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FORMATION OF THE 2-NITRO DERIVATIVE DURING OXIDATION OF 4,5-DIPHENYLIMIDAZOLE TO BENZIL WITH NITRIC ACID

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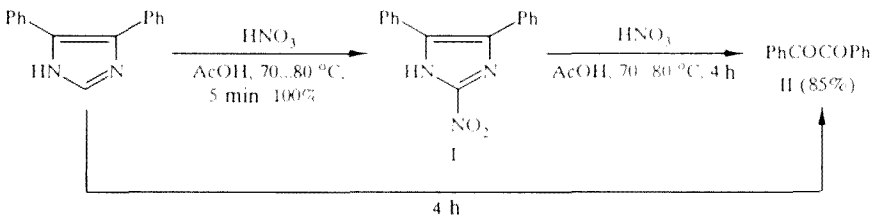
The imidazole ring has high resistance to the destructive action of various oxidizing agents, including nitric acid. The 2-nitro derivatives of imidazole cannot be synthesized by direct substitution in the imidazole ring [1]. However, the boiling of 4,5-diphenylimidazole with a nitrating mixture in acetic acid leads to the formation of 4,5-di(4-nitrophenyl)imidazole or 4,4′-dinitrobenzil [2].

We established that the reaction of 4,5-diphenylimidazole with an excess of nitric acid (more than 2 moles) in glacial acetic acid at 70-80°C for 4 h gave a high yield of benzil (II).



A reduction in the amount of nitric acid to 1-2 moles for 5 min led to the formation of 2-nitro-4,5-diphenylimidazole (I) with a quantitative yield. The latter was also formed quantitatively when the authentic 4,5-diphenylimidazole nitrate that we prepared was heated in acetic acid. The nitration of 4,5-diphenylimidazole and its nitrate only begins above 70°C (TLC). It is curious that N-acetyl-4,5-diphenylimidazole previously obtained by boiling 4,5-diphenylimidazole in acetic anhydride does not react with an excess (1-6 moles) of nitric acid for 4 h.

Thus, 2-nitro-4,5-diphenylimidazole is oxidized to benzil (II) by the action of nitric acid at 70-80°C. Compound (I) reacts with dimethyl sulfate in the presence of pyridine with the formation of 1-methyl-2-nitro-4,5-diphenylimidazole.

2-Nitro-4,5-diphenylimidazole (I) ($C_{15}H_{11}N_3O_2$). The yield was 100%; mp 200°C. Published data [3]: mp 200-202°C. IR spectrum, cm^{-1}: 1530, 1360 (NO_2). PMR spectrum (DMSO-d_6): 10.0 (1H, b, NH), 7.2-7.6 (10H, m, Ph). ^{13}C NMR spectrum (DMSO + Cr^{3+}): 144.3 (C—NO_2), 133.74 ($C_{(4)}$, $C_{(5)}$ of imidazole), 128.89 (Ph, $C_{(1)}$), 126.95 (Ph, $C_{(2)}$, $C_{(3)}$, $C_{(4)}$). Mass spectrum (12 eV), m/z: M^+ 266, $(M - NO_2)^+$ 220.

Benzil (II). The yield was 87%; mp 95-97°C.

1-Methyl-2-nitro-4,5-diphenylimidazole (III) ($C_{16}H_{13}N_3O_2$). The yield was 76%; mp 163-168°C. PMR spectrum (DMSO-d_6): 3.75 (3H, s, Me), 7.1-7.6 (10H, m, Ph).

The elemental analyses of all the synthesized compounds agreed with the calculated data.

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