NITRATION OF 2-PHENYLIMIDAZO[1, 2-a]PYRIDINE

N. O. Saldabol and I. B. Mazheika

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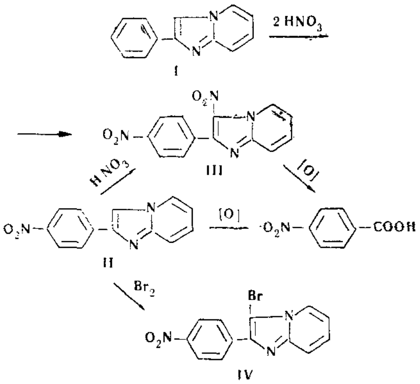
The addition of 2-phenylimidazo[1,2-a]pyridine to a nitrating mixture forms 3-nitro-2-(p-nitrophenyl)imidazo[1,2-a]pyridine; the position of the nitro groups in it has been shown by chemical reactions and by a determination of the dipole moment.

According to Italian authors [1], the action of 0.75 mole of nitric acid on 1 mole of 2-phenylimidazo[1,2-a]pyridine (I) in concentrated sulfuric acid leads to 2-(p-nitrophenyl)imidazo[1,2-a]pyridine (II). We have established that when the order of addition of the reagents is changed, i.e., when I is added to the nitrating mixture, II is not formed but 32% of a dinitro product III is instead obtained. With the use of 2.5 mole of HNO_3 per mole of I, the yield of III increased to 91%. With respect to its mp and UV spectrum, III is identical with the product of the nitration of II. In contrast to II, III does not undergo bromination and does not form a picrate. The oxidation of both II and III with potassium permanganate in an alkaline medium leads to p-nitrobenzoic acid. This shows that the second nitro group does not enter the benzene ring. By analogy with the nitration of imidazo[1,2-a]pyridine [2], it may be assumed that the second nitro group is in position 3 of the imidazopyridine nucleus.



This assumption has been confirmed by a determination of the dipole moment of the dinitro derivative. The value of the dipole moment found experimentally (7.27 D) is close to that calculated vectorially for III (7.4 D) by analogy with previous work [4, 5] and differs considerably from the values of the dipole moments calculated for the two rotational isomers of 2-(o,p-dinitrophenyl)imidazo[1,2-a]-pyridine (4.2 and 7.8 D) and for 5-nitro-2-(p-nitrophenyl)imidazo[1,2-a]pyridine (5.1 D).

EXPERIMENTAL

2-(p-Nitrophenyl)imidazo[1,2-a]pyridine (II) was prepared by a published method [3]. Mp 260–265° C (from CH_3COOH). UV spectrum, λ_{max}, nm (log ε): 272 (4.20), 340 (4.24). Picrate: mp 280° C (washed with ethanol). Found, %: C 48.42; H 2.69; N 18.20%. Calculated for $C_{13}H_9N_3O_2 \cdot C_6H_3N_3$, %: C 48.72, H 2.58, N 17.95.

Results of the Determination of Dipole Moments

f [molar fractions]	ε	d
0.000695	2.2904	1.0318
0.000511	2.2604	1.0316
0.000415	2.2593	1.0314
0.000344	2.2580	—

3-Nitro-2-(p-nitrophenyl)imidazo[1,2-a]pyridine (III). a) With stirring, 3.88 g (20 mM) of I was gradually added to a nitrating mixture consisting of 24 ml of conc. H_2SO_4 and 1.0 ml (15 mM) of 70% HNO_3, and the mixture was stirred for 1 hr and poured onto ice, after which the precipitate was filtered off. Yield 1.81 g (32%). Mp 260–265° C (from CH_3COOH). Found, %: C 54.69; H 2.96; N 20.06. Calculated for $C_{13}H_8N_4O_4$, %: C 54.93; H 2.84; N 19.71. UV spectrum, λ_{max}, nm (log ε): 277 (4.40), 361 (4.07). When the amount of HNO_3 was increased to 2.5 mole/mole of I, the yield of III was 91%.

b) At 15–20° C, 2.39 g (10 mM) of II was added to a mixture of 1.0 ml (15 mM) of 70% HNO_3 and 20 ml of conc. H_2SO_4, and the mixture was stirred for 1 hr and poured onto ice. The precipitate was filtered off and washed with water. Yield 1.86 g (68%). Mp 265° C (from CH_3COOH). No depression of the melting point in admixture with the sample obtained above was observed. Found, %: C 55.01; H 3.05, N 19.78. Calculated for $C_{13}H_8N_4O_4$, %, C 54.93; H 2.84, N 19.71. UV spectrum, λ_{max}, nm (log ε): 278 (4.38), 361 (4.05).

Oxidation of II and III. A 10 mM quantity of II or III was added to 8.0 g of NaOH and 5.5 g of $KMnO_4$ in 120 ml of water, the mixture was heated for 30 min in the boiling water bath, the MnO_2 was filtered off, the filtrate, after cooling, was acidified with hydrochloric acid, the precipitate was filtered off. The mp of 238–240° C (from aqueous dioxane) and the UV spectrum (λ_{max} 260 nm) corresponded to those of p-nitrobenzoic acid.

3-Bromo-2-(p-nitrophenyl)imidazo[1,2-a]pyridine (IV). A 0.52 ml (10 mM) quantity of bromine was added to 2.39 g (10 mM) of II in 40 ml of dioxane, and the mixture was stirred for 1 hr and poured into 200 ml of water, after which the precipitate was filtered off. Yield 1.83 g (57%). Mp 223–225° C (from pyridine). Found, %: Br 25.13; N 13.26. Calculated for $C_{13}H_8BrN_3O_2$, %: Br 25.12; N 13.22%:

The UV spectra were taken on an SF-4a instrument in a solution containing 2 vol.-% of dimethylformamide and 98 vol.-% of ethanol. The dipole moment of III was determined in dioxane solutions at 25° C by the procedure described previously [6].

$$P_{tot} = 1173.76 \text{ cm}^3;\ MR_D = 72.52 \text{ cm}^3;\ \mu = 7.27 \text{ D}$$

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Institute of Organic Synthesis
AS LatvSSR, Riga