SYNTHESIS AND PROPERTIES OF AZOLES AND THEIR DERIVATIVES

XXI.* 1,5-BISHETERYL-3,3-DINITROPENTANES

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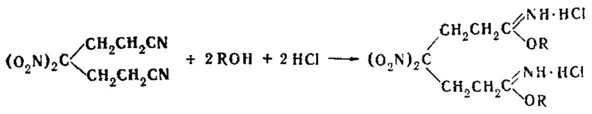
Dihydrochlorides of diimino esters of 4,4-dinitropimelic acid are formed from 4,4-dinitropimelic acid dinitrile and alcohols in the presence of hydrogen chloride. The dihydrochloride of the methyl diimino ester condenses with ethylenediamine, o-phenylenediamine, and o-aminophenol to give the corresponding 1,5-bisheteryl-3,3-dinitropentanes.

Diimino ester dihydrochlorides II-V are obtained in 84-100% yields when dry hydrogen chloride is bubbled through a solution of 4,4-dinitropimelic acid dinitrile (I) and the appropriate alcohol (molar ratio 1:2) in absolute dioxane:



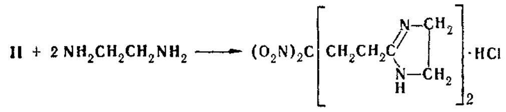
$$(O_2N)_2C\begin{array}{l} CH_2CH_2CN \\ CH_2CH_2CN \end{array} + 2ROH + 2HCl \longrightarrow (O_2N)_2C\begin{array}{l} CH_2CH_2C\begin{array}{l} \!\!=NH\cdot HCl \\ -OR \end{array} \\ CH_2CH_2C\begin{array}{l} \!\!=NH\cdot HCl \\ -OR \end{array} \end{array}$$

II-V

II $R=CH_3$; III $R=C_2H_5$; IV $R=HC=CH_2$; V $R=CH_2CH_2NO_2$

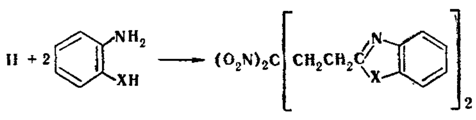
Reactions characteristic for imino ester salts were realized for the dihydrochlorides obtained in this study: II and III were hydrolyzed to dimethyl and diethyl 4,4-dinitropimelates, respectively, and salt II was converted to the diamide by heating and to the dimethyl diimino ester of 4,4-dinitropimelic acid (VI) by treatment with aqueous potassium carbonate solution. Reaction of VI with ammonium chloride gave 4,4-dinitropimelic acid diamidine dihydrochloride.

Salt II readily condenses with ethylenediamine to give 1,5-bis(1',3'-imidazolin-2'-yl)3,3-dinitropentane (VII):



VII

Salt II reacts smoothly with o-phenylenediamine and o-aminophenol to give high yields of the corresponding 3,3-dinitropentanes containing benzimidazolyl or benzoxazolyl groupings in the 1 and 5 positions (VIII and IX):



VIII X=NH; IX X=O

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*See [1] for communication XX.

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EXPERIMENTAL

The IR spectra were recorded with a UR-10 spectrometer. The UV spectra of n-heptane solutions were recorded with a Unicam SP800A spectrophotometer. The individuality of the products was monitored by thin-layer chromatography (TLC) on activity I aluminum oxide [benzene – methanol (12 : 1) for VIII, and benzene – methanol (9 : 1) for IX; the chromatograms were developed with iodine vapors].

4,4-Dinitropimelic Acid Diimino Ester Dihydrochlorides (II-V). The reaction was carried out without access to moisture. Dry hydrogen chloride was bubbled with stirring at 0-5° through a solution of 0.05 mole of nitrile I and 0.1 mole of the appropriate alcohol in 60 ml of absolute dioxane until the solution became saturated, after which the mixture was allowed to stand overnight at 0-5°. It was then held under vacuum to remove the dissolved hydrogen chloride, after which 150 ml of absolute ether was added. The resulting precipitate was removed by filtration and washed with absolute ether until the excess hydrogen chloride had been completely removed. The product was precipitated from glacial acetic acid solution by the addition of absolute ether to give II with mp 102-103° in 100% yield. Found: Cl 20.0%. $C_9H_{18}N_4O_6Cl_2$. Calculated: Cl 20.3%.

Compound III, with mp 99-100°, was obtained in 99.5% yield. Found: Cl 18.7%. $C_{11}H_{22}N_4O_6Cl_2$. Calculated: Cl 18.8%.

Product III, with mp 109-110°, was obtained in 84% yield. Found: Cl 17.7%. $C_{13}H_{18}N_4O_6Cl_2$. Calculated: Cl 17.9%.

Compound V, with mp 93-95°, was obtained in 93% yield. Found: Cl 15.2%. $C_{11}H_{20}N_6O_{10}Cl_2$. Calculated: Cl 15.2%.

4,4-Dinitropimelic Acid Dimethyl Diimino Ester (VI). A total of 7 ml of 33% aqueous potassium carbonate solution was added rapidly with vigorous stirring at 0-5° to a suspension of 6.98 g (20 mmole) of salt II in 80 ml of ether, after which the ether layer was immediately separated, and the aqueous layer was extracted with three 25-ml portions of ether. The ether layer and the extracts were combined and dried with magnesium sulfate at 0°C. The ether was removed by distillation to give 5.2 g (94%) of VI as a colorless undistillable oil. IR spectrum: 1620 (C =N), 3330 (N – H), 1320 and 1590 cm^{-1} [$C(NO_2)_2$].

Starting salt II was recovered in quantitative yield when dry hydrogen chloride was bubbled through a solution of VI in absolute ether at 0°C.

Diethyl 4,4-Dinitropimelate. Water (5 ml) was added to a suspension of 7.54 g (20 mmole) of salt III in 50 ml of ether, and the mixture was stirred at room temperature for 3 h. The aqueous layer was extracted with three 25-ml portions of ether, and the ether layer and extracts were combined and dried with magnesium sulfate. The ether was removed by distillation, and the residue was fractionated in a stream of nitrogen to give 3.86 g (63%) of diethyl 4,4-dinitropimelate with bp 174-175° (2 mm), n_D^{20} 1.4604, and d_4^{20} 1.2695. Found: C 43.4; H 5.9; N 9.4%. $C_{11}H_{18}N_2O_8$. Calculated: C 43.1; H 5.9; N 9.1%. IR spectrum: 1740 (C =O), 1310 and 1575 cm^{-1} [$C(NO_2)_2$].

Dimethyl 4,4-Dinitropimelate. This compound, with mp 44° (from methanol) [2], was obtained in 90% yield from salt II by the method used to prepare the diethyl ester.

4,4-Dinitropimelic Acid Diamide. A 0.87-g (2.5 mmole) sample of salt II was heated at 85-90° until methyl chloride evolution ceased. The reaction mixture was cooled, washed with ether, and dried to give 6.1 g (98%) of 4,4-dinitropimelic acid diamide with mp 97.5-98° (from propanol). Found: C 33.6; H 4.9; N 22.2%. $C_{17}H_{12}N_4O_6$. Calculated: C 33.9; H 4.8; N 22.6%. IR spectrum: 1690 (C =O), 1330 and 1585 cm^{-1} [$C(NO_2)_2$].

4,4-Dinitropimelic Acid Diamidine Dihydrochloride. A 1.07-g (20 mmole) sample of ammonium chloride was added to a solution of 2.76 g (10 mmole) of ester VI in 30 ml of absolute methanol, and the mixture was stirred at room temperature until it became homogeneous, after which it was stirred for another 2 h. It was then evaporated in vacuo to dryness, and the residue was extracted with ether. The ether extracts were discarded. The solid phase was then extracted with glacial acetic acid, and the extract was diluted with three volumes of absolute ether and worked up to give 2.97 g (93%) of 4,4-dinitropimelic acid diamidine dihydrochloride with mp 94-95°. Found: C 26.1; H 5.1; Cl 21.9; N 19.9%. $C_7H_{16}Cl_2N_6O$ Calculated: C 26.3; H 5.0; Cl 22.2; N 20.0%.

1,5-Bis(1',3'-imidazolin-2'-yl)-3,3-dinitropentane (VII). A 3.49-g (10 mmole) sample of salt II was added with stirring at 0° in the course of 30 min to a solution of 1.2 g (20 mmole) of ethylenediamine in 50 ml of absolute methanol, after which the mixture was stirred at 40-50° for 2 h. It was then cooled, and 0.73 g (20 mmole) of hydrogen chloride in 50 ml of absolute methanol was added dropwise. The solution was then evaporated to 50 ml and filtered, and the filtrate was evaporated to dryness to give 3.62 g (97%) of VII with mp 58-60° (from alcohol). Found: C 35.5; H 5.5; N 22.8%. $C_{11}H_{20}Cl_2N_6O_4$. Calculated: C 35.6; H 5.4; N 22.6%. IR spectrum: 1300 and 1610 cm^{-1} [$C(NO_2)_2$].

1,5-Bis(2'-benzimidazolyl)-3,3-dinitropentane (VIII). A mixture of 3.49 g (10 mmole) of salt II and 2.16 g (20 mmole) of o-phenylenediamine in 60 ml of absolute methanol was stirred in 200 ml of cold water containing 1.38 g (10 mmole) of potassium carbonate. The mixture was extracted with five 50-ml portions of ether, and the ether extracts were washed with water and dried with magnesium sulfate. The ether was removed by distillation to give 3.35 g (85%) of VIII with mp 125° (from propyl alcohol). Found: C 57.5; H 4.8; N 20.9%. $C_{19}H_{18}N_6O_4$. Calculated: C 57.8; H 4.6; N 21.3%. IR spectrum: 755, 870, 940, 1030, 1475 (benzimidazole ring); 1325 and 1605 cm^{-1} [$C(NO_2)_2$]. Several narrow bands that are characteristic for substituted benzenes are observed in the UV spectra at ~275 nm, and there is a broad band at 250 nm.

1,5-Bis(2'-benzoxazolyl)-3,3-dinitropenetane (IX). A mixture of 6.98 g (20 mmole) of salt II and 4.36 g (40 mmole) of o-aminophenol in 120 ml of absolute methanol was stirred at 50° for 1 h, after which the cooled reaction mixture was poured with stirring into 300 ml of cold water. The resulting precipitate was removed by filtration, washed with water, and dried to give 7.44 g (94%) of IX with mp 108-109° (from benzene–petroleum ether). Found: C 57.3; H 4.8; N 14.0%. $C_{19}H_{16}N_4O_6$. Calculated: C 57.6; H 4.0; N 14.1%. IR spectrum: 760, 805, 845, 945, 1000, 1150, 1300, 1465 (benzoxazole ring); 1330 and 1575 cm^{-1} [$C(NO_2)_2$]. Several narrow bands that are characteristic for substituted benzenes are observed in the UV spectrum at λ_{max} 275, and there is also a more intense and broader band with a maximum at 233 nm.

LITERATURE CITED

1. G. A. Mikheichev, Petroleum and Gas and Their Products [in Russian], Moscow (1971), p. 168.
2. Z. Herzog, M. H. Gold, and R. D. Geckler, J. Amer. Chem. Soc., 73, 749 (1951).