A Novel Benzyne Displacement Reaction

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Summary Anhydro-3-hydroxy-1-phenylpyridinium hydroxide (1a) and anhydro-3-hydroxy-1-(2',4'-dinitrophenyl)pyridinium hydroxide (1b) each react with benzyne to give 6,7-benzo-8-phenyl-8-azabicyclo[3,2,1]oct-3-en-2one (2).



WE report that the cycloaddition reaction of benzyne with the dinitrophenylpyridinium betaine (1b) is accompanied by a novel displacement of the N-dinitrophenyl group by the benzyne to form the N-phenyl adduct (2), m.p. 192-193° (decomp.) (30% yield) in place of the expected¹ adduct (3). The structure of the adduct (2) was established by elemental analysis and i.r., u.v., and n.m.r. spectral data, and confirmed by independent synthesis. The reaction of the phenyl betaine (1a) with benzyne gave, as expected from previous¹ reactions of pyridinium betaines with dipolarophiles, the adduct (2), identical with that prepared from (1b), in 45% yield.

The reaction now reported represents the sole example of a displacement reaction by benzyne at nitrogen, and is of potential importance as a synthetic method for N-phenyl compounds. The nearest analogy appears to be the displacement of a methyl group from thioanisole by tetrachlorobenzyne to yield tetrachlorophenyl phenyl sulphide reported by Brewer, Heaney, and Ward.² The mechanism and scope of the new reaction are under investigation.

Benzyne was prepared from anthranilic acid and npentyl nitrite.³ Previous unsuccessful attempts⁴ to obtain adducts from benzyne and pyridinium betaines used alternative routes.⁵ Both the dinitrophenylpyridinium betaine and anthranilic acid were recovered unchanged after they had been treated as in the benzyne reaction but in the absence of pentyl nitrite: this shows that the reaction did not involve ring opening and reclosure of the pyridinium ring by the anthranilic acid.

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