Synthesis and Reactivity of *N*-Hydroxybenzimidazolones

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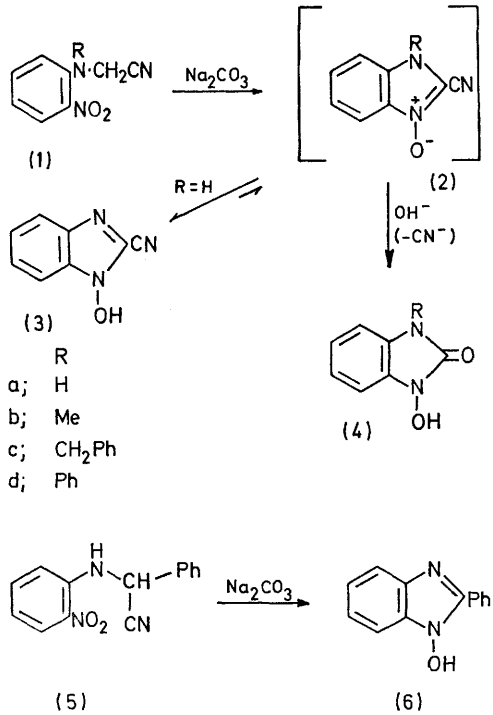
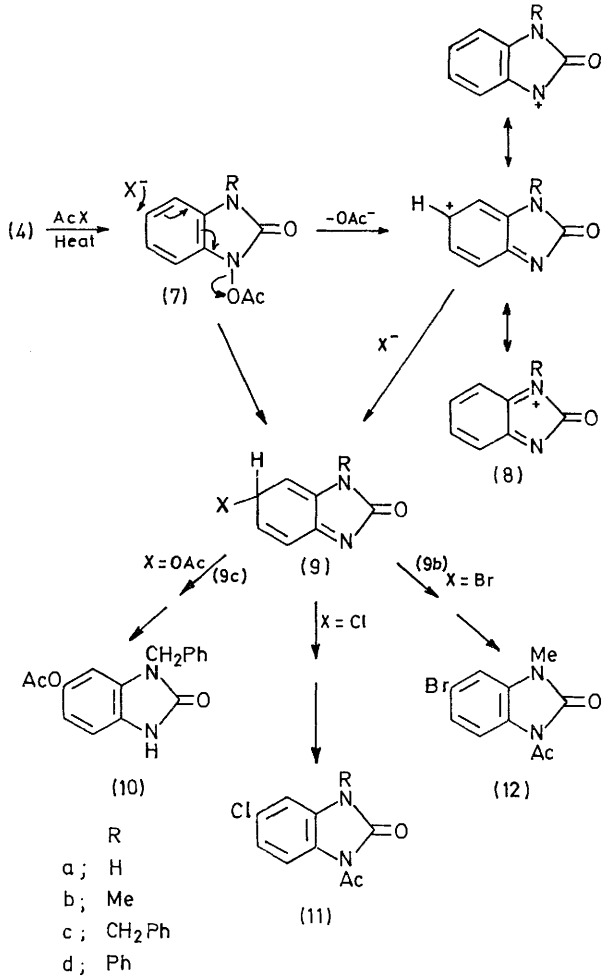
Summary Base-catalysed cyclisation of *N*-substituted 2-nitroanilinoacetonitriles affords *N*-hydroxybenzimidazolones which react with acylating agents to yield 5-substituted benzimidazolones.

FIVE-MEMBERED *N*-oxygenated benzaza-heterocycles are potential sources of heterocyclic nitrenium cations.[1] In this context, *N*-oxygenated benzimidazoles are of particular interest because in these substrates the second nitrogen atom should exert a stabilising effect on nitrenium ion formation. We now describe a general synthetic route to the *N*-hydroxybenzimidazolones (**4**) and their novel reactivity towards acylating agents.†



In a simple extension of previously reported[2] cyclisations, heating (**1a**)[3] with aqueous ethanolic sodium carbonate afforded the benzimidazole (**3**) (77%), m.p. 232°. The



† Satisfactory analysis and spectral data were obtained for all new compounds.

α-phenyl derivative (**5**) cyclised to (**6**) (19%),[4] lending support to the mechanism suggested[5] for the cyanide-catalysed formation of (**6**) from benzylidene-2-nitroaniline. On the other hand, heating the *N*-substituted compounds (**1b**—**d**) with aqueous ethanolic sodium carbonate gave good yields (60—75%) of the cyclic hydroxamic acids (**4b**),[6] m.p. 203°, (**4c**), m.p. 172°, and (**4d**), m.p. 216° which showed enhanced acidity and gave characteristic green colours[7] with $FeCl_3$ in EtOH. The formation of the *N*-hydroxybenzimidazolones (**4**) rather than the *N*-oxides (**2**) in these reactions is in accord with the ready base-catalysed conversion of 2-cyano-3-methylbenzimidazole 1-*N*-oxide (**2b**) into (**4b**).[6]

The cyclic hydroxamic acids (**4**) reacted typically with acetic anhydride at room temperature to afford the *N*-acetoxy-derivatives (**7**) (>90%) showing characteristically[7] high carbonyl absorption at *ca.* 1800 $cm.^{-1}$ However, acetylation at elevated temperature took a different course. Hot acetic anhydride converted (**4c**) into the *C*-acetoxy-product (**10**) (79%), m.p. 180°, while heating the *N*-hydroxy-benzimidazolones (**4b**—**d**) with acetyl chloride in glacial acetic acid afforded (70—80%) the corresponding 1-acetyl-5-chlorobenzimidazolones (**11b**—**d**). Hot acetyl bromide in glacial acetic acid converted the hydroxamic acid (**4b**) into the bromo-compound (**12**) (30%). The 5-position for the entering group in the products is supported by the splitting pattern of the aromatic proton resonances in their ^1H n.m.r. spectra.

The reactions of the *N*-hydroxybenzimidazolones with acylating agents at elevated temperatures are explicable in terms of nucleophilic attack on the *N*-acetoxy-intermediates (**7**) either concertedly with expulsion of the acetoxy-leaving group [(**7**) → (**9**) → (**10**)—(**12**)] or after ionisation to resonance stabilised nitrenium cations[1] [(**7**) → (**8**) → (**9**) → (**10**)—(**12**)] and subsequent acetylation.

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