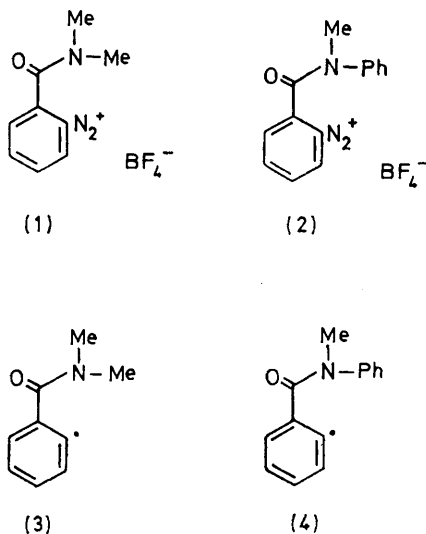


The Formation of *N*-Methylbenzanilide in the Decomposition of 2-(*N*-Methyl-*N*-phenylcarbamoyl)benzenediazonium Fluoroborate in Acetic Acid

By D. H. Hey, G. H. Jones, and M. J. Perkins,* Department of Chemistry, King's College, Strand, London WC2R 2LS

The decomposition of 2-(*N*-methyl-*N*-phenylcarbamoyl)benzenediazonium fluoroborate (2) in acetic [²H]acid gives a monodeuterio-*N*-methylbenzanilide. This and other evidence indicates that the *N*-methylbenzanilide produced in the title reaction is not formed by hydrogen atom abstraction from the solvent. An alternative mechanism involving acetolysis of an arylcopper intermediate is suggested.

It was recently reported that copper-catalysed decomposition of the diazonium salt (1) in glacial acetic acid gives, as a major product, *NN*-dimethylbenzamide (58%), in a process involving hydrogen abstraction from the methyl group of acetic acid (succinic acid was reported to be formed as a by-product).¹ The other major product from this reaction is *N*-methylbenzamide; the demethylation is initiated by intramolecular hydrogen transfer. A minor product (*ca.* 4%) from the copper-catalysed decomposition of 2-(*N*-methyl-*N*-phenylcarbamoyl)benzenediazonium fluoroborate (2) in acetone is benzanilide.^{2,3} *N*-Methylbenzanilide, however, was not detected (less than 0.2% present by g.l.c.). In view of the similar reactivities of acetone and acetic acid towards hydrogen abstraction by aryl radicals,⁴ the apparent absence of *N*-methylbenzanilide from among the products of experiments with compound (2) seemed to conflict with the data on the decomposition of compound (1) in acetic acid.



To investigate this apparent discrepancy, the copper-catalysed decomposition of the diazonium fluoroborate (2) in glacial acetic acid was examined. The products were similar to those found when acetone was employed, except that *N*-methylbenzanilide was formed in *ca.*

¹ A. H. Lewin, A. H. Dinwoodie, and T. Cohen, *Tetrahedron*, 1966, **22**, 1527.

² D. H. Hey, G. H. Jones, and M. J. Perkins, *J.C.S. Perkin I*, 1972, 1162.

³ G. H. Jones, Ph.D. Thesis, London, 1971.

8.5% yield. The following evidence is, however, incompatible with the formation of this additional product in a reaction involving hydrogen abstraction from the methyl group of acetic acid. (i) The *N*-methylbenzanilide is also formed in comparable yield when the solvent is trichloroacetic acid. (ii) The yield of the *N*-methylbenzanilide is drastically reduced by the presence of small concentrations of water. (iii) When the aryl radical (4) was generated in glacial acetic acid by photolysis of the corresponding aryl iodide, no *N*-methylbenzanilide was detected among the products. (iv) The decomposition of the diazonium salt (2) in glacial acetic acid induced by hydrogen iodide similarly failed to produce *N*-methylbenzanilide. (v) The copper-catalysed decomposition of the salt (2) in acetic [²H]acid gave *N*-methylbenzanilide containing one deuterium atom per molecule, in the benzoyl group (g.l.c.-mass spectrum). A lower yield (*ca.* 2%) of the anilide was obtained in this experiment. No attempt has been made to distinguish between two alternative explanations for this reduced yield, namely the presence of D₂O in the acetic acid, or the operation of a kinetic isotope effect.

We tentatively suggest that these results may be explained in terms of formation of the *N*-methylbenzanilide by acetolysis of an arylcopper intermediate.⁵ The inhibition of the reaction by water is at first sight surprising, as this would probably also hydrolyse the arylcopper.⁵ One possibility is that in the present system the role of water might be to inhibit formation of an arylcopper species, possibly by co-ordination with Cu^I to give a species in which reactivity as a scavenger for aryl radicals has been attenuated. A possible analogy is to be found in the oxidation of aralkanes by Mn^{III} in glacial acetic acid.⁶ The competition between two oxidation pathways is markedly affected by the presence of traces of water, and this has similarly been attributed to a dependence on the ligands attached to the metal atom.

These results suggest that the decomposition of the salt (1) in acetic acid may merit further study. It is significant that in that system the presence of a small

⁴ G. A. Russell and A. F. Bridger, *J. Amer. Chem. Soc.*, 1963, **85**, 3754.

⁵ Cf. T. Cohen and A. H. Lewin, *J. Amer. Chem. Soc.*, 1966, **88**, 4521.

⁶ E. I. Hejba, R. M. Dessau, and W. J. Koehl, *J. Amer. Chem. Soc.*, 1969, **91**, 138.

quantity of water substantially reduces the yield of *NN*-dimethylbenzamide.¹

EXPERIMENTAL

2-(*N*-Methyl-*N*-phenylcarbamoyl)benzenediazonium fluoroborate⁷ and 2-iodo-*N*-methylbenzanilide⁸ were prepared as described previously. Analytical procedures were as given elsewhere.⁸

Decomposition of the Diazonium Salt (2).—(i) The salt (1 g) suspended in reagent grade glacial acetic acid (10 ml) at room temperature, and the mixture was stirred under nitrogen. Copper powder (500 mg) was added, and the mixture was stirred for a further 15 min; decomposition of the diazonium salt was then complete (no colour with alkaline β -naphthol). Examination of the organic products by g.l.c. and t.l.c. indicated the formation of benzanilide (4%), *N*-methylphenanthridinone (35%), and a mixture of stereoisomeric spirocyclohexadienyl dimers (*cf.* data for copper-catalysed decomposition given in the Table of ref. 2). In addition, *N*-methylbenzanilide (8.5%) was formed. Prior treatment of the acetic acid with *ca.* 5% acetic anhydride to destroy traces of water was without measurable effect on the yield of this product.

(ii) The diazonium salt (1 g) in glacial acetic acid (10 ml) and water (300 mg) was decomposed as in (i). G.l.c. analysis of the organic products indicated similar yields of *N*-methylphenanthridinone and benzanilide, but only 3% of *N*-methylbenzanilide.

(iii) The diazonium salt (1 g) in glacial acetic acid (10 ml) and water (10 ml) was decomposed as before. The yield of *N*-methylbenzanilide was <0.5% (g.l.c.).

⁷ D. H. Hey, C. W. Rees, and A. R. Todd, *J. Chem. Soc. (C)*, 1967, 1518.

(iv) The diazonium salt (1 g) in a mixture of trichloroacetic acid (5 g) and carbon tetrachloride (15 g) was decomposed with copper as before. The products included *N*-methylbenzanilide (6%).

(v) The diazonium salt (1 g) in acetic [³H]acid (10 ml) was decomposed as before. The organic products included *N*-methylbenzanilide (*ca.* 2%) which was examined by combined g.l.c.–mass spectroscopy. The presence of the parent peak at *m/e* 212 and of a major fragment at *m/e* 106 were consistent with the formulation of the product as a monodeuterio-*N*-methylbenzanilide. Undeuterated material was not detected (< *ca.* 2% present). By analogy with the fragmentation of unlabelled *N*-methylbenzanilide, the fragment ion at *m/e* 106 corresponds to a deuterated benzoyl group, and thus confirms the location of deuterium in the aromatic nucleus.

(vi) The diazonium salt was decomposed in glacial acetic acid by passage of hydrogen iodide, by use of a procedure similar to that described for the reaction in methylene chloride.⁹ *N*-Methylbenzanilide was not formed in this reaction (<0.2% by g.l.c.).

*Photolysis of 2-Iodo-*N*-methylbenzanilide.*—This was carried out in glacial acetic acid, by use of the general procedure described for the reaction in benzene.⁸ The progress of the reaction was monitored by g.l.c.; at no stage was the presence of *N*-methylbenzanilide detected.

We thank the S.R.C. for a Studentship (to G. H. J.) and King's College, London, for financial assistance.

[1/2226 Received, 23rd November, 1971]

⁸ D. H. Hey, G. H. Jones, and M. J. Perkins, *J. Chem. Soc. (C)*, 1971, 116.

⁹ D. H. Hey, G. H. Jones, and M. J. Perkins, *J.C.S. Perkin I*, 1972, 113.