DUAL REACTIVITY OF 2-DIAZO-2-CYANOACETAMIDE RELATIVE TO HYDROGEN SULFIDE

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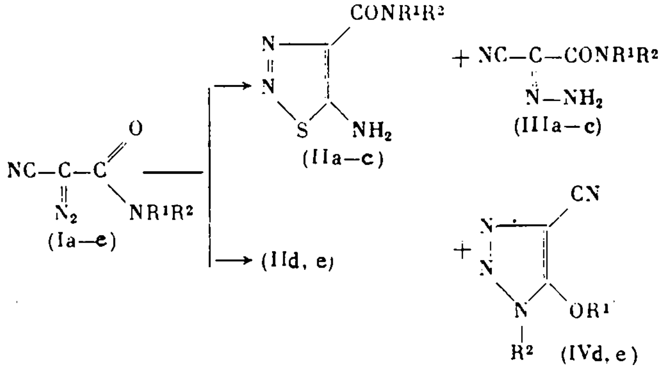
Diazoacetonitrile derivatives react with H_2S in the presence of bases to give 5-amino-1,2,3-thiadiazoles in yields not exceeding 30-50% [1].

In the present work, we studied the reaction of 2-diazo-2-cyanoacetamides (Ia)-(Ie) with H_2S in order to increase the yield of derivatives of 5-amino-1,2,3-thiadiazole-4-carboxylic acid (IIa)-(IIe), which are intermediates in the synthesis of herbicides [2]. The reaction of (Ia)-(Ic) with H_2S in the presence of base proceeds with reduction of the diazo group by hydrogen sulfide to form 2-hydrazono-2-diazoacetamides and elemental sulfur in addition to heterocyclization. The yield of (II) is nonlinearly dependent on the triethylamine concentration (Fig. 1).

The reactions of nitriles with H_2S usually require the use of either a base or high pressure [3]. However, diazoamides (Ia)-(Ie) react with H_2S in the absence of Et_3N and, in the case of (Ia) and (Ib), give thiadizaoles (IIa) and (IIb) in high yield. Amide (Ic) under these conditions forms a mixture of thiadiazole (IIc) and hydrazone (IIIc). Products of intramolecular cyclization, namely, 1-substituted 5-hydroxy-1,2,3-triazole-4-carbonitriles (IVd) and (IVe) were also isolated from the reaction mass in the case of (Id) and (Ie). Products (IVd) and (IVe) are also formed in the absence of H_2S upon heating solutions of (Ia), (Ib), (Id), and (Ie) in ethanol at reflux for 0.5 h.



$R^1 = R^2 = H$(a); $R^1 = H$, $R^2 = Me$(b); $R^1 = R^2 = Me$(c); $R^1 = H$, $R^2 = Ph$(d); $R^1 = H$, $R^2 = C_6H_{11}$(e).

TABLE 1. Product Indices

Compound	Mp, °C (from H_2O, dec.)[a]	Found, %				Chemical formula	Calculated, %				Yield, %
		C	H	N	S		C	H	N	S	
(IIc)	135–136	34.7	4,4	32,6	18.1	$C_5H_8N_4OS$	34.9	4,7	32.5	18.0	76(A)[d]
(IId)	133–134[b]	49.0	3,8	25,7	14.6	$C_9H_8N_4OS$	49.1	3,7	25.4	14.6	69(B)
(IIe)	144[b]	47.5	6,3	25,0	14.1	$C_9H_{14}N_4OS$	47.8	6,2	24.8	14.2	63(B)
(IIc)	115–116[c]	42.7	5,8	40,2	–	$C_5H_8N_4O$	42.9	5,8	40.0	–	70(A)[e]
(IVd)	73	57.8	3,3	30,2	–	$C_9H_6N_4O$	58.1	3,6	30.1	–	22(B)
(IVe)	163	56.4	6,4	29,1	–	$C_9H_{12}N_4O$	56.2	6,3	29.2	–	28(B)

[a] Melting points not corrected.
[b] From ethanol.
[c] From ethyl acetate.
[d] In the presence of an equimolar amount of Et_3N.
[e] In the presence of 0.05 mole Et_3N.

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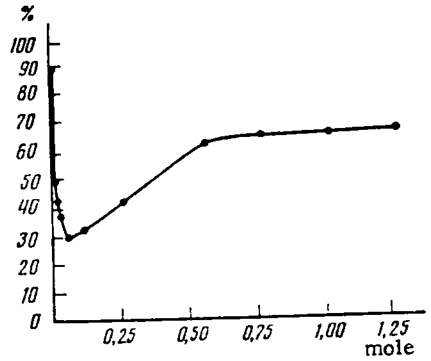

Fig. 1. Dependence of the content of thiadiazole (IIa) in the reaction mixture on the amount of Et_3N taken.

TABLE 2. Spectral Indices of the Products

Compound	IR spectrum (KBr, ν, cm^{-1})	UV spectrum (in EtOH) λ_{max}, nm (log ε)	PMR spectrum (in DMSO-d_6), δ, ppm	Mass spectrum m/z (relative intensity, %)
(IIc)	3390, 3270, 3150(NH), 2950(CH), 1610(CO)	215 sh (3.93), 265(3.88), 289(3.85)	8.0 s (NH_2), 3.2 s ($2CH_3$)	M+ 172(100), 125(91), 101(58), 72(73)
(IId)	3462, 3412, 3340, 3309(NH), 3075, 2940(CH), 1662(CO)	280(4.40)	9.0 s (NH), 8.2 s (NH_2), 8.0–6.5 m (C_6H_5)	
(IIe)	3418, 3285(NH), 2950, 2870(CH), 1640(CO)	257(4.06), 290(3.85)	8,1 d (J=8 Hz NH), 8.0 s (NH_2), 2.2–0.5 m (C_6H_{11})	
(IIIc)	3360, 3330, 3165(NH), 2950, 2900(CH), 2225(CN), 1680(CO)	282(4.10)	9.3 s (NH_2), 3,0 s ($2CH_3$)	M+ 140(100), 124(23), 112(40), 68(74)
(IVd)	3082, 3000(CH), 2270(CN)	215(4.23), 265(4.00)	7.9–7.4 m (C_6H_5)	M+ 186(54), 130(54), 129(48), 103(100)
(IVe)	2955, 2876(CH), 2244(CN)	216(3.83), 258(3.98)	2.2–0.8 m (C_6H_{11})	M+ 192(33), 83(75), 82(83), 55(100)

The mechanisms for the reactions of (Ia)-(Ie) with H_2S in the presence and absence of base are apparently different. In the absence of base, the amide group acts as a base. The reaction rate is sharply diminished upon the replacement of the hydrogen atoms by methyl groups. Thus, the reaction time is 4-5 h for diazoamide (Ia) but 15-20 h for N-methylamide (Ib) and >400 h for N,N-dimethylamide (Ic). Thus, the reactions of (Ia)-(Ie) presumably involve intramolecular coordination of H_2S with the nitrile and carbamoyl groups, which is hindered upon the replacement of a hydrogen atom by a methyl group in the amide moiety.

EXPERIMENTAL

The reactions were monitored and the compound purity was checked by thin-layer chromatography on Silufol UV-245 plates. The mass spectra were taken on an MKh-1303 mass spectrometer at 50 eV under standard conditions. The product indices are given in Tables 1 and 2.

Reactions of 2-Diazo-2-cyanoacetamides with H_2S. A. Ethanol saturated with H_2S and containing 10^{-5}–$1.25 \cdot 10^{-2}$ mole Et_3N was added to 0.01 mole (Ia)-(Ic). The mixture was maintained at about 20°C until starting (Ia)-(Ic) disappeared and concentrated at reduced pressure. The mixtures of (IIa)-(IIc) and (IIIa)-(IIIc) were separated by chromatography on an L 40/100 μm silica gel using 1:15 ethanol—chloroform as eluent. Products (IIa), (IIb), (IIIa), and (IIIb) were identical to those described in our previous work [1].

B. A sample of 0.01 mole (Ia)-(Ie) was dissolved in ethanol. H_2S was introduced at 0°C until the solution was saturated and maintained at about 20°C until starting (Ia)-(Ie) disappeared. The precipitate of (IIa), (IIb), (IId), and (IIe) was filtered off. The filtrate was concentrated and an additional amount of (IIa) and (IIb) was obtained. (IIa) was obtained in 93% yield and (IIb) was obtained in 88% yield. The mixtures of (IIc) and (IIIc), of (IId) and (IVd), and of (IIe) and (IVe) were separated as in method A.

CONCLUSIONS

1. Intramolecular catalysis of the amide group was found in the addition of H_2S to the cyano group of 2-diazo-2-cyanoacetamides to give high yields of amides of 5-amino-1,2,3-thiadiazole-4-carboxylic acid.

2. The reactions of 2-diazo-2-cyanoacetamides with H_2S in the presence of bases give the reduction of the diazo group by hydrogen sulfide in addition to heterocyclization.

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