Novel Oxidation Reduction Reactions Involving Nitro Groups and Methyl Groups in Trifluoromethanesulfonic Acid

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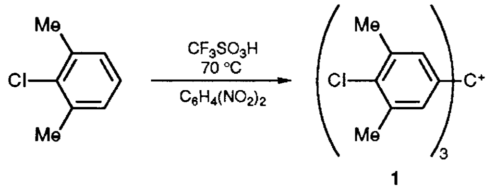
2-Chloro-1,3-dimethylbenzene reacts with *p*-dinitrobenzene in trifluoromethanesulfonic acid at 70 °C to give the corresponding triarylmethyl cation and *p*-diaminobenzene.

The extension of our study of rearrangement reactions in trifluoromethanesulfonic acid from aromatic nitro compounds[1] to aromatic halogeno compounds has revealed an unexpected reaction between some of the aromatic substrates and the *p*-dinitrobenzene present as a ^{1}H NMR standard. Thus, when a solution containing 2-chloro-1,3-dimethylbenzene (0.4 mol dm^{-3}) and *p*-dinitrobenzene (0.14 mol dm^{-3}) is heated in trifluoromethanesulfonic acid (99.1%) for 3 h at 70 °C, the NMR spectrum indicates the formation of the triarylmethyl cation **1** (Scheme 1); this product was



Scheme 1

$$
\begin{array}{c}
C_6H_4(NO_2)_2 + 8C_6H_3Me_2Cl + 8H^+ \\
\downarrow \\
2(C_6H_2Me_2Cl)_3C^+ + C_6H_4(NH_3^+)_2 + 2C_6H_4MeCl + 4H_3O^+
\end{array}
$$

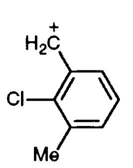
Scheme 2

isolated, after extraction, as the corresponding alcohol and was identified by its elemental analysis, the ^1H and ^{13}C NMR spectra, and the mass spectrum. The only other significant product is *p*-diaminobenzene. In the absence of the *p*-dinitrobenzene, 2-chloro-1,3-dimethylbenzene reacts more slowly to give a very complex mixture of products; the triarylmethyl cation **1** is not formed. In the absence of the 2-chloro-1,3-dimethylbenzene, *p*-dinitrobenzene does not react. In a less acidic solvent (trifluoroacetic acid), no reaction occurs.

3-Chloro-1-methylbenzene also reacts with *p*-dinitrobenzene in trifluoromethanesulfonic acid to give the corresponding triarylmethyl cation. When this reaction was repeated using 3-chloro-1-[^{13}C]methylbenzene, the central carbon atom of the triarylmethyl cation was found to be labelled with ^{13}C to the same extent as the methyl groups. The central carbon is therefore derived from one of the original methyl groups.

From this result and the formation of 1,4-diaminobenzene, the reaction in Scheme 1 appears to require the overall stoichiometry shown in Scheme 2. However, the reaction is not quantitative and the final yield of the triarylmethanol is only about 40% of that expected from this scheme. Minor quantities of a number of other aromatic compounds are formed but 2-chlorotoluene has not been detected; we have shown that it reacts further under these conditions to give a mixture of triarylmethyl cations.

The *p*-dinitrobenzene can be replaced by a number of aromatic nitro compounds (nitrobenzene, 1,3,5-trinitrobenzene, *p*-nitroaniline) without large changes in the reaction rate but reaction did not occur when an aliphatic nitro compound (nitromethane) was used. As outlined above, reaction also occurs with other alkylchlorobenzenes but not with toluene or *m*-xylene; these decompose under the reaction conditions.



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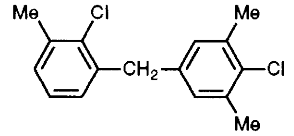

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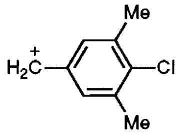

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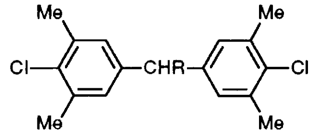

5a; R = H
b; R = OH

From the ^{13}C labelling experiments, we suggest that the reaction in Scheme 1 starts with the oxidation of one of the methyl groups by the nitro compound to form the benzyl cation **2**, and that this is followed by a Friedel–Crafts reaction to form the diarylmethane **3**; this can then undergo a reverse Friedel–Crafts reaction to form the cation **4** and a further Friedel–Crafts reaction to form the diarylmethane **5a**. Further oxidation and substitution reactions of these types would then complete the formation of the triarylmethyl cation. This interpretation is supported by the fact that some of the alcohol **5b** can be extracted from the reaction mixture at early stages of the reaction.

Related sequences of benzylation, debenzylation and rebenzylation have been observed in other Friedel–Crafts reactions.[2] The unusual feature of the present work is the facility with which nitro compounds in this highly acidic medium appear to abstract hydride ions from aromatic methyl groups and are thereby reduced to amino compounds. The range and mechanism of this reaction are currently under investigation.

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References

1 J. V. Bullen, J. H. Ridd and O. Sabek, *J. Chem. Soc., Perkin Trans. 2*, 1990, 1681.
2 C. Serres and E. K. Fields, *J. Am. Chem. Soc.*, 1960, **82**, 4685.