

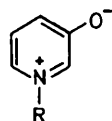
A Novel Benzyne Displacement Reaction

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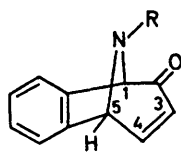
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Summary Anhydro-3-hydroxy-1-phenylpyridinium hydroxide (**1a**) and anhydro-3-hydroxy-1-(2',4'-dinitrophenyl)pyridinium hydroxide (**1b**) each react with benzyne to give 6,7-benzo-8-phenyl-8-azabicyclo[3,2,1]oct-3-en-2-one (**2**).



(1a) R = Ph

(1b) R = 2,4-(NO₂)₂C₆H₃



(2) R = Ph

(3) R = 2,4-(NO₂)₂C₆H₃

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 *n*-pentyl 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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² J. P. N. Brewer, H. Heaney, and T. J. Ward, *J. Chem. Soc. (C)*, 1969, 355.

³ I. Friedman and F. M. Logullo, *J. Org. Chem.*, 1969, **34**, 3089.

⁴ Y. Takeuchi, N. Dennis, A. R. Katritzky, and I. Taulov, 3rd International Congress of Heterocyclic Chemistry, Sendai, Japan, 1971.

⁵ Y. Tamura, N. Tsujimoto, and M. Uchimura, *J. Pharm. Soc. Japan*, 1971, **91**, 72.