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Abstract

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A NEW REARRANGEMENT OF HYDRAZINE DERIVATIVES

PREPARATION OF β-DIALKYLAMINOPROPIONITRILES FROM UNSYMMETRICAL DIALKYLHYDRAZINES AND ACROLEIN

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In an attempt to synthesize the hitherto unknown unsaturated hydrazones by condensation of unsymmetrical dialkylhydrazines with acrolein, we observed a rearrangement of a new type, with formation of β-dialkylaminopropionitriles according to the scheme

$$R_2N-NH_2+CH_2=CH-CHO\rightarrow H_2O+R_2NCH_2-CH_2-C\equiv N.$$

The reaction was carried out with dimethylhydrazine ($R=CH_3$), giving β-dimethylaminopropionitrile in 68% yield, and with diethylhydrazine ($R=C_2H_5$), giving 56% yield. The new rearrangement is characterized by cleavage of the nitrogen–nitrogen bond under very mild conditions–by simple mixing of the reagents in the cold in a weakly acidic medium (addition of acrolein to aqueous solutions of hydrazine salts*).

Rearrangements with cleavage of nitrogen–nitrogen bonds and formation of new nitrogen–carbon bonds, among which the reaction discovered by us belongs, have until now been observed only in the aromatic series (benzidine and semidine rearrangements, conversion of diazoamino compounds into aminoazo compounds, conversions of nitrosamines and nitroamines into C-nitroso and C-nitro compounds, etc.).

Apparently, the reaction with acrolein proceeds through the stage of formation of unsaturated hydrazones $CH_2=CH-CH=N-NR_2$, which in a weakly acidic medium immediately rearrange into aminonitriles. The only known case of formation of nitriles from hydrazine derivatives is the catalytic decomposition of aldehyde phenylhydrazones into nitriles and aniline, discovered by A. E. Arbuzov ([1]), occurring at temperatures of about 200° in the presence of cuprous chloride, i.e., under much harsher conditions.

The β-dialkylaminopropionitriles formed in our case from dialkylhydrazines and acrolein had previously been synthesized by cyanoethylation of secondary amines and are of interest as starting substances for obtaining physiologically active preparations and detergents. For more reliable identification of the products of the reaction described, independent syntheses of β-dimethylaminopropionitrile, β-diethylaminopropionitrile, and a number of their derivatives from acrylonitrile were carried out ([2,3]).

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* In an alkaline medium (when acrolein is added to free dimethylhydrazine), a water-soluble high-molecular-weight substance is formed, which has not yet been investigated further. In a reverse order of mixing the reagents (introduction of dimethylhydrazine into acrolein), a violent explosion occurred, probably as a result of spontaneous polymerization of acrolein.

Experimental Part

Reaction of acrolein with unsymmetrical dimethylhydrazine. 60 g (1 mole) of $(CH_3)_2NNH_2$ (b.p. 62.4–64.0° at 765 mm; $d_4^{20}0.7911; n_D^{20}1.4088$) was added to a cooled solution of 156 g (1 mole) of $NaH_2PO_4 \cdot H_2O$ (chemically pure) in 300 ml of distilled water. To the resulting suspension of small salt crystals, freshly distilled pure acrolein (56 g), stabilized with hydroquinone, was added dropwise over 25 min with ice cooling and constant shaking. After 20 min had elapsed, 120 g of solid caustic potash was gradually added to the reaction mixture. The separated orange organic layer (90 g after drying with solid potassium carbonate and alkali) was distilled on a Vigreux vacuum column with an efficiency of 12 theoretical plates.

The main fraction, b.p. 71.8–72.0° at 20 mm Hg (171–171.5° at 758 mm), was pure β-dimethylaminopropionitrile; yield 67 g (68% of theoretical).

Found, %: C 60.98; 61.11; H 10.30; 10.46; N 28.70; 28.29
$C_5H_{10}N_2$. Calculated, %: C 61.19; H 10.27; N 28.54

Molecular weight (cryoscopically in benzene) 67.5; 98.3; calculated for $C_5H_{10}N_2$ 98.15. Equivalent weight (by titration with 0.1 N HCl with bromophenol blue) 98.25. Calculated for $C_5H_{10}N_2$ 98.15. $d_4^{20}0.8696; n_D^{20}1.4269; n_C^{20}1.4242; \Delta_{FC}86.0; \omega_{FCD}20.17. MR_D$ found 28.98; calculated 28.88 (by Fogel)[3].

An authentic specimen of β-dimethylaminopropionitrile, obtained from dimethylamine and acrylonitrile ([3]), had b.p. 71.8° at 20 mm; $d_4^{20}0.8704; n_D^{20}1.4264; n_C^{20}1.4240; \Delta_{FC}85.2$.

Literature data: b.p. 68° at 18 mm ([10]), 171° at 750 mm ([3]); $d_4^{20}0.8705$ ([3]); $n_D^{20}1.4283$ ([3]).

The melting points of the picrates, hydrochlorides, and iodomethylates of samples of β-dimethylaminopropionitrile synthesized from acrolein and from acrylonitrile practically coincided (see Table 1), and their mixtures showed no melting-point depression.

By saponifying 2.5 g of the substance by boiling with 6.3 g of conc. HCl for 14 hr, 1.2 g (98%) of ammonium chloride and 3.7 g of the hydrochloride of NN-dimethyl-β-alanine were obtained, which after recrystallization from alcohol had m.p. 180–181°. Literature data: m.p. 180.5–182.5° ([4]); 191–192° ([5]).

Equivalent weight (by titration of an alcoholic solution with 0.1 N alcoholic KOH, using phenolphthalein) 80.0; calculated for $(CH_3)_2NCH_2CH_2COOH \cdot HCl$ 78.65.

An authentic specimen of dimethyl-β-alanine hydrochloride prepared analogously from acrylonitrile had m.p. 180–181° and showed no melting-point depression in a mixture with the product obtained from dimethylhydrazine.

Reaction of acrolein with unsymmetrical diethylhydrazine. From 45 g (0.5 mole) of 98% diethylhydrazine ([6]), 78 g of $NaH_2PO_4 \cdot 2H_2O$ in 300 ml of water, and 28 g (0.5 mole) of acrolein, according to the procedure described above, 34.8 g (56%) of β-diethylaminopropionitrile was obtained, b.p. 74.5–75.2° at 9 mm.

Found, %: C 66.49; 66.55; H 11.16; 11.21; N 21.90; 21.97
$C_7H_{14}N_2$. Calculated, %: C 66.62; H 11.18; N 22.20

Equivalent weight (by titration with 0.1 N HCl) 126.6; 126.4; calculated 126.2; $d_4^{20}0.8650; n_D^{20}1.4359; n_C^{20}1.4335; \Delta_{FC}86.1; \omega_{FCD}19.75. MR_D$ found 38.14; calculated 38.18.

The authentic preparation of β-diethylaminopropionitrile, obtained by us by the action of acrylonitrile on diethylamine ([3]), had b.p. 75.2° at 9 mm; d_4^{20} 0.8649; n_D^{20} 1.4355; n_C^{20} 1.4331; ΔF_C 85.0.

Literature data: b.p. 76° at 9 mm ([3]), 76° at 11 mm ([9]), 83.5–84.5° at 13 mm ([7]), 196° at 735 mm ([8]); d_4^{20} 0.8761 ([3,7]), 0.8659 ([9]); n_D^{20} 1.4380 ([3]), 1.4343 ([7]), 1.4356 ([8]), 1.4354 ([9]).

The derivatives of the product of the condensation of acrolein with diethylhydrazine are identical with the analogous derivatives of β-diethylaminopropionitrile (see Table 1) and show no depression of the melting point when mixed with the latter.

Table 1

Melting points of derivatives of β-dimethylamino- and β-diethylaminopropionitriles*

Derivatives	Preparation obtained from the product of the reaction of acrolein with dialkylhydrazine	Authentic preparation (from acrylonitrile)	Literature data
Derivatives of β-dimethylaminopropionitrile			
Picrate	150–151°	150–151°	151° ([2,3])
Hydrochloride	197–198°	201–202°	199° ([2,3])
Iodomethylate	153°	153–154°	152° ([3])
Derivatives of β-diethylaminopropionitrile			
Picrate	84–85°	83–84°	85° ([3,8])
Hydrochloride	119–121°	122–123°	120° ([3])
Iodomethylate	155–156°	155–156°	152° ([3])

* For methods of obtaining the derivatives, see ([3]).

Upon saponification of 6.3 g of the substance by boiling for 12 h with 11.5 g of conc. HCl, 1.78 g of ammonium chloride* and 9.43 g of the hydrochloride of the amino acid were obtained. After recrystallization from alcohol, the salt had m.p. 135–138° and gave no depression of the melting point in a mixture with hydrochloric-acid NN-diethyl-β-alanine (m.p. 137–139°), synthesized from acrylonitrile through β-diethylaminopropionitrile.

Equivalent weight (by titration with alcoholic caustic potash) 91.2, calculated for $(C_2H_5)_2NCH_2CH_2COOH \cdot HCl$ 90.75.

Literature data for hydrochloric-acid NN-diethyl-β-alanine: m.p. 136–138° ([5]).

Infrared spectra of the products of the condensation of acrolein with dialkylhydrazines confirm their identity with authentic preparations of the corresponding dialkylaminopropionitriles. The spectra were recorded on an automatic double-beam infrared spectrophotometer UR-10 (Zeiss, Jena) in the region from 4000 to 650 cm^{-1} with a layer thickness of 25 μ.** In the spectra there are strong absorption bands at 2247 cm^{-1}, characteristic of nitrile groups, and there are no characteristic frequencies of double bonds $C = C$, $C = O$, and $C = N$. The "fingerprint" region in the dimethyl and diethyl derivatives is very rich in bands

* Identified by qualitative reactions and determination of the chloride ion.

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differ sharply, whereas for authentic β-dialkylaminopropionitriles and the corresponding products of the rearrangement under study they coincide completely.

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Note: Figure translations are in progress. See original paper for figures.