NEW HETEROCYCLIC COMPOUNDS CONTAINING TWO PYRAZOLIDONE RINGS

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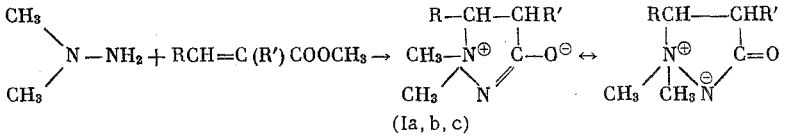
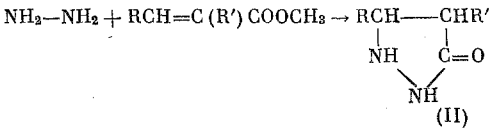
It was shown earlier [1, 2] that cyclic compounds, 1, 1-dimethylpyrazolinium-3-oxides (I), are formed upon reaction of derivatives of α,β-unsaturated acids, for example, their esters, with N, N-dimethylhydrazine



(Ia, b, c)

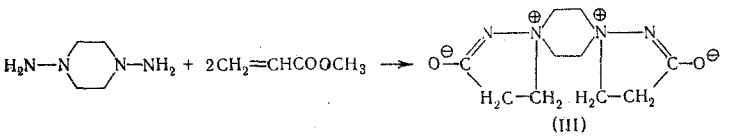
a R=R′=H; b R=H, R′=CH$_3$; c R=CH$_3$, R′=H

There are also many examples in the literature of obtaining pyrazolidones-3 during reactions of α,β-unsaturated acid derivatives with unsaturated hydrazines [3-7]



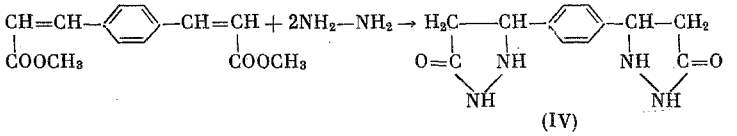
(II)

It could be proposed that compounds containing two pyrazolidone rings in the molecule would be obtained in reactions, for example, of alkylenedihydrazines with methyl acrylate or of hydrazine with di-unsaturated dicarboxylic acids. In fact, we have obtained compound (III) by condensation of N, N′-diamino-piperazine with 2 moles of methyl acrylate



(III)

p-Phenylene-bis-(5-pyrazolidone-3) (IV) was isolated and characterized from the reaction of the methyl ester of 4, 4-phenylenediacrylic acid (p-PhDAA) with hydrazine



(IV)

It should be noted the structure of p-PhDAA hydrazide was earlier assigned to this compound [8].

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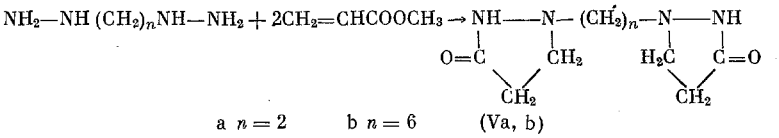
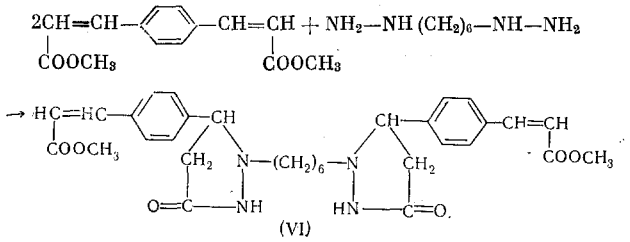
1,2-Dimethylene-bis-(1-pyrazolidone-3) (Va) and 1,6-hexamethylene-bis-(1-pyrazolidone-3) (Vb) were obtained as a result of condensation of alkylenedihydrazines with 2 moles of methyl acrylate.



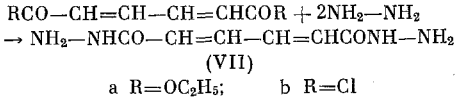
a $n=2$ b $n=6$ (Va, b)

In addition, the analogous compound (VI) with substituents in positions 5, 5' of the pyrazolidone rings was obtained from one molecule of hexamethylenedihydrazine and 2 moles of the dimethyl ester of p-PhDAA



(VI)

All of the compounds (III)-(VI) obtained for the first time were characterized by melting points, solubility, and elemental analysis. Their structure was confirmed by IR spectra. However, pyrazolidone rings could not be obtained upon reaction of the ethyl ester or acid chloride of muconic acid with hydrazine hydrate. In these cases as the reaction product was isolated the dihydrazide of muconic acid (VII), which is similar in its properties to those described in the literature [9]



(VII)

a $R=OC_2H_5$; b $R=Cl$

A reaction does not occur of the dimethyl ester of p-PhDAA or of ethyl muconate with asymmetric dimethylhydrazine (DMH). With the acid chlorides of these same acids their dimethylhydrazides were obtained for the first time.

The structure of the synthesized compounds (bispyrazolidones) makes it possible to propose that polymers having heterocycles in the chain can be obtained upon carrying out reactions between dihydrazines and diunsaturated dicarboxylic acids. Investigation in this direction is being continued.

EXPERIMENTAL

Preparation of Diethylene-bis-(1-pyrazolinium-3-oxide) (III). A solution of 1.74 g of N,N'-diaminopiperazine in 20 ml of water was stirred with 2.58 g of methyl acrylate until the layers disappeared. After standing for 6 h the water was distilled in vacuum and the dry residue was recrystallized from absolute C_2H_5OH, mp 198-200°C. Found: C 53.47; 53.35; H 8.32; 8.29%; mol. wt. 222 (cryoscopically in water). $C_{10}H_{16}N_4O_2$. Calculated: C 53.57; H 7.14%; mol.wt. 224. The IR spectrum taken for (III) as a KBr tablet was unclear evidently due to adduct formation with KBr. An absorption band at 1590 cm^{-1}, indicating the presence of the $-N=\underset{|}{C}-O^{\ominus}$ grouping characteristic for the pyrazolinium-oxide ring [2, 10] and aminoimides [11], was observed in the IR spectrum of (III) in D_2O. The band of stretching vibrations of the C=C bond was absent. The IR spectrum was basically similar to the spectrum of compound (Ia).

Preparation of p-Phenylene-bis-(5-pyrazolidone-3) (IV). We heated 0.016 mole of the dimethyl ester of p-phenylenediacrylic acid and 0.078 mole of hydrazine in a solution of absolute C_2H_5OH on a boiling water bath for 8 h. Isolated and purified (IV) has mp 260° (with dec.). Literature data [8]: mp 258-260° (with dec.). Found: N 22.80; 22.90%. $C_{12}H_{14}N_4O_2$. Calculated: N 22.76%. The authors [8] assigned the structure of p-phenylenediacrylic acid dihydrazide to this compound. The IR spectrum confirms structure (IV). It contains an absorption band at 1670 cm^{-1} (C=O) and also a band of associated hydrogen bonds of the NH group at 3180 cm^{-1}. The absorption band characteristic for stretching vibrations of the C=C group is absent.

Preparation of 1, 2-Dimethylene-bis-(1-pyrazolidone-3) (Va). To a cooled methanol solution of ethylenedihydrazine (0.014 mole), separated from its HCl salt by distillation over solid base, was added 0.028 mole of a solution of methyl acrylate in absolute CH_3OH. Heat evolution was observed upon pouring the solutions together. After standing for several days the solvent was distilled. Compound (Va) was separated from the thick syrup by precipitation from its methanol solution with ether or acetone, mp 169-170° (benzene and alcohol mixture). Compound (Va) is soluble in water and alcohol and insoluble in benzene, acetone, ether. Found: C 48.20; 48.22; H 7.39; 7.57; N 28.12%. $C_8H_{14}N_4O_2$. Calculated: C 48.48; H 7.07; N 28.28%. The IR spectrum contains bands at 1678 cm^{-1} (C=O) and 3195 cm^{-1} (NH). Absorption bands of C=C bonds are not observed.

Preparation of 1, 6-Hexamethylene-bis-(1-pyrazolidone-3) (Vb). Strong heat evolution was observed upon carefully pouring together a solution of hexamethylenedihydrazine (0.9 g) in methanol with 2 ml of methyl acrylate in 10 ml of CH_3OH. After standing for several days in the dark the reaction product was isolated by precipitation with ether; mp 115-116° (acetone). Compound (Vb) is soluble in water, alcohol, benzene; insoluble in ether, cold acetone, $CHCl_3$. Found: C 57.19; 57.14; H 9.09; 9.13; N 22.54; 22.70%. $C_{12}H_{22}N_4O_2$. Calculated: C 56.68; H 8.66; N 22.04%. The IR spectrum confirmed the presence in compound (Vb) of the C=O group (1700 cm^{-1}) and NH group (3200 cm^{-1}). The absorption band of the C=C group was absent. The IR spectrum of (Vb) is similar to that of (Va).

Preparation of the Methyl Ester of 1, 6-Hexamethylene-bis-(1-pyrazolidone-5-p-phenylacrylic Acid) (VI). We heated 0.0147 mole of hexamethylenedihydrazine and 0.0294 mole of p-phenylenediacrylic acid in dimethylformamide at 120° for 12 h. A product was isolated having mp 187-191° and insoluble in the usual organic solvents. Found: C 66.63; 66.65; H 6.95; 6.80; N 9.35; 9.24%. $C_{32}H_{38}N_4O_6$. Calculated: C 66.89; H 6.62; N 9.75%. The IR spectrum contained absorption bands at 3200 cm^{-1} (NH...), 1680 cm^{-1} (C=O), 1730 cm^{-1} ($COOCH_3$), 1665 cm^{-1} (C=C).

Dimethylhydrazide of p-PhDAA. This compound was obtained upon reaction of the acid chloride of p-PhDAA with excess DMH: mp 280-285° (subl.). Found: C 63.21; 63.36; H 7.48; 7.46; N 19.72; 19.34%. $C_6H_{22}N_4O_2$. Calculated: C 63.57; H 7.25; N 18.54%. The absorption band of stretching vibrations of the C=C bond (1645 cm^{-1}) was absent in the IR spectrum.

Dihydrazide of Muconic Acid. The compound was obtained by heating for 8 h the diethyl ester (or acid chloride) of the acid (0.005 mole) in alcohol solution with excess hydrazine hydrate. A product with mp 280-285° (dec.) was isolated after distillation of the solvent and excess hydrazine. Literature data [9]: mp 274°. The IR spectrum contained absorption bands at 1610 (C=C), 3320 cm^{-1} (NH_2), 3200 cm^{-1} (NH...), and 1630 cm^{-1} (C=O).

Dimethylhydrazide of Muconic Acid. This compound was obtained by heating the acid chloride with excess DMH in ether solution. After removal of the solvent and excess DMH the product had mp 245-250° (dec.). Found: N 24.90; 24.79%. $C_{10}H_{18}O_2N_4$. Calculated: N 24.77%. The IR spectrum contained absorption bands at 1615 cm^{-1} (C=C), 3240 cm^{-1} (NH ...), 1640 cm^{-1} (C=O).

Synthesis of Starting Compounds. N, N'-Diaminopiperazine was obtained by nitrosation of piperazine according to Ladenburg [12] and reduction of the obtained nitroso compound according to Ioffe [13]. Isolation of the base from its HCl salt was accomplished by distillation over KOH [14]. The melting point of the anhydrous base was 118-119°. Literature data [14]: mp ~100°. Melting point of the crystallohydrate was 72° ($C_4H_{12}N_4 \cdot 2H_2O$).

The methyl ester and acid chloride of 4, 4'-phenylenediacrylic acid were obtained according to Ruggli and Theilheimer [8]. The methyl ester of p-PhDAA had mp 167-168° (literature data [8]: 168°). The methyl ester and acid chloride of muconic acid were obtained according to [15]. Alkylenedihydrazines were obtained by hydrolysis of the corresponding bissydnones according to Zapevalova et al. [16].

CONCLUSIONS

1. Five heterocyclic compounds have been obtained for the first time and characterized: diethylene-bis-(1-pyrazolinium-3-oxide) (III); p-phenylene-bis-(5-pyrazolidone-3) (IV); 1,2-dimethylene-bis-(1-pyrazolidone-3) (Va); 1,6-hexamethylene-bis-(1-pyrazolidone-3) (Vb); methyl ester of 1,6-methylene-bis-(1-pyrazolidone-3)-5-p-phenyleneacrylic acid (VI), and also the dimethylhydrazides of p-phenylenediacrylic and muconic acids.

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