SYNTHESIS OF 2-VINYLBENZIMIDAZOLE N-OXIDE

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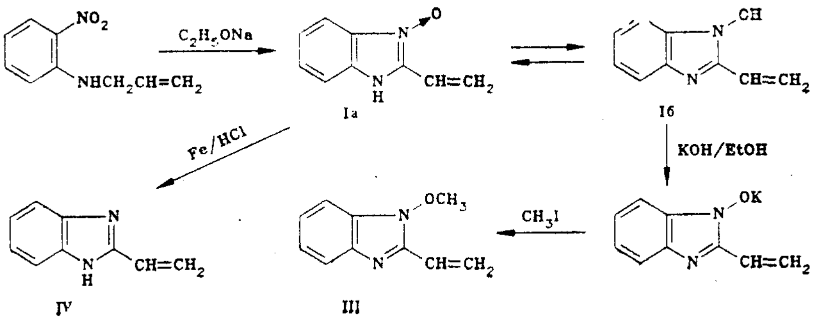
Direct alkylation of o-nitroaniline by allyl bromide with phase-transfer catalysis (50% NaOH, dimethyl sulfoxide, and triethylbenzylammonium chloride) gave o-nitro-N-allylaniline, the reaction of which with sodium ethylate with boiling in alcohol gave 2-vinylbenzimidazole N-oxide (I) in high yield.

With acid treatment or with alkali treatment, sparingly water-soluble oxide I dissolved because of the tautomeric equilibrium Ia ⇄ Ib, which is characteristic of benzimidazole N-oxides [1]. With concentrated HCl, oxide I formed hydrochloride crystals, and with a solution of KOH in alcohol it formed potassium salt (II). In the reaction of rather stable monomer I with methyl iodide in an alkaline medium, 2-vinyl-1-methoxybenzimidazole (III) was formed, which readily polymerized during its recovery from the reaction mixture and during storage, like 2-vinyl-1-methylbenzimidazole [2]. The reduction of oxide I by iron in hydrochloric acid gave known 2-vinylbenzimidazole in 35% yield [2].



The IR spectrum of the compound (in white mineral oil) consisted of bands at 3160-3380 (a strong band of associated NH and OH groups), 3095 and 3000 (=CH_2 and =CH stretching bands), and 1000 and 945 cm^{-1} (out-of-plane =CH and =CH_2 bending bands). The PMR spectrum (CD_3OD) consisted of δ 7.25 (4H, multiplet, H_{arom}), 6.9 (1H, triplet, =CH), 5.75 (2H, doublet, =CH_2), 6.5 (1H, singlet, OH), and 6.3 ppm (1H, singlet, NH). As a result of rearrangements and fragmentation of the molecular ion with m/z 160 (I 2.4%), benzimidazolium with m/z 118 (I 100%), and benzene derivatives with m/z (I, %): 132 (8), 105 (3.0), and 91 (36.1). The nature of fragmentation of M^+ of compound I corresponded to the data of mass spectra of benzimidazole and pyridine N-oxides [1].

2-Vinylbenzimidazole N-Oxide (I). To a solution of sodium ethylate [from 0.46 g (0.02 mole) of sodium and 15 ml of alcohol] was added 1.8 g (0.01 mole) of o-nitro-N-allylaniline, and the whole was boiled for 2.5 h. After cooling, the solution was neutralized with 10% hydrochloric acid, and the resulting precipitate of oxide I was filtered. The yield was 1.61 g (90%) with mp 124-126°C (from aqueous ethanol). Under similar conditions, oxide I was obtained in 45% yield from o-nitro-N-allylacetanilide.

LITERATURE CITED

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