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Preliminary communication

SOME EFFECTS OF TRIFLUOROMETHANESULPHONIC ACID ON MERCURATION IN TRIFLUOROACETIC ACID

G. B. Deacon and M. F. O'Donoghue

Chemistry Department, Monash University, Clayton, Victoria 3168 (Australia)

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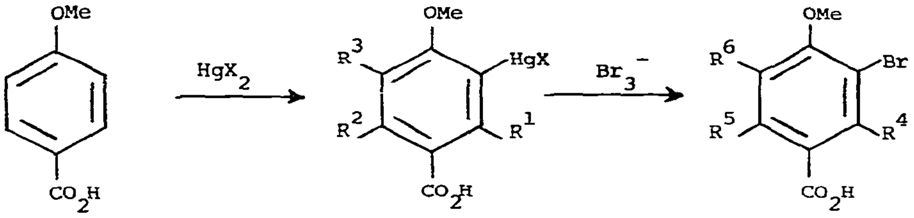
Summary

With suitable choice of conditions, mercuration of 4-methoxybenzoic acid in trifluoroacetic acid with added trifluoromethanesulphonic acid can give predominant 2,5-dimercuration, 2,3,5-trimercuration, or formation of 2,3,4,5-tetramercurated anisole in short reaction times, whereas use of trifluoroacetic acid alone gives 3-mercuration, 3,5-dimercuration or, with long reaction times, 2,3,5-trimercuration.

Addition of trifluoromethanesulphonic acid to a solution of mercuric trifluoroacetate in trifluoroacetic acid generates mercuric trifluoromethanesulphonate [1]. Mercuration of polyfluoroaromatic compounds with this reagent proceeds far more readily than with mercuric trifluoroacetate alone [1], even though this compound is itself an excellent mercurating agent [2]. We now report that use of trifluoromethanesulphonic acid in mercuration of 4-methoxybenzoic acid leads to a change in the preferred dimercuration product, to enhanced polymercuration and to enhanced *ipso* mercuration (decarboxylation).

Mercuration of 4-methoxybenzoic acid with mercuric trifluoroacetate (mole ratio 1:4) in refluxing trifluoroacetic acid for 15 min yielded, after bromodemercuration of the mercuration product, a mixture of unchanged anisic acid, 3-bromo-4-methoxybenzoic acid (scheme 1) and 3,5-dibromo-4-methoxybenzoic acid (scheme 2). By contrast, when trifluoromethanesulphonic acid was added ($CF_3SO_3H : CF_3CO_2H = 3:5$, v/v), a similar reaction for 15 min gave, after bromodemercuration, 2,5-dibromo-4-methoxybenzoic acid as the principal product (scheme 3). The 2,5-dimercurated species appears to result from rearrangement of the expected kinetically favoured 3,5-dimercurated isomer, since cleavage with tribromide ions after 5 min gave 3,5-dibromo-4-methoxybenzoic acid as the main dibromo acid. Presumably, coordination of a carboxyl group to $CF_3SO_3Hg^+$ is more thermodynamically stable than coordination of the methoxy group to a second $CF_3SO_3Hg^+$ group.



<u>Scheme</u> 1. R^1, R^2, R^3, R^4, R^5, $R^6 = H$; $X = CF_3CO_2$

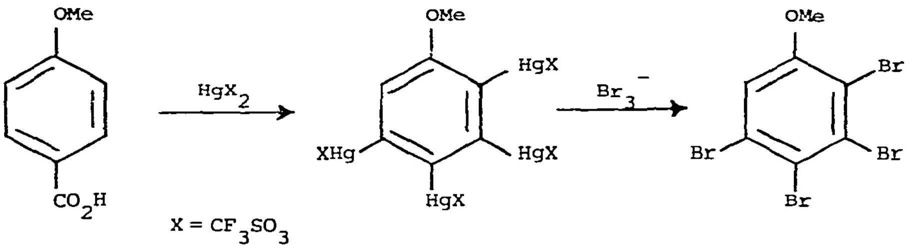
2. R^1, R^2, R^4, $R^5 = H$; $R^3 = HgX$; $R^6 = Br$; $X = CF_3CO_2$ or CF_3SO_3

3. R^1, R^3, R^4, $R^6 = H$; $R^2 = HgX$; $R^5 = Br$; $X = CF_3SO_3$

4. R^1, $R^3 = HgX$; R^2, $R^5 = H$; R^4, $R^6 = Br$; $X = CF_3CO_2$ or CF_3SO_3

Use of a mercuric trifluoroacetate : arene mole ratio of 6:1 in boiling trifluoroacetic acid followed by treatment with tribromide ions gave the following principal products: after 5 min, 3-bromo-4-methoxybenzoic acid (scheme 1), after 15 min, 3,5-dibromo-4-methoxybenzoic acid (scheme 2), and after 180 min, 2,3,5-tribromo-4-methoxybenzoic acid (scheme 4). With addition of trifluoromethanesulphonic acid ($CF_3SO_3H : CF_3CO_2H = 3:5$, v/v), a similar reaction for 15 min gave, after bromodemercuration, predominantly 2,3,5-tribromo-4-methoxybenzoic acid (scheme 4), indicative of major enhancement of polymercuration.

Some decarboxylation (*ipso* mercuration) was observed in all the foregoing reactions but was not of major significance. However, on increasing the $CF_3SO_3H : CF_3CO_2H$ ratio to 1:1 (v/v) with a mercuric salt : arene mole ratio of 6:1, *ipso* mercuration became substantial and the predominant product after bromodemercuration was 2,3,4,5-tetrabromoanisole (scheme 5).



5.

At this stage, it is difficult to see why the one vacant position should be *ortho* to the methoxy group. Certainly, the ready formation of 2,3,5-trimercurated 4-methoxybenzoic acid (scheme 4) suggests that there is no intrinsic difficulty in mercurating both positions *ortho* to methoxy.

A complicating factor in all reactions is the occurrence of partial or substantial precipitation of the polymercurated arenes. In the reaction giving predominantly 2,5-dimercurated 4-methoxybenzoic acid (scheme 3), the bulk of this product is in the insoluble fraction, though it is also the main component of the solution phase.

Our results show that the scope of mercuration by mercuric trifluoroacetate in trifluoroacetic acid is greatly enhanced by addition of trifluoromethanesulphonic acid. This differing and increased reactivity, resulting from formation of mercuric trifluoromethanesulphonate [1], is to be further explored.

Acknowledgement

We are grateful to Dr. J.F.W. McOmie, School of Chemistry, University of Bristol for an authentic sample of 2,3,4,5-tetrabromoanisole.

References

1. G.B. Deacon and D. Tunaley, J. Organometal. Chem., 156 (1978) 403.
2. H.C. Brown and R.A. Wirkkala, J. Amer. Chem. Soc., 88 (1966) 1447; see also C.W. Fung, M. Khorramdel-Vahed, R.J. Ranson, and R.M.G. Roberts, J. Chem. Soc. Perkin Trans. II, (1980) 267.