	5.00 (s)	5.30 (s)	7.15—8.05 (m)[b]	Signal assigned to ring protons may include signal due to $CHBr_3$ [f]
11	2,2,2-Trichloro-1-(4-chlorophenyl)-ethanol[b]	5.23 (s)	5.54 (s)	7.27—7.90 (m)	Signal δ *ca.* 8.23 observed[d]
13	2,2,2-Tribromo-1-(4-chlorophenyl)-ethanol[c]	5.13 (s)[g]	5.50 (s, vbr)[g]	7.20—8.10 (m)[g]	Signal in region of ring protons at δ 7.53 could be $CHBr_3$[f]
17	2,2,2-Trichloro-1-(2,4-dichlorophenyl)-ethanol[b]	5.65 (s)	6.06 (s, br)	7.33—8.33 (m)	Signal assigned to ring protons may include signal due to $CHCl_3$[d]
21	2,2,2-Tribromo-1-(4-nitrophenyl)-ethanol[b,c]	5.31 (s)[c,g]	5.65 (s)[c,g]	7.93—8.38 (m)[c,g]	Signal at δ 7.43 observed.[c] Signal at δ 7.48 observed[b,f]
22	2,2,2-Trichloro-1-(4-nitrophenyl)ethanol[b]	5.44 (d)[g] (*J* 5.6 Hz)	5.67 (d)[g] (*J* 6 Hz)	7.88—8.40 (m)	Signal assigned to ring protons may include signal due to $CHCl_3$[d]
25	2,2,2-Trichloro-1-(4-pyridyl)ethanol[b]	5.32 (s)[g]	5.32 (s, br)[g]	7.60—7.70 (m)[g] 8.53—8.70 (m)[g]	Signal δ *ca.* 8.27 observed[d]

[a] Bands due to ring protons may obscure CHO*H* signal. [b] In $(CD_3)_2SO$. [c] In 50 : 50 $(CD_3)_2SO$–$CDCl_3$. [d] $CHCl_3$ in $(CD_3)_2SO$ gives band at δ 8.27. [e] Benzyl alcohol in Me_2SO: δ(ring) 7.33; δ(CH_2) 4.53. [f] $CHBr_3$ in Me_2SO: δ 7.53. [g] These chemical shifts are reported in ref. 4.

Reaction 11. Some trichloromethane was also formed.

Reaction 12. There was no evidence for formation of dichloromethane.

Reaction 13. To achieve higher solubility of tetrabromomethane, the reaction was carried out in 50:50 (v/v) $(CD_3)_2SO$–$CDCl_3$.

Reaction 14. A ^1H n.m.r. signal at δ 5.30 is tentatively attributed to CH_2Br_2.

Reactions 4, 15, 16, *and* 19. It is possible that the negative outcome is due to low solubility of the halogenoalkane. (The solution was prepared by bubbling gas through solvent for 15 min.)

Reaction 17. The spectrum shows that no aldehyde remains and that some trichloromethane is formed.

Reaction 20, 23, *and* 24. The nitro-group was reduced by tin(II).

Reaction 21. Conditions were as for reaction 13. Reduction of nitro-group was not serious.

Reaction 22. Reduction of nitro-group was not serious.

Reaction 25. Some trichloromethane was detected.

For those combinations of tetrahalogenomethane and tin(II) fluoride with which some of the reactions with aldehydes were to some extent positive, the corresponding reactions with 1,3,5-trinitrobenzene were investigated. With bromotrichloromethane and either tin(II) fluoride or chloride and with tetrabromomethane and tin(II) chloride the characteristic Meisenheimer adducts (**1**) were formed, where X = Cl for the reaction of bromotrichloromethane and X = Br when tetrabromomethane is used. The outcome of these experiments is tabulated (Table 3). The ^1H n.m.r. spectra of the products found under these conditions are given in Table 4.

In the cases of reactions 27—29, 32, and 33 there was no evidence for the formation of a Meisenheimer adduct. A deep red–brown colour was produced immediately on the addition of the tin(II) halide. This is ascribed to reduction of TNB by tin(II) and secondary reactions. To enhance the solubility of tetrabromomethane, a mixture of $(CD_3)_2SO$ and $CDCl_3$ was used as solvent in experiment 26. However, the formation of the Meisenheimer adduct was also detectable when $(CD_3)_2SO$ was used alone. Tribromomethane was observed as an additional product.

^1H N.m.r. measurements were made with a JEOL PMX 60SI instrument at ambient temperature, and ^{13}C n.m.r. measurements with a Bruker WM 250 instrument with normal broadband decoupling at 297 K. For all n.m.r. measurements fully deuteriated solvents were used with tetramethylsilane as internal reference.

The visible spectra were measured with a Pye-Unicam SP-8100 spectrophotometer.

Table 3. Outcome of reactions between TNB and polyhalogenomethanes in the presence of tin(II) halides in $(CD_3)_2SO$ solution

Reaction no.	Tin halide[a]	Halogenomethane	Meisenheimer adduct formed
26	C	CBr_4	Yes
27	C	$CHBr_3$	No
28	C	CCl_4	No
29	F	CCl_4	No
30	C	$CBrCl_3$	Yes
31	F	$CBrCl_3$	Yes
32	C	$CHBr_3$	No
33	C	CF_2Br_2	No

[a] C, $SnCl_2$; F, SnF_2.

Discussion

All the observations are consistent with the notion that CBr_4, $CBrCl_3$, and CCl_4 are reduced by tin(II) salts (either chloride or fluoride) in Me_2SO according to equation (7), (8), or (9). In all

$$CBrCl_3 + Sn^{II} \longrightarrow CCl_3^- + Br^- + Sn^{IV} \quad (8)$$

$$CCl_4 + Sn^{II} \longrightarrow CCl_3^- + Cl^- + Sn^{IV} \quad (9)$$

these cases the reaction products in the presence of added aldehydes are those expected from equations (4) and (5). When TNB is present in place of aldehyde, CBr_4 and $CBrCl_3$ give rise to the Meisenheimer adducts derived from the trihalogenomethyl anions produced according to equation (7) or (8). With tetrachloromethane the formation of the corresponding Meisenheimer adduct is not observed; instead, reduction products of TNB seem to be formed. We infer that, whereas reactions according to equations (7) and (8) are more rapid than the reduction of TNB by Sn^{II}, the reaction of equation (9) cannot compete with that reduction.

For a similar reason, whereas either CBr_4 or $CBrCl_3$ can be used in the preparation of 2,2,2-trihalogeno-1-(4-nitrophenyl)-ethanols, the reaction of CCl_4 with 4-nitrobenzaldehyde is unsuccessful for this purpose, leading instead to reduction of the nitro-group.

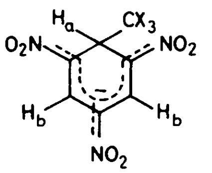
The trend towards lower reactivity as bromine is replaced by chlorine in the reaction of tetrahalogenomethanes with tin(II) salts is continued as chlorine is replaced by fluorine. With none of the fluorine-containing tetrahalogenomethanes studied could we find any evidence for formation of trihalogenomethyl anions. The low tendency for fluorine-containing trihalogenomethyl anions to be formed is consistent with the reluctance of trifluoroacetate anions to break down into trifluoromethyl anions and carbon dioxide.

The enhancement of the stability of carbanions by attachment of the heavier halogens to the carbanionic centre is also borne out by the negative outcome of all our preparative experiments with trihalogenomethanes. The indication of probable formation of dibromomethane in experiment 14 (using tribromomethane) may suggest that transient formation of the carbanion $CHBr_2^-$ is nevertheless possible in Me_2SO solutions.

Table 4. ^1H N.m.r. chemical shifts (relative to Me_4Si) for the Meisenheimer adduct (**1**)[a] formed by the reaction of TNB with trihalogenomethyl anions

Reaction no.	X[a]	$\delta(H_a)$	$\delta(H_b)$	Comments
26	Br	6.30 (t)[b]	8.55 (d)[b] (J 2.6 Hz)	Solvent 50:50 $(CD_3)_2SO$—$CDCl_3$ and $(CD_3)_2SO$ Also observation of band at δ 7.33[d] Visible spectrum[f] $\lambda_{max.}$ 433 and 501 nm[g]
30, 31	Cl	6.31 (t)[c]	8.55 (t)[c] (J 2.5 Hz)	Solvent Me_2SO Also observation of band at δ 8.23[e] Visible spectrum[f] $\lambda_{max.}$ 431 and 505 nm[h]

[a]



(**1**)

[b] Reported for Meisenheimer adduct (**1**; X = Br) $\delta(H_a)$ 6.28 (t), $\delta(H_b)$ 8.52 (d), J_{ab} 2.8 Hz. [c] Reported for Meisenheimer adduct (**1**; X = Cl) $\delta(H_a)$ 6.25 (t), $\delta(H_b)$ 8.48 (d), J_{ab} 2.6 Hz. [d] $CHBr_3$ in Me_2SO δ 7.53. [e] $CHCl_3$ in Me_2SO δ 8.27. [f] ^1H N.m.r. solutions diluted with Me_2SO to enable the visible spectrum to be measured. [g] (**1**; X = Br) Absorption maxima at 433 and 502 nm are reported in ref. 2. [h] (**1**; X = Cl) Absorption maxima at 431 and 507 nm are reported in ref. 2.

Acknowledgements

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