SYNTHESIS AND PROPERTIES OF AZOLES AND THEIR DERIVATIVES

XVII.* 1-(2-CYANOETHYL)-2-SUBSTITUTED 2-IMIDAZOLINES

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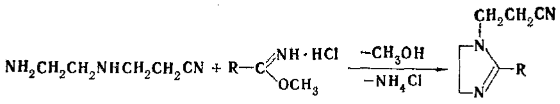
A method is proposed for the synthesis of 1-(2-cyanoethyl)-2-substituted 2-imidazolines; the method is based on reaction of N-(2-cyanoethyl)ethylenediamine with the hydrochlorides of methyl imino esters of carboxylic acids.

2-Substituted imidazolines containing a 2-cyanoethyl group in the 1 position may be of interest as intermediates for the synthesis of other functional derivatives of 2-substituted imidazolines and various heterocyclic compounds containing an imidazolyl grouping in the molecule. There recently was a communication [2] regarding the addition of some 2-alkylimidazolines to the activated double bond of acrylonitrile in the presence of ion-exchange resins. In the present research we decided to use condensation of the hydrochlorides of methyl imino esters of carboxylic acids with N-(2-cyanoethyl)ethylenediamine (I) for the preparation of 1-(2-cyanoethyl)-2-substituted imidazolines. In studying this reaction we found that 1,2-disubstituted imidazolines (IIIa-e) are formed in high yields under mild conditions.



I II a-e III a-e

II, III a $R = CH_3$; b $R = C_6H_5CH_2$; c $R = C_6H_5$; d $R = NO_2C(CH_3)_2CH_2CH_2$; e $R = CH_3C(NO_2)_2CH_2CH_2$

Compounds IIIa-e are hygroscopic, quite soluble in alcohols and methylene chloride, and insoluble in hydrocarbons and ether. They cannot be purified by vacuum distillation. Thus decomposition with the formation of 2-methyl-2-imidazoline was observed during an attempt to vacuum distill imidazoline IIIa at 100° (1 mm). Compounds IIIa-e were therefore purified with a column filled with Al_2O_3.

The IR spectra of IIIa-e contain an absorption band at 2240 cm^{-1}, which is related to the C≡N stretching vibrations, and an intense absorption band at 1605-1615 cm^{-1}, which is related to the C = N stretching vibrations [3].

EXPERIMENTAL

N-(2-Cyanoethyl)ethylenediamine (I). This compound was obtained in 70% yield by cyanoethylation of ethylenediamine (the molar ratio of ethylenediamine to acrylonitrile was 2 : 1) and had bp 97-98° (1 mm) and n_D^{20} 1.4720 [4].

1-(2-Cyanoethyl)-2-methyl-2-imidazoline (IIIa). A 5.42-g (0.05 mole) sample of methyl iminoacetate hydrochloride (IIa) [5] was added with stirring at 0° to a solution of 5.65 g (0.05 mole) of I in 25 ml of absolute methanol, and the mixture was stirred at 0° for 1 h and at 60° for 2 h. It was then cooled to 0°, and a solution of sodium methoxide (1.15 g of sodium in 20 ml of methanol) was added dropwise. The precipi-

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*See [1] for communication XVI.

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TABLE 1. 1-(2-Cyanoethyl)-2-Substituted 2-Imidazolines

Compound	Picrates									Yield, %
	mp, °C	crystallization solvent	empirical formula	found, %			calc., %			
				C	H	N	C	H	N	
IIIa	137—139	Methanol	$C_7H_{11}N_3 \cdot C_6H_3N_3O_7$	41,9	3,7	22,6	42,1	3,8	22,7	88
IIIb	98—100	Methanol	$C_{13}H_{15}N_3 \cdot C_6H_3N_3O_7$	51,0	4,1	19,2	51,3	4,1	19,0	90
IIIc	104,5—105	Cyclohexane	$C_{12}H_{13}N_3 \cdot C_6H_3N_3O_7$	72,3	6,5	20,9	72,3	6,5	21,1	92
IIId	125—125,5	Ethanol	$C_{11}H_{18}N_4O_2 \cdot C_6H_3N_3O_7$	43,3	4,8	21,0	43,7	4,8	20,9	94

tate was removed by filtration, and the filtrate was passed through a column filled with activity-II Al_2O_3. The solvent was removed by distillation, and the residual oil was vacuum-dried over KOH.

Compounds IIIb-d were similarly obtained from IIb [5], IIc [6], and IId [7], respectively. The yields of the products and the properties of their picrates are presented in Table 1.

1-(2-Cyanoethyl)-2-(3,3-dinitrobutyl)-2-imidazoline (IIIe). A 4.56-g (0.019 mole) sample of methyl 4,4-dinitroiminovalerate hydrochloride (IIe) [8] was added with stirring at 0° to a solution of 2.15 g (0.019 mole) of I in 20 ml of absolute methanol, after which the mixture was stirred at 0° for 1 h and at 40° for 2 h. It was then cooled to 0°, and a solution of 0.73 g (0.02 mole) of dry HCl in 10 ml of absolute methanol was added dropwise. The precipitate was removed by filtration, the filtrate was evaporated, and the residue was vacuum-dried. Storage in the cold for 48 h gave 4.77 g (93%) of the hydrochloride of IIIe with mp 142-143° (absolute methanol). Found: N 22.7; Cl 11.5%. $C_{10}H_{15}N_5O_4 \cdot HCl$. Calculated: N 22.9; Cl 11.6%.

LITERATURE CITED

1. G. A. Shvekhgeimer, E. V. Arslanov, and A. Baranski, Roczn. Chem., 46, 2381 (1972).
2. V. I. Isagulyants, V. I. Frolov, V. A. Tromfimov, R. I. Fedorova, and A. Yu. Adzhiev, Zh. Prikl. Khim., 48, 2120 (1970).
3. A. Bellamy, Infrared Spectra of Complex Molecules, Wiley (1958).
4. A. P. Terent'ev and A. N. Kost, Zh. Obshch. Khim., 20, 2069 (1950).
5. A. Pinner, Die Imidoather und ihre Derivate, Berlin (1892).
6. G. I. Braz, G. V. Myasnikova, A. Ya. Yakubovich, V. P. Bazov, I. E. Kardash, and A. N. Pravednikov, Khim. Geterotsikl. Soedin., 215 (1967).
7. V. P. Dukhovskoi, V. D. Tyurin, and G. A. Shvekhgeimer, Trudy Moskovsk Inst. Neftekhim. i Gazovoi Prom., Neftekhim i Neftepererabotka, 3, 12 (1969).
8. G. A. Shvekhgeimer and G. A. Mikheichev, Khim. Geterotsikl. Soedin., 678 (1971).