Acid-catalysed Transformation of Hexamethylazoxybenzene. An Unusual Product in the Wallach Rearrangement

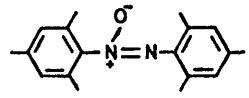
By E. BUNCEL* and R. A. Cox

(*Department of Chemistry, Queen's University, Kingston, Ontario, Canada*)

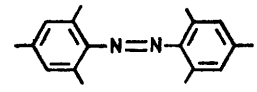
Summary 2,2',4,4',6,6'-Hexamethylazoxybenzene reacts in strong sulphuric acid media to yield 4-hydroxymethyl-2,2',4',6,6'-pentamethylazobenzene; a reaction pathway for this novel process is suggested.

HEXAMETHYLAZOXYBENZENE (**1**) should be suitable for the evaluation of current theories concerning the mechanism of the acid-catalysed Wallach rearrangement, since structurally this substrate places restrictions on available rearrangement pathways. In particular, the absence of vacant *ortho* or *para* positions precludes the occurrence of a "normal" rearrangement[1] (*e.g.* azoxybenzene → *p*-hydroxyazobenzene).

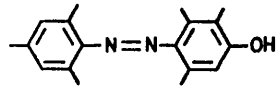
Among the pathways possible for this substrate in strong sulphuric acid media, the following are the most probable from precedents recorded for related systems.[1] (i) Formation of hexamethylazobenzene (**2**), by analogy with the reported reduction of hexabromoazoxybenzene to the azo-derivative in strong acid.[2] (ii) Skeletal rearrangement accompanying attack on aromatic carbon, with formation of the azophenol (**3**), provided that analogy can be drawn with the Bamberger rearrangement.[3] (iii) Formation of a dicationic intermediate, $ArN^{+}{\equiv}N^{+}Ar$, as postulated in the rearrangement of azoxybenzene;[4] this might be sufficiently



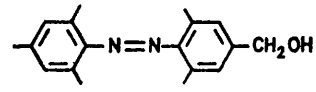
(**1**)



(**2**)



(**3**)



(**4**)

stabilized to allow its detection, or it might partake in some novel process(es) which could be characteristic of that species.

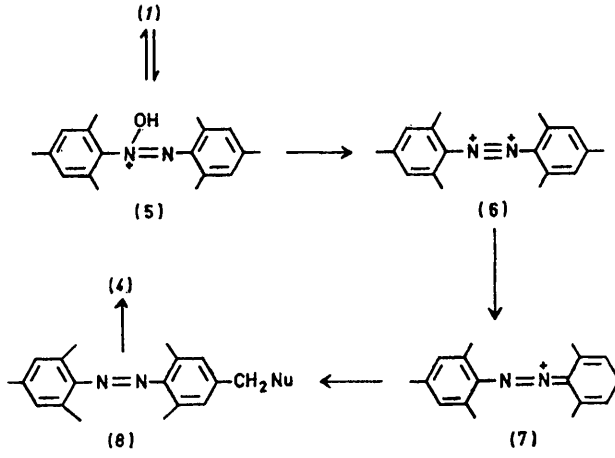
The reaction of (**1**)† in sulphuric acid has been examined spectrophotometrically. In 84·1% H_2SO_4 at 44·4°, with a

† The substrate (**1**) was synthesized by oxidation of the azo-derivative (**2**) and characterized spectrally as well as by elemental analysis.

substrate concentration of 5×10^{-5}M, one observes a decrease in absorption at 387 nm, ascribed to the conjugate acid of (**1**), and the appearance of an absorption peak at 463 nm due to a new species, with an isosbestic point occurring at 373 nm. Reaction is complete after 1h, yielding a solution of stable absorption (ϵ_{463} 28,400). Though the product absorption is characteristic of an azo compound, it differs quantitatively from that of (**2**) in this medium (λ_{max} 475 nm, ϵ_{475} 35,100). Similarly the product spectrum does not correspond to that of (**3**) in this medium (λ_{max} 488 nm, ϵ_{488} 32,900). That the product is non-phenolic is indicated by the fact that its spectrum in alkaline methanolic solution is virtually unchanged from that in neutral medium. Product isolation was achieved by treatment of a 6×10^{-4}M solution in 85·6% H_2SO_4 at 44·4° for 10 half-lives and work-up. Characterization by n.m.r. i.r., and mass spectrometry, as well as by elemental analysis, showed that the product was in fact the alcohol (**4**). The acetyl derivative of (**4**) was prepared and similarly characterized.

A possible mechanism for the transformation of (**1**) is shown in the Scheme and involves an equilibrium protonation (**5**), followed by a second proton transfer with loss of H_2O yielding the dicationic intermediate (**6**). Proton loss to give the quinoid structure (**7**) is followed by nucleophilic attack to yield the product, either directly or *via* the intermediate sulphate ester (**8**) (Nu = OSO_3H).[5] However, the spectral behaviour in the kinetic run shows that the intermediate (**6**) is not present in significant concentration.

The reaction course observed for hexamethylazoxybenzene differs fundamentally from that recorded for related systems. Unlike the hexabromoazoxybenzene case, in the present system reduction is shown to be a negligible process, at least under kinetic conditions. Contrast may also be drawn with 4,4′-dimethylazoxybenzene which gives 2-hydroxy-4,4′-dimethylazobenzene in the Wallach rearrangement,[6] and with the Bamberger rearrangement of 4-methylphenylhydroxylamine which yields products derived from migration of the methyl group.[3] A possible rationalization of the Wallach rearrangement results for



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methyl substituted azoxybenzenes, such as (**1**) and 4,4′-dimethylazoxybenzene, may be suggested on the basis of formation of a metastable dicationic intermediate, $ArN{\equiv}NAr^{++}$, which leads to *ortho*-hydroxy-substitution in the cases when a vacant *ortho* position is available, and to proton loss yielding a hydroxymethyl product when the *ortho* and *para* positions are blocked. It may also be concluded that the Bamberger and the Wallach rearrangements differ basically in their intimate mechanisms, despite an apparent formal analogy of these processes.

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