Brief Communications

The addition reaction of acrylonitrile and methylacrylate to *N*-(5R-1,3,4-thiadiazol-2-yl)dithiocarbamates

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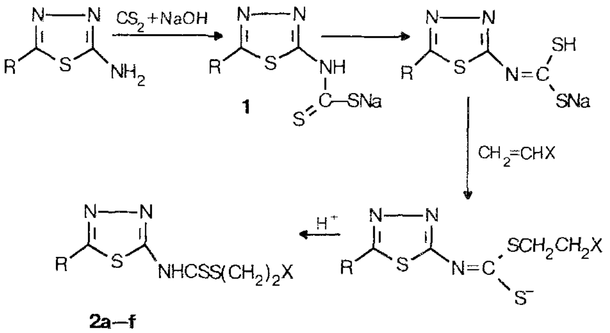
A new type of dithiocarbamic acid derivatives, *S*-(2-X-ethyl) ethers of *N*-(5R-1,3,4-thiadiazol-2-yl)-dithiocarbamic acids (X = CN, COOMe), has been synthesized by the reaction of sodium *N*-(1,3,4-thiadiazol-2-yl) dithiocarbamates with acrylonitrile and methylacrylate.

Key words: cyanoethylation, addition of methylacrylate, 2-cyano(methoxycarbonyl) ethyl 5R-1,3,4-thiadiazol-2-yl dithiocarbamates.

Salts and ethers of dithiocarbamic acid, which manifest activity towards pathogenic fungi and nematodes,[1,2] play an importantt role among synthetic chemical agents for plant protection. To find promising fungicides in the series of 1,3,4-thiadiazol-2-yl dithiocarbamates we studied the addition of acrylonitrile (AN) and methylacrylate (MA) to sodium *N*-(5R-1,3,4-thiadiazol-2-yl) dithiocarbamates (**1**). Although there is some information in the literature that such unsaturated compounds as acetylene can be added to dithiocarbamates to form vinyl ethers,[3] there are no data about reaction **1** with AN and MA.

Our preliminary experiments have shown that the compounds **1** add to AN and MA at room temperature to form in some cases the desired products in quantitative yields. The reaction is accompanied by an exothermal effect and requires 4—5 h to go to completion. The reaction results in the formation of *S*-(2-cyanoethyl) (**2a—f**) and 2-(methoxycarbonyl)ethyl (**3a—f**) ethers of *N*-(5R-1,3,4-thiadiazol-2-yl)dithiocarbamic acids (see Table 1).



2a—f
3a—f

R = H (**a**), Me (**b**), Et (**c**), Pr (**d**), CF_3 (**e**), $PhCH_2S$ (**f**).
X = CN (**2**), COOMe (**3**).

High reactivity of dithiocarbamates **1** towards AN and MA seems to be caused by the predominance of the imidothiocarbonic tautomeric form. Compounds **1** were

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†Deceased.

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Table 1. Characteristics of compounds **2a—f** and **3a—f**

Compound	Yield (%)	M.p./°C	Empirical formula	Found/Calculated (%)		
				C	H	S
S-(2'-Cyanoethyl) *N*-(1,3,4-thiadiazol-2-yl) dithiocarbamate (**2a**)	88.7	175-176	$C_6H_6N_4S_3$	31.41 31.28	2.67 2.62	41.89 41.76
S-(2'-Cyanoethyl) *N*-(5-methyl-1,3,4-thiadiazol-2-yl) dithiocarbamate (**2b**)	91.7	176—177	$C_7H_8N_4S_3$	34.70 34.40	3.40 3.29	39.42 39.36
S-(2'-Cyanoethyl) *N*-(5-ethyl-1,3,4-thiadiazol-2-yl) dithiocarbamate (**2c**)	80.0	162—163	$C_8H_{10}N_4S_3$	37.27 37.22	3.50 3.90	37.01 37.23
S-(2'-Cyanoethyl) *N*-(5-propyl-1,3,4-thiadiazol-2-yl) dithiocarbamate (**2d**)	80.8	149—150	$C_9H_{12}N_4S_3$	39.89 39.67	4.81 4.44	35.66 35.30
S-(2'-Cyanoethyl) *N*-(5-trifluoromethyl-1,3,4-thiadiazol-2-yl) dithiocarbamate (**2e**)	93.6	161—162	$C_7H_5F_3N_4S_3$	28.93 28.17	1.86 1.69	32.08 32.24
S-(2'-Cyanoethyl) *N*-(5-benzylthio-1,3,4-thiadiazol-2-yl) dithiocarbamate (**2f**)	97.5	189—190	$C_{13}H_{12}N_4S_3$	43.85 44.29	3.57 3.43	36.02 36.38
S-(2'-Methoxycarbonylethyl) *N*-(1,3,4-thiadiazol-2-yl) dithiocarbamate (**3a**)	83.6	145—146	$C_7H_9N_3O_2S_3$	31.52 31.92	3.61 3.44	37.34 36.52
S-(2'-Methoxycarbonylethyl) *N*-(5-methyl-1,3,4-thiadiazol-2-yl) dithiocarbamate (**3b**)	83.4	135—136	$C_8H_{11}N_3O_2S_3$	34.69 34.63	4.02 3.99	34.80 43.68
S-(2'-Methoxycarbonylethyl) *N*-(5-ethyl-1,3,4-thiadiazol-2-yl) dithiocarbamate (**3c**)	87.2	123—124	$C_9H_{13}N_3O_2S_3$	37.22 37.09	4.79 4.49	33.51 33.01
S-(2'-Methoxycarbonylethyl) *N*-(5-propyl-1,3,4-thiadiazol-2-yl) dithiocarbamate (**3d**)	77.3	99—100	$C_{10}H_{15}N_3O_2S_3$	40.00 39.32	5.09 4.95	31.04 31.49
S-(2'-Methoxycarbonylethyl) *N*-(5-trifluoromethyl-1,3,4-thiadiazol-2-yl) dithiocarbamate (**3e**)	98.7	185—186	$C_8H_8F_3N_3O_2S_3$	28.53 28.99	2.60 2.89	29.35 29.03
S-(2'-Methoxycarbonylethyl) *N*-(5-benzylthio-1,3,4-thiadiazol-2-yl) dithiocarbamate (**3f**)	95.9	125—126	$C_{14}H_{15}N_3O_2S_3$	44.13 43.61	4.17 3.92	33.01 33.27

synthesized according to the previously described method.[4]

The physicochemical characteristics and data of the elemental analysis of the obtained products **2a—f** and **3a—f** are presented in Table 1, the spectral parameters of these compounds are listed in Table 2.

Table 2. Spectral parameters of compounds **2a—f** and **3a—f**

Compound	IR spectrum (ν/cm^{-1})					NMR spectrum (δ)	
	CN	CO	NCSS	NH	Ht	SCH$_2$	CH$_2$X
2a	2260	—	1130	3450	1570	3.35	2.75
2b	2250	—	1110	3450	1540	3.37	2.90
2c	2260	—	1120	3440	1560	3.40	2.98
2d	2260	—	1130	3450	1570	3.40	2.95
2e	2260	—	1170	3440	1590	3.47	2.97
2f	2250	—	1130	3450	1570	3.42	2.94
3a	—	1735	1170	3440	1550	3.41	2.95
3b	—	1730	1170	3440	1550	3.35	2.76
3c	—	1740	1170	3450	1540	3.32	2.75
3d	—	1730	1170	3440	1550	3.32	2.75
3e	—	1740	1150	3450	1580	3.42	2.78
3f	—	1740	1150	3450	1580	3.35	2.77

Experimental

IR spectra were obtained on a UR-20 spectrometer in a thin layer on KBr prisms (4000—400 cm^{-1}), NMR spectra were recorded on a Tesla-BS-587C instrument with an operating frequency of 80 MHz in DMSO-d$_6$ solutions (HMDS as the internal standard). Melting points of crystalline substances were determined on glass plates with a Boetius instrument.

The starting 2-amino-5R-1,3,4-thiadiazoles were prepared according to the known procedures.[5-8]

General procedure for the synthesis of 2 and 3. 2-Amino-5R-1,3,4-thiadiazole (0.05 mol) and carbon disulfide (0.06 mol) were dissolved in 25—40 ml of DMF. Sodium hydroxide (0.05 mol) as a 40% solution was added with vigorous mixing, the mixture was additionally stirred for 2—3 h. AN (0.05 mol) (for the preparation of **2a—f**) or MA (0.05 mol) (for the preparation of **3a—f**) was added dropwise to the obtained solution of dithiocarbamate **1** for 20—30 min. The mixture was stirred for 4—5 h. The solution was diluted with a 3—4-fold amount of water and acidified with hydrochloric acid to pH 1—2. The desired product was precipitated and filtered off and recrystallized from alcohol or aqueous dioxane.

Compounds **2**, **3** are yellow crystalline substances with a specific odor.

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Chemiluminescence by the interaction of XeO_3 and the products of photolysis of uranyl solutions in sulfuric acid

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Using the chemiluminescence oxidation of U(IV) and H_2O_2 with xenon trioxide as a model, it has been found that during the photolysis of solutions of UO_2SO_4 in sulfuric acid in the absence of any organic compounds, the accumulation of $U(SO_4)_2$ and H_2O_2 takes place as a result of the reaction of the primary products of the photoreduction of uranyl ion, *i.e.*, UO_2^+ and the $\cdot OH$ radical.

Key words: uranyl, xenon trioxide, hydrogen peroxide, photolysis, chemiluminescence.

The decomposition of organic compounds in the presence of uranyl salts irradiated by light have been known for more than hundred years.[1] The detachment of the hydrogen atom (or electron) from a donor SH_2 is the main photochemical reaction of the uranyl ion (UO_2^{2+}):

$$^*UO_2^{2+} + SH_2 \rightarrow UO_2^+ + {}^\cdot SH + H^+, \tag{1}$$

Taking into account the high oxidation potential (E^0 = 2.7 V) of the electron-excited uranyl ion, it was assumed[2] that photoreduction of UO_2^{2+} can also occur in the absence of organic compounds in an aqueous solution:

$$^*UO_2^{2+} + H_2O \rightarrow UO_2^+ + {}^\cdot OH + H^+, \tag{2}$$

$${}^\cdot OH + {}^\cdot OH \rightarrow H_2O_2, \tag{3}$$

$$2\ UO_2^+ + 4\ H^+ \rightarrow UO_2^{2+} + U^{4+} + 2\ H_2O. \tag{4}$$

It has also been suggested that some portion of the UO_2^{2+} ions and $\cdot OH$ radicals leave the cage and participate in reactions (3) and (4) to form the U(IV) and H_2O_2 accumulating in the solutions. However, direct proof of the validity of the photoreduction mechanism of UO_2^{2+} by H_2O has not yet been found.[3]

We attempted for the first time to study the photolysis of UO_2^{2+} in aqueous solutions of H_2SO_4 (0.2—1.0 *M*) using chemiluminescent (CL) methods based on the possibility of determining small amounts (~ 10^{-9} mol/L) of uranium(IV) on the background of a great excess (~10^{-1} mol/L) of UO_2^{2+} by means of the CL oxidation of uranium(IV) with xenon trioxide.[4]

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