SYNTHESIS OF 2,4-DISUBSTITUTED THIAZOLES

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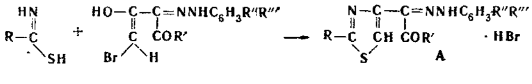
By the reaction of thiourea, thioacetamide, and thiobenzamide with arylhydrazones of γ-bromoacetic ester [1], with boiling for several hours in absolute ethanol, we have obtained previously unreported thiazolium salts (table)


A

When the salts IV and VI were recrystallized from aqueous ethanol, the free bases were obtained. The reaction of IV with hydrazine hydrate in absolute ethanol gave the hydrazide VIII, which by condensation with phenyl isothiocyanate, was converted into the corresponding phenyl thiosemicarbazide **IX**.

The structure A was confirmed by the IR absorption spectra. The IR spectra have the characteristic frequencies for C=O (1700–1675 cm^{-1}) and C=N (1620–1580 cm^{-1}) and bands of a disubstituted thiazole ring (1340–1300, 1080–1040, 970–930, 880–700 cm^{-1}) [2, 3].

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2,4-Disubstituted Thiazole Derivatives*

Compound	R**	R″	Mp, °C***	Empirical formula	Found, %				Calculated,%				Yield, %
					C	H	N	S	C	H	N	S	
I	NH_2	o-CH_3O	197—199	$C_{14}H_{16}N_4O_3S \cdot HBr$	42.37	4.16	—	7.80	41.90	4.27	—	7.99	97
II	NH_2	p-CH_3O	168—169	$C_{14}H_{16}N_4O_3S \cdot HBr$	42.23	4.24	14.17	7.56	41.90	4.27	13.96	7.99	69
III	NH_2	o-C_2H_5O	190—190.5	$C_{17}H_{22}N_4O_4S \cdot HBr$	43.88	5.04	—	6.60	44.44	5.15	—	6.98	56
IV	CH_3	p-CH_3O	72—73	$C_{15}H_{17}N_3O_3S$	—	—	13.02	9.61	—	—	13.15	10.03	74
V	CH_3	p-CH_3	138—143 (decomp.)	$C_{15}H_{17}N_3O_2S \cdot HBr$	—	—	10.47	8.20	—	—	10.93	8.34	64
VI	C_6H_5	p-CH_3O	105	$C_{20}H_{19}N_3O_3S$	—	—	11.13	8.23	—	—	11.01	8.40	53
VII	C_6H_5NH	H	190—192	$C_{19}H_{18}N_4O_2S \cdot HBr$	—	—	12.56	7.15	—	—	12.52	7.16	69
VIII	CH_3	p-CH_3O	158—160	$C_{13}H_{15}N_5O_2S$	—	—	22.81	10.35	—	—	22.93	10.50	100
IX	CH_3	p-CH_3O	180 (decomp.)	$C_{20}H_{20}N_6O_2S_2$	—	—	18.95	14.42	—	—	19.07	14.55	70

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*I, II, IV–IX R‴ = H; III R‴ = 5-OC_2H_5.

**I–VII R′ = OC_2H_5; VIII R′ = $NHNH_2$; IX R′ = $NHNHCSNHC_6H_5$.

***I–III, V, and VII were recrystallized from absolute ethanol, VIII from a mixture of ethanol and dioxane (1:2), and IX from a mixture of ethanol and acetone (1:1).

REACTION OF BENZIMIDAZOLE AND 2-METHYLBENZIMIDAZOLE WITH 1-NITROPROP-1-ENE

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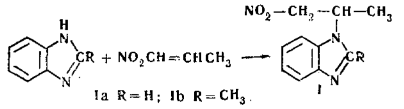
1-Nitroalkyl derivatives of benzimidazole have not been described in the literature. We have obtained the previously unknown 1-(β-nitroisopropyl)benzimidazole (**Ia**) and 1-(β-nitroisopropyl)-2-methylbenzimidazole (**Ib**) by the addition of 1-nitroprop-1-ene to benzimidazole and 2-methylbenzimidazole, respectively. By the action of zinc and hydrochloric acid, **Ia** was reduced to 1-(β-aminoisopropyl)benzimidazoles (**II**).



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%

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

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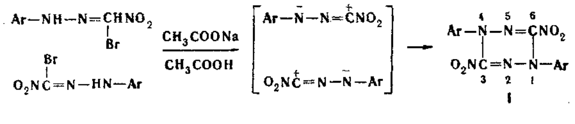
The reaction of the arylhydrazones of bromonitroformaldehyde with sodium acetate in acetic acid leads to the splitting out of bromine and the formation of 1,4-diaryl-3,6-dinitro-1,2,4,5-tetrazines (I), which have not been reported in the literature. In their structure, these compounds are similar to 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]:



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.

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