SYNTHESIS AND PROPERTIES OF AZOLES AND THEIR DERIVATIVES

VI.* HETEROCYCLIC COMPOUNDS CONTAINING γ,γ-DINITROBUTYL RADICALS

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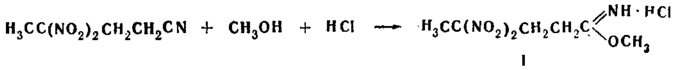
The reaction of 4,4-dinitrovaleronitrile with hydrogen chloride and methanol gives the hydrochloride of the methyl imino ester of 4,4-dinitrovaleric acid. The latter is converted to the free imino ester, amide, and methyl ester of 4,4-dinitrovaleric acid. The same hydrochloride readily condenses with ethylenediamine, o-phenylenediamine, or o-aminophenol to give, respectively, imidazoline, benzimidazole, or benzoxazole, which contain a γ,γ-dinitrobutyl radical in the 2-position. The methyl imino ester of 4,4-dinitrovaleric acid is rapidly converted to 2,4,6-tris(γ,γ-dinitrobutyl)-1,3,5-triazine at room temperature.

In developing our studies of the synthesis and transformations of nitroalkyl-substituted heterocyclic compounds, we have investigated the use of 4,4-dinitrovaleronitrile as the starting compound for this purpose. It was found that this nitrile readily reacts with methanol and hydrogen chloride in ether to give 98% of the hydrochloride of the methyl imino ester of 4,4-dinitrovaleric acid (I).

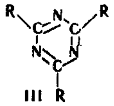


$$H_3CC(NO_2)_2CH_2CH_2CN + CH_3OH + HCl \longrightarrow H_3CC(NO_2)_2CH_2CH_2C\begin{cases}NH\cdot HCl\\ OCH_3\end{cases}$$

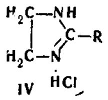
I

The structure of I was confirmed by reactions characteristic for imino ester hydrochlorides: it was hydrolyzed to methyl 4,4-dinitrovalerate, converted to the amide of the same acid by the Pinner rearrangement and, by treatment with triethylamine, converted to the free imino ester (II), a rather unstable compound which is converted rapidly to the corresponding triazine (III) at room temperature. The latter was also obtained in high yield by heating II with a catalytic amount of I.

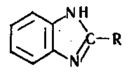
Heating I with ethylenediamine in alcohol gives the hydrochloride of the corresponding imidazoline (IV). The corresponding benzimidazole (V) and benzoxazole (VI) are obtained in even higher yields by brief heating of I with o-phenylenediamine or o-aminophenol in methanol. The structures of IV-VI were confirmed by their IR spectra from 500 to 3500 cm^{-1}.



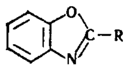
III



IV



V



VI

R = $CH_2CH_2C(NO_2)_2CH_3$

EXPERIMENTAL

Hydrochloride of the Methyl Imino Ester of 4,4-Dinitrovaleric Acid (I). Dry hydrogen chloride was passed with vigorous stirring at −5 to 0° through a solution of 8.65 g (0.05 mole) of 4,4-dinitrovaleronitrile and 1.6 g (0.05 mole) of absolute methanol in 50 ml of absolute ether until the solution was saturated. The precipitate was filtered without access to moisture and washed with absolute ether until the chloride ions were removed to give 11.95 g (98%) f I with mp 110° (by precipitation from glacial acetic acid with absolute ether). Found %: Cl 14.9. $C_6H_{12}N_3O_5Cl$. Calculated %: 14.7.

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*See [1] for communication V.

I. M. Gubkin Moscow Institute of the Petrochemical and Gas Industry. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 698-699, May, 1971. Original article submitted February 27, 1970.

Methyl 4,4-Dinitrovalerate. Water (5 ml) was added to a suspension of 7.26 g (0.03 mole) of I and 40 ml of ether, and the mixture was stirred at room temperature for 2 h. The ether layer was then removed, and the aqueous layer was extracted with ether. The ether layer and the ether extracts were combined, dried with $MgSO_4$, and fractionated in a nitrogen stream to give 5.22 g (84%) of methyl 4,4-dinitrovalerate with bp 125-127° (4 mm) and n_D^{20} 1.4554 [2].

4,4-Dinitrovaleramide. Compound I [2.42 g (0.01 mole)] was heated to the melting point, during which decomposition with methyl chloride evolution was observed. When the frothing had ceased, the temperature was raised to 115-120°, and the mixture was held at this temperature for 10 min. The reaction product was extracted with hot benzene, and the extracts were evaporated to dryness to give 1.63 g (91%) of 4,4-dinitrovaleramide with mp 76° [from cyclohexane–benzene (3 : 7)]. Found %: C 31.4; H 4.7; N 21.1. $C_5H_9N_3O_7$. Calculated %: C 31.4; H 4.8; N 21.9.

Methyl Imino Ester of 4,4-Dinitrovaleric Acid (II). A mixture of 7.26 g (0.03 mole) of I and 3.04 g (0.03 mole) of triethylamine in 50 ml of ether was stirred vigorously for 1.5 h, the precipitate was filtered and washed with ether, and the ether was removed by distillation to give 5.85 g (95%) of II with bp 112-114° (1.5 mm). The imino ester was rapidly converted to III on standing.

2,4,6-Tris(γ,γ-dinitrobutyl)-1,3,5-triazine (III). A mixture of 2.57 g (0.0125 mole) of II and 0.08 g (0.0003 mole) of I was heated at 140° for 2 h, cooled, and extracted with hot benzene to give 2.15 g (84%) of III with mp 79-80° (from petroleum ether). Found %: C 34.6; H 4.6; N 24.3. $C_{15}H_{21}N_9O_{12}$. Calculated %: C 34.7; H 4.1; N 24.3. IR spectrum: 1560, 1570, 1410, 1250, 800 (triazine ring); 1595; 1330 cm^{-1} $C(NO_2)_2$.

2-(γ,γ-Dinitrobutyl)-2-imidazoline Hydrochloride (IV). A mixture of 2.42 g (0.01 mole) and 0.6 g (0.01 mole) of ethylenediamine in 25 ml of absolute alcohol was refluxed for 1.5 h, cooled to 0°, and 15 ml of absolute alcohol containing 0.7 g of hydrogen chloride was added. The resulting precipitate was filtered, and the filtrate was evaporated to dryness to give 2.17 g (86%) of IV with mp 173° (decomp.). Found %: C 33.2; H 5.3; N 22.2; Cl 14.3. $C_7H_{13}N_4O_4Cl$. Calculated %: C 33.3; H 5.2; N 22.2; Cl 14.3. IR spectrum: 1600 and 1320 cm^{-1} [$C(NO_2)_2$].

2-(γ,γ-Dinitrobutyl)benzimidazole (V). A mixture of 2.42 g (0.01 mole) of I and 1.08 g (0.01 mole) of o-phenylenediamine in 25 ml of absolute methanol was refluxed for 1 h, cooled, and 50 ml of cold water containing 1 g (0.01 mole) of sodium carbonate was added. The precipitate was washed with cold water to give 2.46 g (96%) of V with mp 191-193° (decomp., from benzene). Found %: C 50.2; H 4.7; N 20.8. $C_{11}H_{12}N_4O_4$. Calculated %: C 50.0; H 4.6; N 21.0. IR spectrum: 1480, 1000, 1020, 980, 875, 735 (benzimidazole ring); 1620 and 1325 cm^{-1} [$C(NO_2)_2$].

2-(γ,γ-Dinitrobutyl)benzoxazole (VI). A mixture of 2.42 g (0.01 mole) of I and 1.09 g (0.01 mole) of o-aminophenol in 25 ml of absolute methanol was refluxed for 1 h, cooled, 50 ml of water containing 1 g of sodium carbonate was added, and the mixture was extracted with ether. The ether extracts were dried over $MgSO_4$ and evaporated to dryness to give 2.45 g (95%) of VI with mp 50-51° (from petroleum ether). Found %: C 49.6; H 4.3; N 15.6. $C_{11}H_{12}N_3O_5$. Calculated %: C 49.8; H 4.2; N 15.8. IR spectrum: 745, 800, 838, 958, 1010, 1155, 1200, 1240, 1292, 1450, 1560 (benzoxazole ring); 1328, 1608 cm^{-1} [$C(NO_2)_2$].

LITERATURE CITED

1. V. P. Dukhovskoi, V. D. Tyurin, and G. A. Shvekhgeimer, in: Scientific-Technical Reviews. Chemistry and Petroleum Refining, Vol. 3 [in Russian], Moscow (1969), p. 12.
2. H. Shechter and L. Zeldin, J. Am. Chem. Soc., 73, 1276 (1951).