11. L. M. Korotaeva, T. Ya. Rubinskaya, M. Ya. Botnikov, and V. P. Gul'tyai, Izv. Akad. Nauk SSSR, Ser. Khim., 637 (1988).

REARRANGEMENT OF 5-AMINO-1,2,3-THIADIAZOLE-4-CARBOTHIOAMIDES

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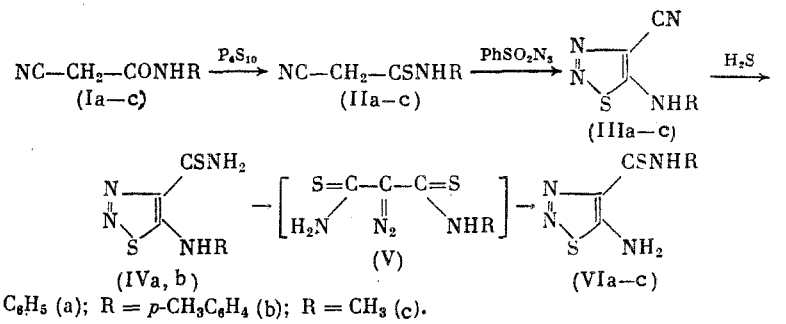
1,2,3-Thiadiazole-4-carbothioamides are little-studied compounds and are represented in the literature by single examples [1, 2]. To prepare new 5-amino-1,2,3-thiadiazole-4-carbothioamides, of interest for biological tests [1], we carried out their synthesis from cyanoacetamides (I) consecutively by selective thionation by phosphorus decasulfide P_4S_{10} with the formation of thioamides (II), by the reaction of (II) with benzenesulfonyl azide [3], and, finally, by sulfhydrylation of the prepared nitriles (III) to 1,2,3-thiadiazole-4-carbothioamides (IV) and (VI).



R = C_6H_5 (a); R = p-$CH_3C_6H_4$ (b); R = CH_3 (c).

In a study of the reactions of compounds (IIIa-c) with hydrogen sulfide in the presence of catalytic amounts of bases [4], we observed that 5-(arylamino)- and 5-(methylamino)1,2,3-thiadiazole-4-carbothioamides (IV) are rearranged to isomeric thioamides (VI). In addition, in the case of N-aryl substituents, as a result of the reaction a mixture of isomers (IV) and (VI) is formed; according to the data of ^{13}C and ^1H NMR spectra, the mixture consists of 75% compound (IV) and 25% thiadiazole (VI), its rearrangement product. The signals in the ^1H and ^{13}C NMR spectra were assigned on the basis of their comparison with the spectra of model compounds.

Replacement of the aryl substituent by a methyl group led to the formation of individual 5-amino-1,2,3-thiadiazole-4-(N-methylcarbothioamide) (VIc), described by us previously [2].

The observed reaction is a new rearrangement of 5-(N-aryl)- and 5-(N-methylamino)1,2,3-thiadiazoles to 4-(N-aryl)- and 4-(N-methylthiocarbamoyl)-1,2,3-thiadiazoles, respectively, and the first example in the series of cyclic compounds in which methyl and aryl groups are "transferred" from the nitrogen atom of the amino group to the nitrogen atom of the thioamide group.

The conversion of compound (IV) to thiadiazole (VI) can occur either by double transamination or by ring cleavage to diazo thione (V) with subsequent ring formation at the sulfur atom of the unsubstituted thioamide group.

The first mechanism seems unlikely because of the very low basicity of the amino and thioamide groups in compound (IV). Because it is known that 5-amino-1,2,3-thiadiazoles are labile compounds and are facilely rearranged with ring cleavage to isomeric 5-mercapto-1,2,3-triazoles [5], the second mechanism seems more likely.

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TABLE 1. Spectral Characteristics of the Synthesized Substances

Compound	Yield, %	Mp. °C	IR spectrum, ν, cm^{-1}	Mass spectrum, m/z (rel. intensity of peaks, %)	PMR spectrum, δ, ppm	^{13}C NMR spectrum, δ, ppm
(IIIa)	15	165–168	3244, 3151, 3035 (NH) 2248 (CN)	M+202 (40) 174 (100), 146 (26), 142 (46)	7,3–7,5 m (C_6H_5), 11,1 s (NH)	
(IIIb)	38	185	3270 (NH) 2250 (CN)	M+216 (57), 188 (100), 187 (46), 173 (44)	2,2 s (CH_3), 7,3–7,6 m (C_6H_4), 10,9 s (NH)	23.0 (CH_3), 112,5 (CN), 188,8 (C^4), 167,6 (C^5)
(IIIc)	64	138	3240, 3130, 3045 (NH), 2235 (CN)	M+140 (100), 112 (10), 111 (8), 70 (19)	3,0 d (CH_3), 9,2 s (NH)	113,1 (CN), 172,3 (C^5)
(IVa)	82	120–121	3318, 3170 (NH) 2940 (CH)	M+236 (100), 191 (77), 175 (31), 148 (27)	7,1–7,9 m (C_6H_5), 9,9 d ($CSNH_2$), 12,7 s (NH)	137,86 (C^4), 162,8 (C^5), 186,5 (C=S)
(IVb)					7,1–7,9 m (C_6H_5), 9,1 s (NH_2), 11,8 s (CSNH)	137,5 (C^4), 168,4 (C^5), 184,1 (C=S)
(VIa)	50	130	3400, 3290, 3200 (NH) 2930 (CN)	M+250 (100), 205 (98), 105 (50), 91 (81)	2,2 s (CH_3), 7,1–7,5 m (C_6H_4), 9,9 d ($CSNH_2$), 12,6 s (NH)	20,4 (CH_3), 137,5 (C^4), 163,4 (C^5) 186,4 (C=S)
(VIb)					2,3 s (CH_3, 7.1–7,5 m (C_6H_4), 9.1 s (NH_2), 11,8 s (CSNH)	20.7 (CH_3), 136.0 (C^4), 168.2 (C^5), 183,9 (C=S)

EXPERIMENTAL

The course of the reactions and the purity of the prepared substances were monitored by thin-layer chromatography on Silufol UV-254 plates. Infrared spectra were recorded on a UR-20 spectrometer with tablets of KBr. PMR spectra were obtained on Perkin–Elmer R-12B (60 MHz) and Bruker WP-80 (80.13 MHz) instruments in DMSO-d_6, and the internal standard was TMS. The ^{13}C NMR spectra were recorded on a Bruker WP-80 spectrometer (20.13 MHz) in DMSO-d_6, and the internal standard was TMS. The mass spectra were recorded on a Varian MAT-311A instrument (voltage 70 eV).

2-Cyanothioacetamides (IIa-c). The appropriate cyanoacetamide (I) (1 mole) and 0.5 mole of P_4S_{10} were suspended in 1.5 liters of xylene, and the whole was boiled for 30 min. The hot solution was decanted and cooled to 0°C. The precipitate was filtered and crystallized from alcohol. With respect to their physicochemical constants, compounds (IIa-c) were identical to cyanoacetamides prepared by the method of [6].

5-(N-Methyl(or aryl)amino)-1,2,3-thiadiazole-4-carbonitriles (IIIa-c). Compound (II) (1 mole) was suspended in a solution of 0.1 mole of Na in 1 liter of abs. EtOH, and 1 mole of benzenesulfonyl azide was added with stirring at 5-15°C. The precipitate that formed for 10 min was filtered and crystallized from water or alcohol.

Sulfhydrylation of Nitriles (IIIa-c). Nitrile (III) (1 mole) was dissolved in 1 liter of an organic solvent [ether was used in the case of (IIIa) or (IIIc), and EtOH was used in the case of (IIIb)], 0.1 mole of the catalyst (EtONa or Et_3N) was added, and the whole was saturated with dry H_2S at 0°C. The reaction mixture was heated to 75°C in an autoclave for 30 min (the sulfhydrylation of thiadiazole (IIIc) occurred at 0-5°C). The precipitate that formed after cooling was filtered and crystallized from EtOH.

The physicochemical constants and spectral characteristics of the synthesized substances are given in Table 1. The elemental analysis data correspond to the calculated data.

CONCLUSIONS

A new rearrangement in the series of 5-amino-1,2,3-thiadiazole-4-carbothioamides was observed.

LITERATURE CITED

1. V. A. Bakulev and V. S. Mokrushin, Khim. Geterotsikl. Soedin., 1011 (1986).
2. E. F. Dankova, V. A. Bakulev, V. S. Mokrushin, and Yu. M. Shafran, Khim. Geterotsikl. Soedin., 1429 (1985).
3. M. Regitz, in: Newer Methods of Preparative Organic Chemistry, W. Foerst (ed.), Verlag Chemie G. M. B. H., Academic Press (1977), p. 201.
4. E. N. Zil'berman, Reactions of Nitriles [in Russian], Khimiya, Moscow (1972), p. 183.
5. J. Goerdler and G. Gnad, Chem. Ber., 99, 1619 (1966).
6. A. D. Grabenko, P. S. Pel'kis, and L. N. Kulaeva, Zh. Obshch. Khim., 32, 2248 (1962).

O-ALKYLCHLOROFORMIMINO O-ALKYL METHYLPHOSPHONATES

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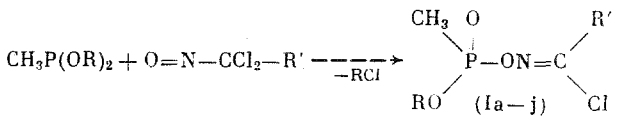
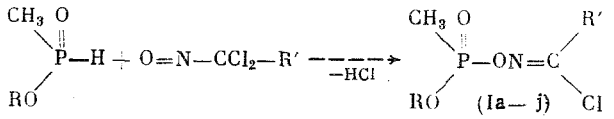
Derivatives of phosphorous acid react with α-chloro-α-nitrosoalkanes forming the corresponding phosphorylated oximes (the Allen reaction) [1, 2]. Derivatives of phosphonous acid were not studied in this reaction. With the object of enlarging the concept of the limitations of the utilization of the Allen reaction for the synthesis of phosphorylated oximes, we studied the reaction of O,O-dialkyl methylphosphonites and O-alkyl methylphosphonites with 1,1-dichloro-1-nitrosoalkanes; this resulted in the formation of the corresponding O-alkylchloroformimino O-alkyl methylphosphonates (I).



R = C_2H_5, R′ = CH_3 (a); R = C_3H_7, R′ = CH_3 (b); R = C_4H_9, R′ = = CH_3 (c); R = i-C_3H_7, R′ = C_2H_5 (d); R = C_4H_9, R′ = C_2H_5 (e); R = = C_5H_{11}, R′ = C_2H_5 (f); R = C_3H_7, R′ = C_3H_7 (g); R = C_4H_9, R′ = C_3H_7 (h); R = C_4H_9, R′ = i-C_3H_7 (i); R = C_4H_9, R′ = C_4H_9 (j).

The phosphonates (I) were synthesized directly from the O-alkyl methylphosphonites with the yield of 50-60%.



The structure of the phosphonates (I) was determined from the data of the elemental analysis, and the PMR, ^{31}P NMR, and IR spectroscopies. The phosphonate structure of (I) is unambiguously confirmed by the chemical shifts of the nuclei of the P atoms in the region of 33-35 ppm. The doublet of the methyl group is characteristic of the PMR spectra at 1.5-

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