OXIDATION OF 4-AMINO-1,3-DIMETHYLPYRAZOLE

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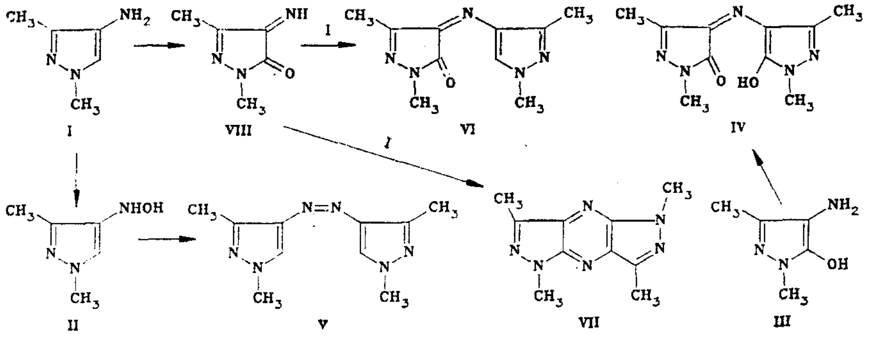
UDC 547.772.1.04:542.943

It is known that 4,5-diamino-1-methylpyrazole and 4-amino-1,3-dimethylpyrazole (I) are unstable in air [1, 2]. We found that amine I is completely oxidized in 5 days, forming, according to TLC data (Silufol U-254; chloroform-acetone, 20:1), a mixture of products. Compounds with M^+ 127, 216, 218 and 219 were recorded using the chromato-mass spectrometry. A structure of 4-hydroxylamino-(II) or 4-amino-5-hydroxy-1,3-dimethylpyrazole (III) may be ascribed to the product with M^+ 127. We synthesized compound III, and by its oxidation obtained 1,3-dimethyl-4-[(1,3-dimethyl-5-hydroxy-4-pyrazolyl)imino]pyrazol-5(1H)-one (IV). The absence of compounds III and IV, according to TLC data, in the oxidation products of amine I indicates the formation of hydroxylaminopyrazole II. The compound with M^+ 218 was not preparatively isolated, but the presence in its mass spectrum of a peak with m/z 123 makes it possible to ascribe to it the structure of 1,1',3,3'-tetramethyl-4-azopyrazole (V), in the molecular ion of which the $C_{(4)}$—N bond is cleaved by electron impact.

Compounds with M^+ 219 and 216, respectively — 1,3-dimethyl-4-[(1,3-dimethyl-4-pyrazolyl)-imino]pyrazol-5(1H)-one (VI) and 1,3,5,7-tetramethylpyrazolo[4,5-b]pyrazolo[5,4-b']pyrazine (VII) — were isolated and characterized by the data of PMR, IR and mass spectra, and electronic absorption spectra. The formation of compounds VI and VII is possibly preceded by the oxidation of amine I into 4-imino-4,5H-pyrazol-5-one (VIII), which reacts with the initial aminopyrazole I (see also [3, p. 286; 4]).



Thus, the position 5 in the molecule of 4-aminopyrazoles is the "vulnerable" one. The presence of a methyl group in it, for example, results in stability towards oxidation of 4-amino-1,5-dimethylpyrazole.

Compound IV. A 2.5 g portion of compound III [5] was reduced by hydrazine hydrate according to the method in [2]. After the separation of the catalyst, air was bubbled through the solution for 4 h at 40...50°C. The solvent was distilled off, the residue was dissolved in chloroform and 0.7 g (38%) of compound IV was isolated by TLC on a plate (silica gel 5/40, benzene), mp 195-196°C. UV spectrum (in ethanol), λ_{max}, nm (ε): 347 (12000), 446 (13400); (ethanol + NaOH): 340 (13000), 536 (11000). IR spectrum (KBr): 1636 (C=O), 1585 cm^{-1} (C=N). PMR spectrum ($CDCl_3$): 2.16 (s, 3-CH_3); 3.46 (s, 1-CH_3); 17.40 ppm (s, OH). M^+ 235.

Compound VI, mp 128...130°C, R_f 0.24. IR spectrum (in ethanol), λ_{max} nm (ε): 229 (10000), 360 (20800). IR spectrum (KBr): 1595 (C=N), 1680 cm^{-1} (C=O). PMR spectrum ($CDCl_3$): 2.20 (s, C—CH_3); 2.43 (s, C—CH_3); 3.39 (s, N—CH_3); 3.89 (s, N—CH_3); 9.05 ppm (s, 5-H).

Compound VII, mp 178...180°C, R_f 0.39. IR spectrum (in ethanol) λ_{max} nm (ε): 233 (19660), 313 (11550), 418 (4500), 427 (4400). IR spectrum (KBr): 1635 cm^{-1} (C=N). PMR spectrum ($CDCl_3$): 2.70 (s, 3- and 7-CH_3); 4.16 ppm (s, 1- and 5-CH_3).

D. I. Mendeleev Moscow Chemical Engineering Institute, Moscow 125820. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 998-999, July, 1989. Original article submitted July 4, 1988; revision submitted November 11, 1988.

0009-3122/89/2507-0838$12.50

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SYNTHESIS OF NITROGEN-CONTAINING CRYPTANDS UNDER INTERPHASE CATALYSIS CONDITIONS

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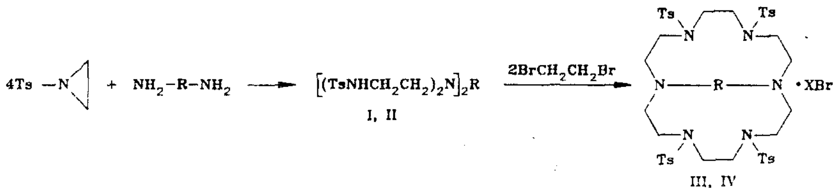
UDC 547.717'898.07:541.128

The cryptands, which are macrobicyclic compounds, have a greater selective ability to form complexes with metal ions than the monocyclic crown compounds. However, up to the present time, their synthesis remained multi-stage and complex [1].

We have developed a method for the synthesis of cryptands based on the reaction of tetrakis(tosylamidoethyl)alkylenediamines I and II with 1,2-dibromoethane under the interphase catalysis conditions.



$Ts=CH_3C_6H_4SO_2$; I, III $R=CH_2CH_2$; II, IV $R=-(CH_2)_6-$; III X=K; IV X=H

Diamines I and II were obtained by the reaction of tosylaziridine with ethylene- and hexamethylenediamines at 80°C in DMFA in a yield of 80...85% (the molar ratio of the corresponding reagents was equal to 4:1). The cyclization of diamines I and II with 1,2-dibromoethane was carried out in a chloroform—water two-phase system in the presence of 50% solution of KOH and an equimolar amount of triethylbenzylammonium chloride. The reaction proceeds at 55...60°C for 6 h. Under these conditions, diamine I reacts with 1,2-dibromoethane and forms a complex – 4,7,13,16-tetratosyl-1,4,7,10,13,16-hexaazabicyclo[8,8,2]-cosane potassium bromide (III) [yield 60%, mp 107...108°C. IR spectrum (KBr): 1590 (C_6H_4), 1320, 1130 cm^{-1} (SO_2). PMR spectrum ($CDCl_3$), ε: 2.39 (s, CH_3), 3.28 (m, CH_2N), 7.72 ppm (C_6H_4)] – while diamine II forms 4,7,13,16-tetratosyl-1,4,7,10,13,16-hexaazabicyclo[8.8.6]-tetracosane hydrobromide (IV) [yield 65%, mp 115°C. IR spectrum (KBr): 1590 (C_6H_4), 1310, 1130 cm^{-1} (SO_2). PMR spectrum ($CDCl_3$), δ: 2.39 (s, CH_3), 3.28 (m, CH_2N), 7.74 ppm (m, C_6H_4)].

The data of the elemental analysis of compounds I-IV correspond to the calculated values.

Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Irkutsk 664033. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, p. 1000, July, 1989. Original article submitted July 15, 1988; revision submitted November 15, 1988.

0009-3122/89/2507-0839$12.50