ERRATA

REACTION OF 2-AMINO-1-ALKYLBENZIMIDAZOLES WITH NITROSYLSULFURIC ACID

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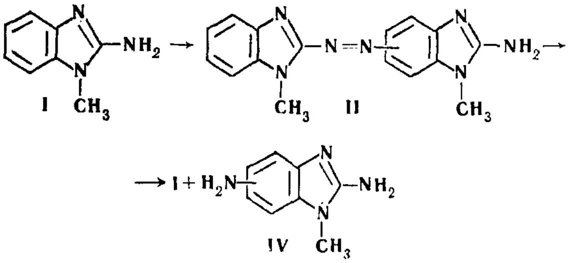
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 3, No. 1, pp. 186–187, 1967

UDC 547.785.5+542.958.3

When studying the possibility of diazotizing the amino group at position 2 in imidazole systems, we found that reaction of 2-amino-1-methylbenzimidazole (I) [1] in conc H_2SO_4, at 0–2°, with nitrosylsulfuric acid, in the presence of conc H_3PO_4 [2], gives a mixture of two isomeric diazo compounds II. It was isolated from the solution after pouring onto ice and making alkaline, yield 80%. 2-Amino-1-ethylbenzimidazole (III) reacted similarly. It can be assumed that I is first converted to a diazo compound (see [1]), which quickly undergoes diazo coupling with a second molecule of amine. However, since I and 2-dimethylamino-1-methylbenzimidazole in aqueous or acetic acid solution do not undergo coupling with diazonium salts, prepared from 2, 4-dinitroaniline and sulfanilic acid, the mechanism of formation of II requires study.



a 2, 5'-diazo compound
b 2, 6'-diazo compound

a 2, 5-diamino derivative
b 2, 6-diamino derivative

When the mixture II was recrystallized from pyridine, the isomer IIa first separates as orange plates, mp 307–308° (decomp, ex pyridine). Found: C 63.26; H 4.97; N 32.24%. Calculated for $C_{16}H_{15}N_7$. C 62.94; H 4.95; N 32.11%. From a pyridine solution ether precipitated the isomer IIb, crimson needles, mp 311–312° (decomp, ex EtOH). Found: C 63.07; H 4.95; N 32.23% Calculated for $C_{16}H_{15}N_7$. C 62.94; H 4.95; N 32.11%.

The structures of the diazo compounds obtained were established by reducing them to I and the diamines IV. IIa gave 2, 5-diamino-1-methylbenzimidazole (IVa), as its dipicrate mp 244–245° (in the free state the diamines IV are unstable). Found: N 22.72%. Calculated for $C_8H_{10}N_4 \cdot 2C_6H_3N_3O_7$. N 22.58%. IIb gave the dipicrate of 2, 6-diamino-1-methylbenzimidazole (IVb), mp 264–265°. Found: C 38.98; H 2.59; N 22.78%. Calculated for $C_8H_{10}N_4 \cdot 2C_6H_3N_3O_7$. C 38.73; H 2.60; N 22.58%. The position of the amino group in IV was shown by synthesis: identical diamines IVa, b were obtained by reducing 5-nitro-2-amino-1-methylbenzimidazole and its 6-nitro isomer [3].

Treatment of I and III with nitrous acid in 20–40% sulfuric acid leads to slow diazotization (check coupling with R salt), accompanied by further changes. In agreement with the results of [1], there was practically no reaction at 5° in 2 N HCl. Only 20% diazo compound was obtained when a solution of III in glacial AcOH was treated at 20°, over a period of 2–3 hr, with dry sodium nitrite [4].

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29 March 1966

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SYNTHESIS OF DERIVATIVES OF PYRROLO[1, 2-*a*]BENZIMIDAZOLE

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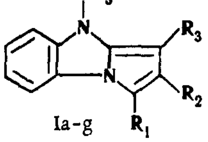
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 3, No. 1, pp. 187–188, 1967

UDC 547.785.5+547.741

The last number of KhGS [1] contained a letter to the Editor from P. M. Kochergin, A. A. Druzhinina, and R. M. Palei. In this connection, it should be mentioned that one of us has been occupied since 1963 [2–5] with the synthesis and study of the properties of ten π-electron heterocyclic compounds, analogs of indolizine. Continuing along those lines, we have synthesized a large number of derivatives of pyrrolo[1, 2-*a*]benzimidazole (I):



Ia-g

Some of these compounds have been described in the author's abstract of a thesis by F. S. Babichev, issued in May 1965 [6]. We established that good yields of I derivatives were obtained by heating quaternary salts of 1, 2-dialkylbenzimidazoles and α-halogenoketones with sodium carbonate solution in the presence of a small amount of sodium sulfite, which stops oxidation of I bases. Pyrrolo[1, 2-*a*] benzimidazoles readily undergo electrophilic substitution of position 1 or 3 of the molecules are vacant.

Ia. $R_1=R_3=H$, $R_2=CH_3$. yield 46%, mp 90° (ex MeOH). Found: N 15.19, 15.25%. Calculated for $C_{12}H_{12}N_2$. N 15.21%. Ib. $R_1=R_3=H$, $R_2=C_6H_5$. mp 114° (ex EtOH). Found: N 11.51; 11.68%. Calculated for $C_{17}H_{14}N_2$. N 11.39%. Ic. $R_1=H$, $R_2=R_3=CH_3$, 50% yield, mp 99° (ex MeOH). Found: N 14.12, 14.32%. Calculated for $C_{13}H_{14}N_2$. N 14.13%. Id. $R_1=CH_3$, $R_2=C_6H_5$, $R_3=H$, yield 74%, mp 145–146° (ex

MeOH). Found: N 10.51, 10.60%. Calculated for $C_{18}H_{16}N_2$. N 10.76%. Ie. $R_1=R_2=CH_3$, $R_3=H$, yield 69%, mp 96° (ex MeOH). Found: N 14.02, 14.16%. Calculated for $C_{13}H_{14}N_2$. N 14.13%. If. $R_1=H$, $R_2=C_6H_5$, $R_3=CH_3$, yield 78%, mp 167° (ex EtOH). Found: N 10.44, 10.53%. Calculated for $C_{18}H_{16}N_2$. N 10.76%. Ig. $R_1=R_2=R_3=CH_3$ (perchlorate), mp 194–195° (ex glacial AcOH). Found: Cl 11.51, 11.52%. Calculated for $C_{14}H_{16}N_2 \cdot HClO_4$: Cl 11.34%.

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6 April 1966

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