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A Simple, One-Step, Conversion of Aniline into Benzyne

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Summary Reaction of aniline with acetic anhydride, pentyl nitrite, and 2,3,4,5-tetraphenylcyclopentadienone, in benzene, gives the corresponding benzyne adduct (32%) while *p*-chlorobenzoyl nitrite and preformed acetanilide gives the adduct in 50·5% yield.

PREVIOUS communications from our laboratories[1] have dealt with the production of arynes and aryne precursors in the decomposition in solution of *N*-nitrosoacylanilides *via* the isomeric diazonium acetates. In accord with this, benzenediazonium acetate has recently been shown to give benzyne (37% based on PhN_2^+).[2] Two classes of behaviour have been identified, one being the special case of a t-butyl group *ortho* to the diazonium function (Scheme). This special effect has been confirmed by the observation[3] that *in situ* diazotisation by butyl nitrite[4] of 2,5-di-t-butylaniline leads to the corresponding aryne rather than the "normal" radical products observed with a large series of other anilines.[4]

Following these observations we have investigated the *in situ* diazotisation of aniline in the presence of acetate ions. This did *not* give benzyne as might have been expected from the foregoing, particularly from our observation of the formation of benzyne from *N*-nitrosoacetanilide (*via* the diazonium acetate). Thus, the reported case[3] of 2,5-di-t-butylaniline is unique and does not, as it stands, represent a general route to arynes. We have now discovered the reason for this and, in so doing, have devised a simple one-step conversion of aniline into benzyne. Thus, it has been shown in our laboratories[5] that benzyne formation from *N*-nitrosoacylanilides is suppressed by water. Since water is produced in the *in situ* diazotisation of anilines by pentyl nitrite,[4]

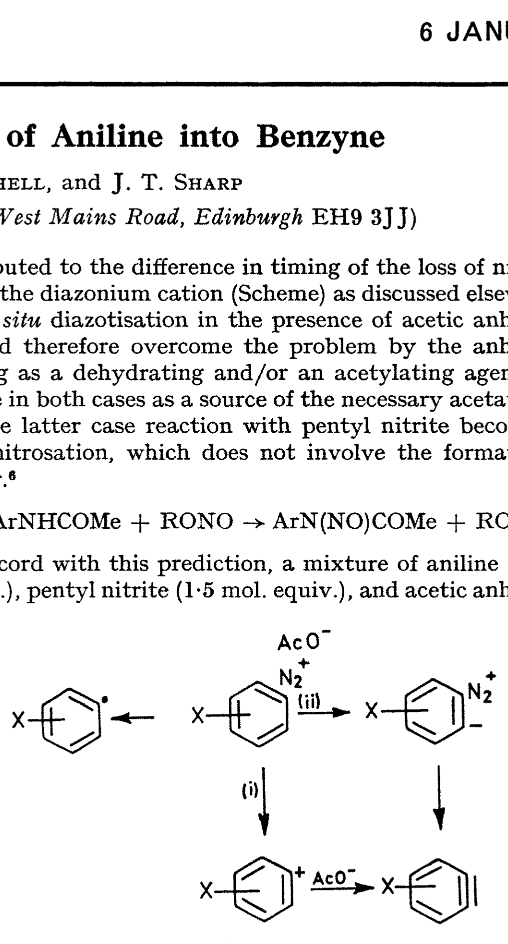
$$ArNH_2 + RONO + PhH \rightarrow ArPh + ROH + N_2 + H_2O$$

the failure of this method, in the presence of acetate ions, as a route to arynes, becomes clear. The unique success, even in the presence of water, in the *o*-t-butyl case[3] can be attributed to the difference in timing of the loss of nitrogen from the diazonium cation (Scheme) as discussed elsewhere.[1]

In situ diazotisation in the presence of acetic anhydride should therefore overcome the problem by the anhydride acting as a dehydrating and/or an acetylating agent (and hence in both cases as a source of the necessary acetate ion). In the latter case reaction with pentyl nitrite becomes *in situ* nitrosation, which does not involve the formation of water.[6]

$$ArNHCOMe + RONO \rightarrow ArN(NO)COMe + ROH$$

In accord with this prediction, a mixture of aniline (1 mol. equiv.), pentyl nitrite (1·5 mol. equiv.), and acetic anhydride (3 mol. equiv.) in benzene (34 mol. equiv.), at 80°, overnight, in the presence of 2,3,4,5-tetraphenylcyclopentadienone (1 mol. equiv.), gave 1,2,3,4-tetraphenylnaphthalene in 32% yield. *m*-Bromo-, *m*-chloro-, *m*-methoxy-, and *m*-methyl-anilines behave similarly, but *p*-toluidine gave a very low yield (*cf.* ref. 1c). Triptycene (10%) was obtained from aniline in the presence of anthracene.



SCHEME

(i) When X = *o*-Bu^t (not inhibited by furan or water).
(ii) Does not occur in presence of water or furan.

In a control experiment, acetanilide and pentyl nitrite in benzene under similar conditions gave the benzyne adduct in 8% yield only.

The reaction, which follows the pattern previously established[1] of suppression of the formation of benzyne by furan, appears to be the simplest route to benzyne so far recorded and has considerable potential, currently being evaluated, as a useful method for the production of certain, but not necessarily all, arynes, under mild conditions.

Added in proof. Modification of the reaction is likely to lead to still better results: thus the more efficient system, *p*-chlorobenzoyl nitrite/preformed acetanilide, leads to the isolation of the benzyne adduct in 50·5% yield.

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[1] (a) J. I. G. Cadogan and P. G. Hibbert, *Proc. Chem. Soc.*, 1964, 338; (b) J. I. G. Cadogan, *J. Pure and Appl. Chem.*, 1967, **15**, 153; (c) D. L. Brydon, J. I. G. Cadogan, D. M. Smith, and J. B. Thomson, *Chem. Comm.*, 1967, 727; (d) J. I. G. Cadogan, J. Cook, M. J. P. Harger, and J. T. Sharp, *ibid.*, 1970, 299; *J. Chem. Soc.* (B), 1970, in the press; (e) J. I. G. Cadogan in "Essays in Free Radical Chemistry," *Chem. Soc. Special Publ. No.* 24, 1970, 71.

[2] C. Rüchardt and C. C. Tan, *Angew. Chem. Internat. Edn.*, 1970, **9**, 522.

[3] R. M. Franck and K.Yanagi, *Tetrahedron Letters*, 1966, 2905; *J. Amer. Chem. Soc.*, 1968, **90**, 5814.

[4] J. I. G. Cadogan, *J. Chem. Soc.*, 1962, 4257; J. I. G. Cadogan, D. A. Roy, and D. M. Smith, *J. Chem. Soc.* (*C*), 1966, 1249.

[5] J. I. G. Cadogan, D. M. Smith, and J. B. Thomson, unpublished; J. I. G. Cadogan, M. J. P. Harger, and J. T. Sharp, *Amer. Chem. Soc. Div. Petrol. Chem.*, 1969, **14**, p. C19.

[6] E. B. McCall and E. J. Blackman, B.P. 929093 (*Chem. Abs.*, 1963, **59**, 12,704).