ISSN 1070-4280, Russian Journal of Organic Chemistry, 2010, Vol. 46, No. 3, pp. 459–460. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © A.O. Chunaev, E.A. Stepanov, P.P. Purygin, 2010, published in Zhurnal Organicheskoi Khimii, 2010, Vol. 46, No. 3, pp. 463–464.

SHORT COMMUNICATIONS

Reaction of *N*,*N*-Dimethylaniline with *N*-Cyanoazoles according to Electrophilic Aromatic Substitution Pattern

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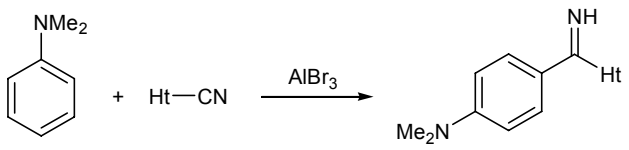
Received May 25, 2009

DOI: 10.1134/S1070428010030309

N-Cyanoazoles are highly reactive organic compounds and important intermediate products in the synthesis of numerous derivatives containing an azole ring. Owing to high polarity of the cyano group, *N*-cyanoazoles are capable of acting as electrophilic reagents in electrophilic aromatic substitution reactions.

In the present communication we report on the synthesis of some imines via electrophilic aromatic substitution of hydrogen in *N*,*N*-dimethylaniline by *N*-cyanoimidazole, *N*-cyanobenzimidazole, *N*-cyano-1,2,3-benzotriazole, and *N*-cyano-2-methylimidazoles. Initial *N*-cyanoazoles **Ia**–**Id** were prepared according to standard procedures. We were the first to demonstrate that the above listed *N*-cyanoazoles react with *N*,*N*-dimethylaniline in the presence of anhydrous aluminum bromide to give *para*-substituted imines in good yields (65–74%). Azole-containing imines **IIa**–**IId** were characterized by sharp melting points and R_f values, and their structure was confirmed by elemental analyses and ^{1}H NMR spectra.

Nitrobenzene was found to be appropriate solvent for carrying out reactions of *N*-cyanoazoles **Ia**–**Id** with *N*,*N*-dimethylaniline. High polarity and dissolving power of nitrobenzene ensure homogeneity of the reaction mixture throughout the process. On the other hand, nitrobenzene itself is not involved in the reaction because of the presence of a strong electron-withdrawing nitro group in its molecule.



Ia–Id **IIa–IId**

Ht = 1*H*-imidazol-1-yl (**a**), 2-methyl-1*H*-imidazol-1-yl (**b**), 1*H*-benzimidazol-1-yl (**c**), 1*H*-1,2,3-benzotriazol-1-yl (**d**).

***N*,*N*-Dimethyl-4-[azolyl(imino)methyl]anilines IIa–IId (*general procedure*).** Anhydrous aluminum bromide, 4 g, was dissolved in 50 ml of anhydrous nitrobenzene on cooling in an ice–salt bath, and a solution of 15 mmol of *N*-cyanoazole **Ia**–**Id** in 20 ml of anhydrous nitrobenzene was slowly added dropwise under stirring at 6°C. The mixture turned yellow–orange. It was stirred for 1 h, and a solution of 1.9 ml (1.82 g, 15 mmol) of *N*,*N*-dimethylaniline in 15 ml of anhydrous nitrobenzene was added. The mixture turned red or blue and was stirred for 4 h, the solvent was distilled off under reduced pressure (3 mm), and the tarry residue was extracted with anhydrous chloroform. The solvent was distilled from the extract on a rotary evaporator under reduced pressure (water-jet pump) at a bath temperature not exceeding 40°C. The crystalline product was stored in a vacuum desiccator over calcium chloride.

4-[1*H*-Imidazol-1-yl(imino)methyl]-*N*,*N*-dimethylaniline (IIa). Yield 2.12 g (66%), mp 186°C (from benzene), R_f 0.56. ^{1}H NMR spectrum, δ, ppm: 3.2 br.s (6H, NMe_2), 5.9 s (1H, NH), 7.2 d (2H, *o*-H), 7.5 m (2H, 4-H, 5-H), 7.8 m (2H, *m*-H), 8.1 br.s (1H, 2-H). Found, %: C 67.38; H 6.48; N 26.14. $C_{12}H_{14}N_4$. Calculated, %: C 67.29; H 6.54; N 26.17.

4-[Imino(2-methyl-1*H*-imidazol-1-yl)methyl]-*N*,*N*-dimethylaniline (IIb). Yield 2.22 g (65%), mp 168°C (from benzene), R_f 0.65. ^{1}H NMR spectrum, δ, ppm: 2.5 s (3H, 2-CH_3), 3.2 br.s (6H, NMe_2), 6.2 s (1H, NH), 7.2 d (2H, *o*-H), 7.5 m (2H, 4-H, 5-H), 7.6–7.7 m (2H, *m*-H). Found, %: C 68.53; H 6.97; N 24.50. $C_{13}H_{16}N_4$. Calculated, %: C 68.42; H 7.02; N 24.56.

4-[1*H*-Benzimidazol-1-yl(imino)methyl]-*N*,*N*-dimethylaniline (IIc). Yield 2.12 g (74%), mp 205°C (from benzene), R_f 0.73. ^{1}H NMR spectrum, δ, ppm: 3.2 br.s (6H, NMe_2), 5.9 s (1H, NH), 7.2 d (2H, *o*-H),

7.6–8.0 m (6H, *m*-H, 4-H–7-H), 8.3 br.s (1H, 2-H). Found, %: C 72.80; H 6.04; N 21.16. $C_{16}H_{16}N_4$. Calculated, %: C 72.73; H 6.04; N 21.21.

4-[1*H*-1,2,3-Benzotriazol-1-yl(imino)methyl]-*N*,*N*-dimethylaniline (IId). Yield 2.86 g (72%), mp 175°C (from benzene), R_f 0.66. ^{1}H NMR spectrum, δ, ppm: 3.2 br.s (6H, NMe_2), 5.9 s (1H, NH), 7.3 d (2H, *o*-H), 7.6 m (2H, 5-H, 6-H), 7.8 m (2H, 4-H, 7-H), 8.3 m (2H, *m*-H). Found, %: C 67.96; H 5.64; N 26.40. $C_{15}H_{15}N_5$. Calculated, %: C 67.92; H 5.66; N 26.42.

The ^{1}H NMR spectra were recorded from solutions in $CDCl_3$ on a Bruker Avance II 300 spectrometer (300 MHz) using tetramethylsilane as internal reference. The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates using ethyl acetate as eluent.