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FORMATION OF FUSED RING SYSTEMS BY THE REDUCTIVE CYCLISATION OF ARYL HALIDES

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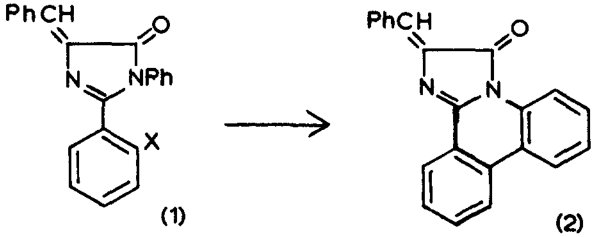
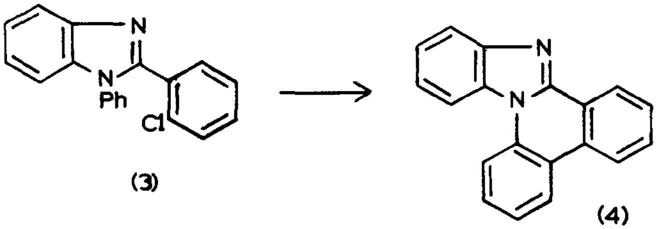
Aromatic radical-anions carrying a halogeno-substituent usually decompose by fragmentation of the carbon-halogen bond.[1,2] In appropriately substituted compounds this reaction is followed by cyclisation of the radical so generated on an adjacent benzene ring.[3] The overall reaction constitutes a new synthesis of condensed aromatic systems the scope of which still remains to be explored. Here we describe two further examples of the reaction both proceeding in excellent yield.

2-(2-Bromophenyl)-4-benzylidene-Δ^2-oxazolin-5-one reacted[4] with aniline in acetic acid containing sodium acetate to give (1, X = Br), m.p. 170-171°. Reduction at a mercury cathode (-1.4 V versus s.c.e.) in anhydrous dimethylformamide gave (2), yellow needles m.p. 269-270° which showed the correct analytical and m.s. data and was not identical with the known (1, X = H), m.p. 180°.[5]



(1) (2)



(3) (4)

2-Aminodiphenylamine with *o*-chlorobenzoyl chloride gave a diaroyl derivative which afforded (3), m.p. 162-163°, on heating with *o*-chlorobenzoyl chloride at 200°. Reduction of (3) at a mercury cathode (-2.1 V *versus* s.c.e.) in anhydrous dimethylformamide gave (4), colourless needles m.p. 151-152° not identical to the known 1,2-diphenylbenzimidazole, m.p. 112°.[6]

In both these reductive cyclisations the radical-anion is the reactive intermediate first formed. It undergoes cleavage of the carbon-halogen bond rapidly relative to other processes which such an intermediate can undergo and this is important for obtaining a good yield of the cyclised product. Previously[2] we showed that if the potential for formation of the radical-anion is less negative than -1.6 V fragmentation of an attached chloro-substituent will be relatively slow so that other reactions terminate the life of the species. Bromine substituted radical-anions do not fragment the carbon-halogen bond if the potential for their formation is less negative than -1.2 V. These considerations dictated the use of a bromo-substituent in the synthesis of (2). The corresponding bromo-compound could surely also be used in the synthesis of (4).

References

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