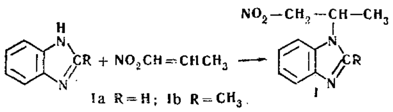

Ia R=H; Ib R=CH$_3$

I

1-(β-Nitroisopropyl)benzimidazole (Ia). In drops, 1.74 g (0.02 mole) of 1-nitroprop-1-ene [1] was added with stirring to a solution of 2.36 g (0.02 mole) of benzimidazole in 15 ml of absolute ethanol. Then the reaction mixture was kept at room temperature for 2 hr, the ethanol was distilled off, and the residual oil was washed with ether and extracted with chloroform. The extract was dried over magnesium sulfate, and the chloroform was distilled off. Yield 3.15 g (77%) of **Ia.** Mp of the picrate 168–169° C (ethanol). Found, %: C 43.86; H 3.31; N 19.68. Calculated for $C_{10}H_{11}N_3O_2 \cdot C_6H_3N_3O_7$, %: C 44.25; H 3.25; N 19.35. IR spectrum of **Ia**, cm^{-1}: 1602 (C=N), 1540, 1374 (NO$_2$), 1280 (C–N), 780, 743 (C–H, o-disubstituted benzene ring).

1-(β-Nitroisopropyl)-2-methylbenzimidazole (Ib). This was obtained similarly. Yield 82%. Mp 118–119° C (benzene-petroleum ether). Found, %: C 60.46; H 6.01; N 18.87. Calculated for $C_{11}H_{13}N_3O_2$, %: C 60.26; H 5.98; N 19.17. IR spectrum, cm^{-1}: 1597 (C=N), 1538, 1366 (NO$_2$), 1287 (C–N), 775, 758 (C–H, o-disubstituted benzene ring).

1-(β-Aminoisopropyl)benzimidazole (II). This was obtained by the reduction of Ia with zinc in an aqueous ethanolic solution of hydrochloric acid. Yield 75%. Mp of the dihydrochloride 257–259° C (ethanol-ether). Found, %: Cl 28.71; N 16.73. Calculated for $C_{10}H_{13}N_3 \cdot 2HCl$, %: Cl 28.58; N 16.93%

REFERENCE

1. G. D. Buckley, C. W. Scaife, J. Chem. Soc., 1947, 1471.

9 August 1968

Moscow Institute of the Petro-
Chemical and Gas Industry

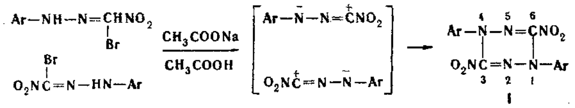
SYNTHESIS OF 1,4-DIARYL-3,6-DINITRO-1,2,4,5-TETRAZINES

L. S. Pupko, A. I. Dychenko, and P. S. Pel'kis

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 5, No. 4, pp. 759–760, 1969

UDC 547.883.07:543.422.4.6

The reaction of the arylhydrazones of bromonitroformaldehyde with sodium acetate in acetic acid leads to the splitting out of bromine and the formation of 1,4-diaryl-3,6-dinitro-1,2,4,5-tetrazines (I), which have not been reported in the literature. In their structure, these compounds are similar to the 1,4-diaryl-3,6-dihydro-1,2,4,5-tetrazines [1–3]. Compounds I are obtained by heating arylhydrazones of bromonitroformaldehyde [4] in glacial acetic acid with anhydrous sodium acetate by an intermolecular condensation mechanism or by the 1,3-bipolar formation of the ring [5]:



I

The compounds I that we synthesized form small faintly-colored crystals with a metallic luster soluble in all the usual organic solvents and insoluble in water. In the UV region they have two absorption maxima, at 275-285 and 377-385 nm (in ethanol). The presence in the IR spectrum of a C=N absorption band at 1590–1610 cm^{-1} and the results of a molecular-weight determination confirm the formation of the tetrazine ring.

1,4-Diphenyl-3,6-dinitro-1,2,4,5-tetrazine. A mixture of 2.44 g (0.01 mole) of the phenylhydrazone of bromonitroformaldehyde and 2.46 g (0.3 mole) of finely-ground anhydrous sodium acetate in 35 ml of glacial acetic acid was heated in the oil bath at 100–120° C for 3 hr. After cooling, the reaction mixture was poured into ice water. The light yellow precipitate that deposited was filtered off, washed with water to neutrality, and dried. Yield 0.73 g (45%). Mp 98–100° C (from ethanol). Found, %: N 25.48, 25.58; mol. wt. 428, 373. Calculated from $C_{14}H_{10}N_6O_4$, %: N 25.76; mol. wt. 395.

1,4-Di-p-bromophenyl-3,6-dinitro-1,2,4,5-tetrazine. Yield 80%, mp 158–160° C (from ethanol). Found, %: Br 33.00, 33.18; N 17.16, 17.04; C 35.15; H 1.73. Calculated for $C_{14}H_8Br_2N_6O_4$, %: Br 33.06; N 17.35; C 34.71; H 1.65.

1,4-Di-p-chlorophenyl-3,6-dinitro-1,2,4,5-tetrazine. Yield 63% mp 145–146° C (from ethanol). Found, %: N 21.31, 21.35. Calculated for $C_{14}H_8Cl_2N_6O_4$, %: N 21.26

1,4-Di-(o,p-dichlorophenyl)-3,6-dinitro-1,2,4,5-tetrazine. Yield 95%, mp 100-102° C (from ethanol). Found, %: N 17.83, 17.93. Calculated for $C_{14}H_6Cl_4N_6O_4$, %: N 18.1.

REFERENCES

1. S. Ruhemann, J. Chem. Soc., 55, 242, 1889.
2. F. D. Chattaway and A. J. Walker, J. Chem. Soc., 892, 1925.
3. M. O. Lozinskii and P. S. Pel'kis, ZhOKh, 4, 798, 1965.
4. L. S. Pupko, G. A. Lanchuk, and A. I. Dychenko, Ukr. khim. zh., 19, 610, 1963.
5. R. Huisgen, Proc. Chem. Soc., 4701, 1961.
6. L. Bellamy, Infrared Spectra of Complex Molecules [Russian translation], IL, Moscow, 319, 1957.

23 September 1968

Institute of Organic Chemistry AS
UkrSSR, Kiev