The Decomposition of Trihalogenoacetic Acids in Dimethyl Sulphoxide: a Mild Route from Carbonyl Compounds to Trihalogenomethylethanol and Trihalogenomethyl Ketones

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Solutions of trichloro- and tribromo-acetic acid in dimethyl sulphoxide in the presence of carbonyl compounds react at room temperature to give insoluble products corresponding to the addition of $H-CX_3$ across the carbonyl double bond.

Solutions of trichloroacetic acid in dimethyl sulphoxide (DMSO) have recently been shown to decompose in the cold with formation of the trichloromethyl anion as an unstable primary product.[1] The production of the anion is clearly indicated by trapping it with 1,3,5-trinitrobenzene, so as to prevent its conversion into chloroform or dichloromethylene.

We now report that a similar trapping reaction can be achieved with other species susceptible to attack by reactive nucleophiles. In particular, a solution of trichloroacetic acid and a carbonyl compound in DMSO yields, on being kept at room temperature for *ca.* 1 h, a solution from which the addition compound $RR'C(OH)CCl_3$ (**1**) can be isolated in high yield. Such secondary or tertiary alcohols, containing the trichloromethyl group, and the corresponding trichloromethyl ketones (formed by oxidation of secondary alcohols) are of interest not only as potentially useful products whose high biological activity[2] has recently been recognised but also as precursors in other synthetic applications.[3] Compounds of this type have hitherto been prepared only by procedures that are either more drastic or cumbersome and expensive.[3,4] The examples given in Scheme 1(a), (b), and (c) describe the application of our method to some typical preparations and show that good yields are achieved under notably mild conditions. The example given in Scheme 1(b) shows that tribromoacetic acid closely resembles trichloroacetic acid in its behaviour and synthetic utility. The new compounds had ^1H and ^{13}C n.m.r. spectra consistent with the expected structures.

$$CX_3CO_2H + ArCHO \xrightarrow[\text{room temp.}]{\text{DMSO } (n \text{ cm}^3)} \underset{(\mathbf{1})}{ArCH(OH)CX_3}$$

Scheme 1. (a) X = Cl, (2.1 g of acid), Ar = 4-nitrophenyl (1.4 g), *n* = 50; (**1**) isolated in 60% yield; crystallised from n-heptane; m.p. 107—108 °C (lit.[5] 109 °C). (b) X = Br, (2.7 g of acid), Ar = 4-nitrophenyl (1.05 g), *n* = 10; (**1**) isolated in 60% yield, crystallised from dichloromethane and then n-hexane, m.p. 118—120 °C (new compound). (c) X = Cl (2.15 g of acid), Ar = 4-pyridyl (1.0 g), *n* = 20; (**1**) isolated in 65% yield, crystallised from benzene, m.p. 136—138 °C (new compound).

Oxidation to the corresponding ketones can be carried out by standard literature methods.[6] It can be performed *in situ* by addition of acetic anhydride and keeping the mixture at room temperature for a day. The preparation of α,α,α-trichloro-4-nitroacetophenone can thus be achieved in 50% yield from 4-nitrobenzaldehyde.

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