Trichloroacetic Acid in Dimethyl Sulphoxide as a Source of Trichloromethyl Anions: Formation of an Adduct and Substitution Product with 1,3,5-Trinitrobenzene

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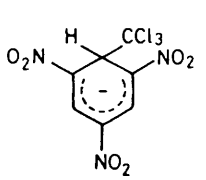
Solutions of trichloroacetic acid in dimethyl sulphoxide generate trichloromethyl anions which can be trapped by species susceptible to nucleophilic attack, such as 1,3,5-trinitrobenzene; the procedure is preparatively useful.

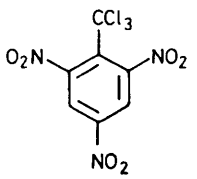
Trichloromethyl anions (CCl_3^-) are generally accepted to be reaction intermediates in the hydrolysis of chloroform under basic conditions.[1] The ions generated under these conditions are unstable and decompose into chloride ions and the carbene $:CCl_2$ which then undergoes reactions characteristic of that species. It has also been inferred that trichloromethyl anions are intermediate in the thermal decomposition of trichloroacetate ions into carbon dioxide and chloroform,[2] the latter resulting from the protonation of the intermediate.

We now report a convenient and mild general method for the generation of trichloromethyl anions under conditions such that it is possible to trap them efficiently before their conversion into either chloroform or dichlorocarbene. The recommended procedure is to dissolve dry trichloroacetic acid in dimethyl sulphoxide (DMSO) in the presence of a reagent susceptible to nucleophilic attack. In this solvent the decomposition reaction takes place at room temperature and without the addition of any catalyst. It occurs much more readily than the reported reaction of sodium trichloroacetate in dimethoxyethane.[3] The reaction has a half-life of the order of 15 min for solutions containing trichloroacetic acid at concentrations in the range 0.1—0.5 M and 1,3,5-trinitrobenzene, in the presence of which it yields the highly coloured Meisenheimer adduct anion (**1**). This is readily identified by its u.v.–visible and n.m.r. spectrum.[4] It can be oxidised *in situ* to 1-trichloromethyl-2,4,6-trinitrobenzene (**2**), *e.g.* by addition of a solution of bromine in pyridine.[5]

To examine the extent to which a concurrent decomposition of the trichloromethyl anion might be occurring in our system, the decomposition of trichloroacetic acid in DMSO was also performed (without added trinitrobenzene) in the presence of



(1)



(2)

cyclohexene. Under these conditions chloroform is the predominant reaction product and the formation of the carbene adduct[6] is not detectable in ^{13}C n.m.r. spectra.

It has previously been noted that solutions of trichloroacetic acid in DMSO give rise to a short-lived mutagen.[7] Our experiments suggest that the species concerned is the trichloromethyl anion.

The rapid decarboxylation of trichloroacetic acid in DMSO is readily explained by the solvating properties of the solvent. These lead to stabilisation of the hydrogen ion, so as to produce a solution that contains on the one hand relatively unreactive hydrogen ions (and hydrogen-bonded trichloroacetic acid),[8] and on the other hand poorly solvated and hence unstable trichloroacetate ions, which readily decompose. The low reactivity of the solvated proton allows other electrophiles to compete effectively in the reaction with the trichloromethyl anion.

The foregoing considerations suggest other experimental conditions that lead to a similar production of trichloromethyl and similar anions. First, solutions of salts of trichloroacetic acid in DMSO readily undergo thermal decarboxylation at room temperature. The decomposition of sodium trichloroacetate in DMSO leads to the isolation of the previously reported sodium salt[4] of (**1**). Secondly, solvents of similar solvating properties (*i.e.* highly polar and non-hydroxylic) are also (but less) effective. The formation of (**1**) has been observed on decomposing trichloroacetic acid in tetrahydrofuran or pyridine. Thirdly, tribromoacetic acid similarly undergoes decarboxylation, with formation of trihalogenomethyl anions.

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