

SYNTHESIS OF 4,5-DISUBSTITUTED 1,3,4-DITHIAZOLIDINE 3,3-DIOXIDES*

M. ZBÍROVSKÝ^a, R. SEIFERT^a, and Š. TRUHLÍK^b

^a Department of Organic Technology,

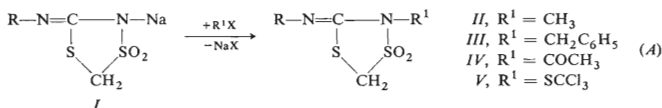
Prague Institute of Chemical Technology, 166 28 Prague 6 and

^b Research Institute of Agrochemical Technology, 810 04 Bratislava

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N-Alkylation and N-acylation of sodium salts of 5-(subst. imino)-1,3,4-dithiazolidine 3,3-dioxides *I* afforded total 34 methyl, benzyl, acetyl, and trichloromethylthio derivatives *II–V* which were characterised in several cases by IR and ¹H-NMR spectra. Compounds *II–V* were tested as herbicides and fungicides; the activity was low.

The recently reported¹ 5-(subst. imino)-1,3,4-dithiazolidine 3,3-dioxides *I* can be alkylated or acylated in the form of alkali metal salts according to equation (A) with the formation of derivatives *II–V* (Table I).



For R see Table I; X = Cl, I

The alkylations were accomplished by methyl iodide (compounds *II*) and benzyl chloride (compounds *III*). The acylations were performed with the use of acetyl chloride (compounds *IV*) and trichloromethanesulfonyl chloride (compounds *V*). In all cases, the reactions proceed in high yields.

When compared with the starting 5-(subst. imino)-1,3,4-dithiazolidine 3,3-dioxides¹, the IR spectra of all the present N⁴-substituted derivatives lack the bands of N—H vibrations. Groups of compounds *IV* and *V* exhibit specific bands of substituents²: compounds *IV* display a vibration of the C=O group at 1705 cm⁻¹ or a split band at 1705–1720 cm⁻¹ (*IVf*) or at 1725 cm⁻¹ (*IVe*); compounds *V* show a CCl₃ vibration at 830 cm⁻¹. The ¹H-NMR spectrum of compound *Iia* has been reported earlier¹; the data of some derivatives of the group *III* and *IV* are shown in Table II. All the spectra agree with expectations.

* Part VIII in the series Organic Herbicides; Part VII: This Journal 42, 2672 (1977).

TABLE I
4,5-Disubstituted 1,3,4-Dithiazolidine 3,3-Dioxides II—V

Com- pound	R R ¹	M.p., °C	Formula (mol.wt.)	Calculated/Found				
				% C	% H	% Cl/ /Br	% N	% S
<i>Ila</i>	C ₆ H ₅ CH ₃	180—181 ^a	C ₉ H ₁₀ N ₂ O ₂ S ₂ (242.3)	44.61	4.16	—	11.56	24.46
				44.53	4.31	—	11.80	24.20
<i>Ilb</i>	C ₆ H ₅ CH ₂ CH ₃	111—113 ^b	C ₁₀ H ₁₂ N ₂ O ₂ S ₂ (256.3)	46.85	4.72	—	10.93	25.02
				47.10	4.94	—	10.75	25.01
<i>Ilc</i>	2-CH ₃ C ₆ H ₄ CH ₃	158—160 ^c	C ₁₀ H ₁₂ N ₂ O ₂ S ₂ (256.3)	46.85	4.72	—	10.93	25.02
				46.58	4.79	—	10.73	25.06
<i>Ild</i>	3-CH ₃ C ₆ H ₄ CH ₃	123—125 ^d	C ₁₀ H ₁₂ N ₂ O ₂ S ₂ (256.3)	46.85	4.72	—	10.93	25.02
				47.04	4.92	—	10.67	24.86
<i>Ile</i>	4-CH ₃ C ₆ H ₄ CH ₃	127—129 ^e	C ₁₀ H ₁₂ N ₂ O ₂ S ₂ (256.3)	47.85	4.72	—	10.93	25.02
				47.10	4.91	—	10.71	24.74
<i>Ilf</i>	3-ClC ₆ H ₄ CH ₃	147—148 ^a	C ₉ H ₉ ClN ₂ O ₂ S ₂ (276.8)	39.42	3.28	12.81	10.12	23.17
				39.67	3.49	12.91	9.92	22.89
<i>Ilg</i>	4-ClC ₆ H ₄ CH ₃	118—120 ^c	C ₉ H ₉ ClN ₂ O ₂ S ₂ (276.8)	39.42	3.28	12.81	10.12	23.17
				39.23	3.39	13.06	10.11	23.01
<i>Ilh</i>	4-BrC ₆ H ₄ CH ₃	137—139 ^d	C ₉ H ₉ BrN ₂ O ₂ S ₂ (321.2)	33.65	2.82	24.87	8.72	19.96
				33.92	3.00	24.93	8.80	19.71
<i>Ili</i>	2,5-Cl ₂ C ₆ H ₃ CH ₃	143—145 ^f	C ₉ H ₈ Cl ₂ N ₂ O ₂ S ₂ (311.2)	34.74	2.59	22.78	9.00	20.61
				34.52	2.69	22.93	8.75	20.81
<i>Ilj</i>	3,4-Cl ₂ C ₆ H ₃ CH ₃	141—143 ^a	C ₉ H ₈ Cl ₂ N ₂ O ₂ S ₂ (311.2)	34.74	2.59	22.78	9.00	20.61
				34.92	2.84	23.04	8.96	21.01
<i>Ilk</i>	3-NO ₂ C ₆ H ₄ CH ₃	145—147 ^d	C ₉ H ₉ N ₃ O ₄ S ₂ (287.3)	37.62	3.16	—	14.62	22.32
				37.75	3.33	—	14.60	22.39
<i>IIla</i>	C ₆ H ₅ CH ₂ C ₆ H ₅	161—162 ^a	C ₁₅ H ₁₄ N ₂ O ₂ S ₂ (318.4)	56.58	4.43	—	8.80	20.14
				56.81	4.62	—	9.05	19.90
<i>IIlb</i>	C ₆ H ₅ CH ₂ CH ₂ C ₆ H ₅	143—145 ^a	C ₁₆ H ₁₆ N ₂ O ₂ S ₂ (332.4)	57.81	4.85	—	8.43	19.28
				57.74	4.93	—	8.25	18.96
<i>IIlc</i>	2-CH ₃ C ₆ H ₄ CH ₂ C ₆ H ₅	134—135 ^c	C ₁₆ H ₁₆ N ₂ O ₂ S ₂ (332.4)	57.81	4.85	—	8.43	19.28
				57.55	4.76	—	8.19	19.01
<i>IIld</i>	3-CH ₃ C ₆ H ₄ CH ₂ C ₆ H ₅	116—118 ^d	C ₁₆ H ₁₆ N ₂ O ₂ S ₂ (332.4)	57.81	4.85	—	8.43	19.28
				58.05	5.04	—	8.25	19.03

TABLE I
 (continued)

Compound	R R ¹	M.p., °C	Formula (mol.wt.)	Calculated/Found				
				% C	% H	% Cl/ /Br	% N	% S
IIIe	4-CH ₂ C ₆ H ₄ CH ₂ C ₆ H ₅	128—130 ^c	C ₁₆ H ₁₆ N ₂ O ₂ S ₂ (332·4)	57·81	4·85	—	8·43	19·28
				57·86	4·60	—	8·31	19·45
III _f	2-ClC ₆ H ₄ CH ₂ C ₆ H ₅	62—64 ^b	C ₁₅ H ₁₃ ClN ₂ O ₂ S ₂ (352·9)	51·06	3·71	10·05	7·94	18·17
				51·12	3·61	10·01	7·84	17·98
III _g	3-ClC ₆ H ₄ CH ₂ C ₆ H ₅	168—170 ^c	C ₁₅ H ₁₃ ClN ₂ O ₂ S ₂ (352·9)	51·06	3·71	10·05	7·94	18·17
				51·32	3·95	10·26	7·87	17·90
III _h	4-ClC ₆ H ₄ CH ₂ C ₆ H ₅	144—145 ^c	C ₁₅ H ₁₃ ClN ₂ O ₂ S ₂ (352·9)	51·06	3·71	10·05	7·94	18·17
				50·89	3·60	10·10	7·70	18·43
III _i	4-BrC ₆ H ₄ CH ₂ C ₆ H ₅	148—150 ^g	C ₁₅ H ₁₃ BrN ₂ O ₂ S ₂ (397·3)	45·34	3·28	20·11	7·05	16·14
				45·56	3·15	19·72	6·88	16·43
III _j	2,5-Cl ₂ C ₆ H ₃ CH ₂ C ₆ H ₅	91—93 ^a	C ₁₅ H ₁₂ Cl ₂ N ₂ O ₂ S ₂ (387·3)	46·52	3·12	18·31	7·23	16·55
				46·70	3·40	18·41	7·34	16·28
III _k	3,4-Cl ₂ C ₆ H ₃ CH ₂ C ₆ H ₅	118—120 ^g	C ₁₅ H ₁₂ Cl ₂ N ₂ O ₂ S ₂ (387·3)	46·52	3·12	18·31	7·23	16·55
				46·27	3·37	18·59	7·09	16·47
III _l	3-NO ₂ C ₆ H ₄ CH ₂ C ₆ H ₅	188—189 ^d	C ₁₅ H ₁₃ N ₃ O ₄ S ₂ (363·4)	49·58	3·61	—	11·56	17·65
				49·68	3·78	—	11·77	17·95
IV _a	C ₆ H ₅ COCH ₃	163—165 ^a	C ₁₀ H ₉ N ₂ O ₃ S ₂ (270·3)	44·43	3·73	—	10·36	23·72
				44·70	3·74	—	10·10	24·15
IV _b	C ₆ H ₅ CH ₂ COCH ₃	210—212 ^c	C ₁₁ H ₁₁ N ₂ O ₃ S ₂ (284·4)	46·46	4·25	—	9·85	22·25
				46·51	4·25	—	10·05	22·65
IV _c	2-CH ₃ C ₆ H ₄ COCH ₃	188—189 ^c	C ₁₁ H ₁₁ N ₂ O ₃ S ₂ (284·4)	46·46	4·25	—	9·85	22·55
				46·58	4·30	—	9·84	22·28
IV _d	3-ClC ₆ H ₄ COCH ₃	248—250 ^b	C ₁₀ H ₉ ClN ₂ O ₃ S ₂ (304·8)	39·41	2·98	11·63	9·19	21·04
				39·33	3·04	11·75	8·98	20·87
IV _e	4-BrC ₆ H ₄ COCH ₃	215—216 ^a	C ₁₀ H ₉ BrN ₂ O ₃ S ₂ (349·2)	34·39	2·60	22·88	8·02	18·36
				34·67	2·55	22·51	7·82	18·56
IV _f	2,5-Cl ₂ C ₆ H ₃ COCH ₃	186—188 ^f	C ₁₀ H ₈ Cl ₂ N ₂ O ₃ S ₂ (339·2)	35·41	2·38	20·90	8·26	18·90
				35·58	2·46	21·13	8·06	18·54
V _a	C ₆ H ₅ SCCl ₃	190—191 ^f	C ₉ H ₇ Cl ₃ N ₂ O ₂ S ₃ (377·7)	28·62	1·87	28·16	7·42	26·47
				28·73	2·11	28·21	7·18	25·33

TABLE I
(continued)

Com- pound	R R ¹	M.p., °C	Formula (mol.wt.)	Calculated/Found				
				% C	% H	% Cl/ /Br	% N	% S
<i>Vb</i>	2-CH ₃ C ₆ H ₄ SCCl ₃	138–140 ^c	C ₁₀ H ₉ Cl ₃ N ₂ O ₂ S ₃ (391.7)	30.66	2.32	27.15	7.15	24.55
				30.40	2.44	27.46	6.96	24.86
<i>Vc</i>	4-CH ₃ C ₆ H ₄ SCCl ₃	163–165 ^c	C ₁₀ H ₉ Cl ₃ N ₂ O ₂ S ₃ (391.7)	30.66	2.32	27.15	7.15	24.55
				30.80	2.09	26.94	6.89	24.24
<i>Vd</i>	2-ClC ₆ H ₄ SCCl ₃	181–183 ^c	C ₉ H ₆ Cl ₄ N ₂ O ₂ S ₃ (412.2)	26.23	1.47	34.41	6.80	23.32
				26.50	1.70	34.70	6.71	23.53
<i>Ve</i>	4-ClC ₆ H ₄ SCCl ₃	83–85 ^c	C ₉ H ₆ Cl ₄ N ₂ O ₂ S ₃ (412.2)	26.23	1.47	34.41	6.80	23.32
				26.44	1.56	34.03	6.83	23.12

Solvents in crystallisations: ^a acetone; ^b n-heptane-tetrachloromethane (4 : 1; v/v); ^c tetrachloromethane-chloroform (4 : 1); ^d chloroform; ^e tetrachloromethane; ^f tetrachloromethane-chloroform (1 : 1); ^g acetic acid; ^h chloroform-acetone (2 : 1).

TABLE II

The ¹H-NMR Chemical Shifts of Proton Signals in Some Compounds of Group III and IV (ppm, δ scale; s, singlet; m, multiplet)

Com- pound	CH ₂ s ^a	CH ₂ s ^b	CH ₃ s ^c	CH m ^d
<i>IIIg</i>	4.41	5.08	—	6.80–7.55
<i>IIIi</i>	4.76	5.11	—	7.00–7.75
<i>IIIk</i>	4.81	5.16	—	7.00–7.86
<i>IIIl</i>	4.43	5.13	—	7.00–8.40
<i>IVa</i>	4.74	—	1.98	7.06–7.76
<i>IVe</i>	4.72	—	1.98	7.53–7.82
<i>IVf</i>	4.32	—	2.07	7.26–7.62

^a Dithiazolidine ring; ^b benzyl group; ^c acetyl group; ^d aromatic ring.

The compounds of groups *II* to *V* and the appropriate starting 5-(subst. imino)-1,3,4-dithiazolidine 3,3-dioxides were tested as herbicides and fungicides. In all the cases, the biological activity was low.

EXPERIMENTAL

Melting points (uncorrected) were taken on a heated microscope stage (Kofler block). The IR spectra were recorded on a Perkin-Elmer apparatus with the use of the KBr method. The $^1\text{H-NMR}$ spectra were measured in deuteriochloroform (with compound *IIIk*, in hexadeuterio-dimethyl sulfoxide) on a Varian XL 100 apparatus (hexamethyldisilane as internal standard): The starting 5-(subst. imino)-1,3,4-dithiazolidine 3,3-dioxides¹ (*I*) and trichloromethanesulfonyl chloride³ were prepared by reported procedures. Methyl iodide, benzyl chloride, acetyl chloride and other chemicals were of Analytical Grade (Lachema, Brno, Czechoslovakia).

4-Methyl- and 4-Benzyl-5-(subst. imino)-1,3,4-dithiazolidine 3,3-Dioxides (*II* and *III*)

A solution of the appropriate dithiazolidine *I* (0.05 mol) in methanol (20 ml) and a solution of the respective alkyl halide (0.06 mol; 8.5 g of methyl iodide or 7.6 g of benzyl chloride) in methanol (20 ml) were added to methanolic sodium methoxide prepared from sodium (1.4; 0.06 gramatom) and methanol (60 ml). The mixtures were refluxed (2–6 h) until the alkaline reaction and the starting dithiazolidin *I* disappeared (as determined by moistened pH papers and thin-layer chromatography on Silufol UV₂₅₄ silica gel sheets from Kavalier Glassworks, Votice, Czechoslovakia, with the use of dichloromethane as eluant and detection in UV light) and taken down under diminished pressure on a rotatory evaporator. The residues were washed with water, dried (yields of 85–95%), and (if required) purified by crystallisation (Table I).

4-Acetyl- and 4-Trichloromethylthio-5-(subst. imino)-1,3,4-dithiazolidine 3,3-Dioxides (*IV* and *V*)

The appropriate dithiazolidine *I* (0.05 mol) was dissolved in methanolic sodium methoxide prepared from sodium (1.4 g; 0.06 gramatom) and methanol (60 ml). Toluene (180 ml) was then added (in order to precipitate the sodium salts) and the azeotropic mixture of solvents was removed (along with the remaining toluene) by distillation at ordinary pressure. Chloroform (50 ml) was added to the residual sodium salts with stirring at 20°C followed by a solution of the respective acyl chloride (0.06 mol; 4.7 g of acetyl chloride or 10.9 g of trichloromethanesulfonyl chloride) in chloroform (20 ml); the solution of the acyl chloride was added portionwise over 10 min. The stirring was continued for 10 min, the mixtures evaporated, the residues washed with water, dried (yields of about 80–90%), and (if required) purified by crystallisation (Table I).

Biological Assays

The herbicidal activity of compounds *II–V* was examined in both preemergent and postemergent application on the plants *Avena sativa*, *Fagopyrum vulgare*, *Sinapis alba*, *Panicum miliaceum*, and *Lepidium sativum*. The fungicidal activity was tested on the organisms *Erysiphe polyphaga*, *Er. graminis*, and *Phytophthora infestans* (on living plants), then on *Botrytis cinerea*, *Fusarium nivale*, and *Sclerotinia (in vitro)*, and finally on *Tilletia foetida* (model test).

Elemental analyses, IR spectra, and $^1\text{H-NMR}$ spectra were carried out in Central Laboratories, Prague Institute of Chemical Technology.

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