SYNTHESIS OF 5-(SUBST. IMINO)-1,3,4-DITHIAZOLIDINE 3,3-DIOXIDES BY REACTION OF ISOTHIOCYANATES WITH CHLOROMETHANESULFONAMIDE*

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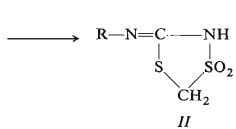
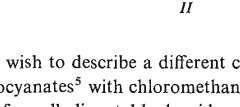
The title compounds *II* are formed in alkaline medium by the N-addition of chloromethanesulfonamide to aromatic or aliphatic isothiocyanates and spontaneous cyclisation of the assumed addition compounds *I*. The structure of compounds *II* is in accord with their chemical and spectral (IR, ^{1}H-NMR, and mass spectra) behaviour.

From the numerous nucleophilic additions to isothiocyanates[1,2], relatively little has been reported on the N-additions of amides (alkali metal salts of benzenesulfonamide[3], 3-nitrobenzenesulfonamide[3], methanesulfonamide[3], acetamide[4]) affording the corresponding acylated thioureas.



I



II

(*A*)

In the present paper we wish to describe a different course of the reaction of aromatic and aliphatic isothiocyanates[5] with chloromethanesulfonamide in the presence of an equimolar amount of an alkali metal hydroxide, see Scheme (*A*). The expected primary adducts *I* cannot be isolated in the present case since the subsequent removal of hydrogen chloride and cyclisation result in the formation of 5-(subst.imino)-1,3,4-dithiazolidine 3,3-dioxides (*II*) in 70–80% yields (Table I).

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The results of reaction (*A*) were compared under analogous conditions with those obtained in additions of methanesulfonamide to some of the above aromatic isothiocyanates; in the latter case, the reaction afforded normal, non-cyclic products.

TABLE I
5-(Subst. Imino)-1,3,4-dithiazolidine 3,3-Dioxides *II*

Compound R	M.p., °C	Formula (mol.wt.)	Calculated/Found				
			% C	% H	% Cl Br	% N	% S
IIa	180–182[a]	$C_8H_8N_2O_2S_2$	42·09	3·53	—	12·27	28·09
C_6H_5		(228·3)	42·28	3·67	—	12·31	27·82
IIb	135–137[b]	$C_9H_{10}N_2O_2S_2$	44·61	4·16	—	11·56	26·46
$2\text{-}CH_3C_6H_4$		(242·3)	44·77	4·28	—	11·29	26·20
IIc	209–211[c]	$C_9H_{10}N_2O_2S_2$	44·61	4·16	—	11·56	26·46
$3\text{-}CH_3C_6H_4$		(242·3)	44·72	4·19	—	11·32	26·17
IId	193–195[d]	$C_9H_{10}N_2O_2S_2$	44·61	4·16	—	11·56	26·46
$4\text{-}CH_3C_6H_4$		(242·3)	44·82	4·27	—	11·64	26·33
IIe	160–161[e]	$C_9H_{10}N_2O_3S_2$	41·85	3·90	—	10·84	24·82
$2\text{-}CH_3OC_6H_4$		(258·3)	41·86	3·97	—	10·80	25·09
IIf	134–136[d]	$C_8H_7ClN_2O_2S_2$	36·57	2·68	13·49	10·66	24·41
$2\text{-}ClC_6H_4$		(262·7)	36·74	2·80	13·62	10·61	24·65
IIg	229–231[f]	$C_8H_7ClN_2O_2S_2$	36·57	2·68	13·49	10·66	24·41
$3\text{-}ClC_6H_4$		(262·7)	36·90	2·82	13·31	10·36	24·29
IIh	239–241[g]	$C_8H_7ClN_2O_2S_2$	36·57	2·68	13·49	10·66	24·41
$4\text{-}ClC_6H_4$		(262·7)	36·80	2·86	13·28	10·83	24·12
IIi	230–232[f]	$C_8H_6Cl_2N_2O_2S_2$	32·33	2·03	23·86	9·43	21·58
$2,5\text{-}Cl_2C_6H_3$		(297·2)	32·60	2·21	23·94	9·32	21·29
IIj	249–251[f]	$C_8H_6Cl_2N_2O_2S_2$	32·33	2·03	23·86	9·43	21·58
$3,4\text{-}Cl_2C_6H_3$		(297·2)	32·62	2·23	24·11	9·50	21·60
IIk	260–262[f]	$C_8H_7BrN_2O_2S_2$	31·28	2·30	26·01	9·12	20·88
$4\text{-}BrC_6H_4$		(307·2)	31·48	2·40	26·18	9·16	20·76
IIl	255–257[e]	$C_8H_7N_3O_4S_2$	35·16	2·58	—	15·38	23·46
$3\text{-}NO_2C_6H_4$		(273·3)	35·42	2·80	—	15·34	23·19
IIm	258–260[f]	$C_8H_7N_3O_4S_2$	35·16	2·58	—	15·38	23·46
$4\text{-}NO_2C_6H_4$		(273·3)	35·36	2·36	—	15·51	23·30
IIn	124–126[h]	$C_9H_{10}N_2O_2S_2$	44·44	4·14	—	11·52	26·37
$C_6H_5CH_2$		(243·2)	44·68	4·31	—	11·25	26·14
IIo	60–62[i]	$C_5H_8N_2O_2S_2$	31·24	4·19	—	14·57	33·36
$CH_2{=}CHCH_2$		(192·3)	31·45	4·30	—	14·80	33·30

Solvents in crystallisations: [a] chloroform–ethanol (5 : 2, v/v); [b] tetrachloromethane; [c] chloroform–acetone (2 : 1); [d] tetrachloromethane–chloroform (4 : 1), [e] ethanol; [f] acetone; [g] acetone–chloroform (5 : 1); [h] tetrachloromethane–chloroform (1 : 1); [i] water–ethanol (4 : 1) or water.

The required reaction times and the yields of compounds *II* (*IIa* – 14 h, 84%; *IIe* – 17 h, 73%; *IIf* – 22 h, 68%) are very similar to those observed in the formation of substituted thioureas from methanesulfonamide (14 h, 82%; 18 h, 76%; 21 h, 70%). In additions of both methanesulfonamide and chloromethanesulfonamide, the relatively slow formation of the adduct type *I* may be regarded as the rate determining step while the subsequent loss of hydrogen chloride and cyclisation are very fast in the case of chloromethanesulfonamide.

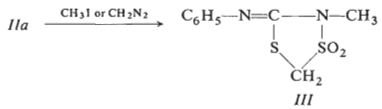
The expected structure of dithiazolidine derivatives *II* is in accord with chemical properties such as stability towards mercuric oxide in refluxing ethanol[6] (proof of the sulfide sulfur in a cycle) or the acidic behaviour of the —NH— group (induction effect of the vicinal —SO_2— group) manifesting itself in the formation of salts with solutions of alkali metal hydroxides (the salts are mostly poorly soluble in water). 5-Phenylimino-1,3,4-dithiazolidine 3,3-dioxide (*IIa*) was successfully N-methylat-

TABLE II

Characteristic Bands in IR Spectra (cm^{-1}) of 5-Allylimino- and 5-Phenylimino-1,3,4-dithiazolidine 3,3-Dioxides (*IIo* and *IIa*, resp.) and the N-Methyl Derivative *III*

IIo	*IIa*	*III*	*IIo*	*IIa*	*III*
3 260 (s)	3 280 (s)				1 115 (s)
	3 200 (w)			1 075 (w)	1 070 (m)
	3 140 (m)			1 055 (w)	
3 050 (m)	3 090 (m)	3 080 (w)	1 030 (m)	1 025 (w)	1 020 (w)
3 015 (w)	3 000 (m)	3 060 (w)	980 (m)	955 (s)	950 (s)
		3 020 (m)	915 (s)	905 (m)	
2 960 (m)	2 940 (m)	2 945 (w)	860 (w)	852 (m)	875 (w)
		2 920 (w)		845 (w)	
1 645 (m)	1 605 (s)	1 600 (s)		825 (m)	820 (w)
1 595 (s)	1 575 (vs)	1 570 (vs)		810 (w)	795 (s)
1 535 (m)	1 555 (s)		770 (w)	760 (s)	760 (w)
	1 495 (m)	1 490 (m)	745 (w)	745 (w)	745 (m)
	1 485 (m)	1 460 (w)		710 (w)	700 (s)
1 430 (m)	1 445 (m)	1 445 (m)	670 (w)	685 (m)	670 (w)
1 405 (w)		1 440 (s)	640 (w)	620 (w)	625 (m)
1 395 (w)	1 380 (w)	1 360 (s)		610 (w)	615 (m)
1 350 (w)		1 351 (s)	585 (m)	585 (m)	605 (m)
1 300 (s)	1 315 (vs)	1 305 (s)		575 (w)	560 (m)
1 260 (s)	1 255 (m)	1 285 (s)		530 (m)	535 (m)
1 190 (s)	1 175 (vs)	1 190 (s)		500 (m)	
1 120 (s)	1 120 (vs)	1 135 (s)		470 (s)	480 (s)

ed with the formation of compound *III*, see equation (*B*). Compound *IIa* reacts slowly with bromine to afford the corresponding 4-bromophenyl derivative (identical with compound *IIk*).



(*B*)

The IR and ^{1}H-NMR spectra of compounds *II* exhibit the expected absorption bands and signals of characteristic groups. The spectra of the particular compounds *II* are very similar, some differences being due to various substituents on the aromatic ring and the like. Only some examples are therefore shown in Table II. Thus, bands in the 2920 to 3090 cm^{-1} region correspond to stretching vibrations of CH_3, CH_2, and CH in the aromatic ring. At 1485 cm^{-1}, the bending vibration of CH_2 manifests itself. In the 1600 to 1485 cm^{-1} region, the spectrum exhibits very intense bands of the skeletal C=C vibration of the aromatic ring which coalesce with the C=N vibration[7] (an intense band at 1600 cm^{-1}, accompanied by bands at 1645 and 1535 cm^{-1} is also present in the spectrum of the 5-allylimino derivative *IIo*). Bands at 1120 (*IIa*, *IIo*) or 1115 cm^{-1} (*III*) correspond to the symmetrical stretching vibration of the SO_2 group while the asymmetric vibration of this group manifests itself at 1315 cm^{-1}. Bands of the NH group vibrations at 3260 cm^{-1} (*IIo*) are split with compound *IIa* (due to measurement in KBr, *cf.*[8]) and absent in the spectrum of com-

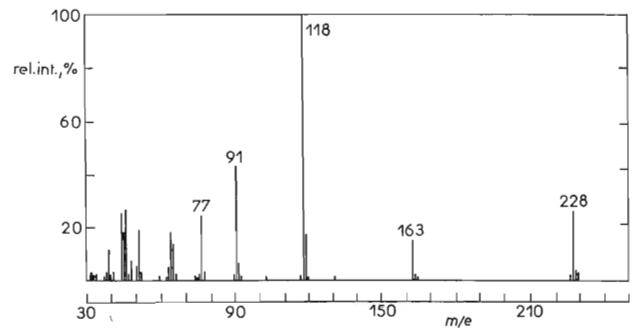


FIG. 1
Mass Spectra of 5-Phenylimino-1,3,4-dithiazolidine 3,3-Dioxide (*IIa*)

pound *III*. The ^{1}H-NMR spectrum of 5-phenylimino-1,3,4-dithiazolidine 3,3-dioxide (*IIa*) exhibits a CH_2 singlet at 4·75 ppm (δ scale), a multiplet of aromatic protons at 7·06 to 7·70 ppm (integral intensity ratio, 2 : 5), and a broad NH signal at 11·10 ppm (the integral intensity is approximately by 30% lower than the theoretical value, probably due to the existence of tautomeric structures). The ^{1}H-NMR spectrum of compound *III* exhibits a singlet of NCH_3 protons at 3·47 ppm, a CH_2 singlet at 4·68 ppm, and a multiplet of aromatic protons at 7·51 ppm while the NH signal is lacking. Integral intensities agree with expectations.

The structure of the present dithiazolidine derivatives *II* is also supported by the mass spectra of compound *IIa* and the corresponding N-methyl derivative *III* (Figs 1 and 2). The fragmentation pattern is similar in both cases except for one intermediary stage). Potential structures of the particular fragments are shown in Scheme 1; the paths proposed are supported by a relatively ready formation of substituted carbodiimides from compounds containing the —N—C(—S)—N— grouping in some other degradations (thermal or by chemical agents)[9].

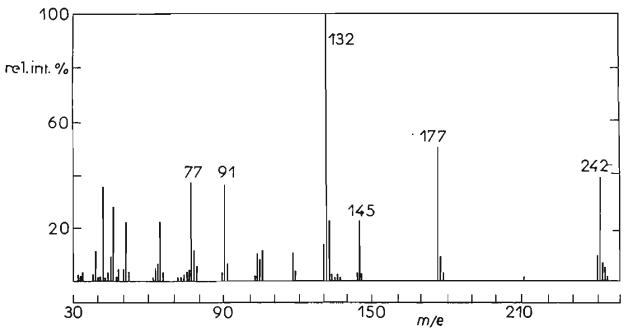
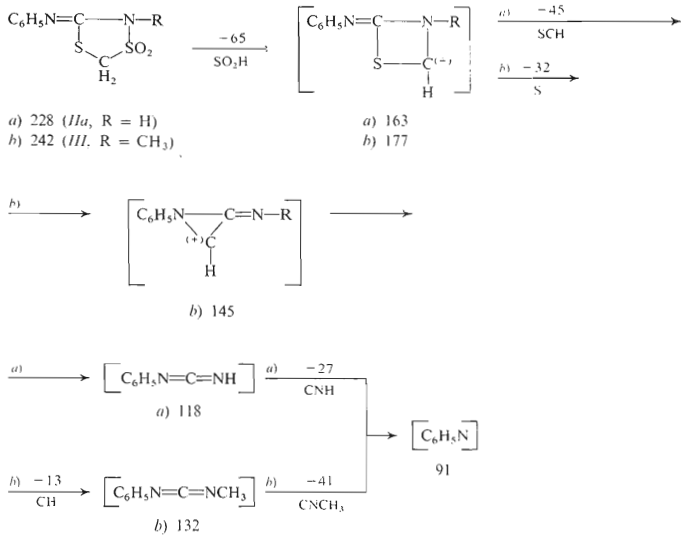


FIG. 2

Mass Spectra of 4-Methyl-5-phenylimino-1,3,4-dithiazolidine 3,3-Dioxide (*III*)



SCHEME 1

EXPERIMENTAL

Melting points (uncorrected) were taken on a heated microscope stage (Kofler block). The IR spectra were recorded on a Perkin-Elmer apparatus by the KBr method. The ^{1}H-NMR spectra were measured on a Varian XL 100 apparatus at 100 MHz in hexadeuteriodimethyl sulfoxide (hexamethyldisilane as internal standard). The mass spectra were taken on a Varian MAT-311 apparatus by the DADI technique[10] (direct inlet at 25°C, the ion source temperature 200°C, ionising potential 70 eV. The starting compounds (chloromethanesulfonamide[11], methanesulfonamide[12], isothiocyanates[13–17]) were prepared by reported procedures.

5-(Subst.Imino)-1,3,4-dithiazolidine 3,3-Dioxides *II*

A solution of the appropriate aromatic or aliphatic isothiocyanate (0·50 mol) and chloromethanesulfonamide (0·55 mol; 71·3 g) in acetone (300 ml) was treated at 50°C over 30 min with 0·55 mol of sodium hydroxide (or potassium hydroxide but not pyridine or triethylamine) in 30 ml of water. The mixture was stirred at 50°C for 8 to 24 h until the alkalinity dropped below pH 8·5 (moistened pH paper). The decreasing amount of the isothiocyanate was determined by thin-layer chromato-

graphy on ready-for-use Silufol UV_{254} (Kavalier Glassworks, Votice, Czechoslovakia) silica gel sheets (ethyl acetate as eluant; detection in UV light). When the reaction was complete, the mixture was acidified with hydrochloric acid and taken down on a rotatory evaporator at 50°C. The residue was washed with water, dried, and washed with two 50 ml portions of cold chloroform (except for *IIo* which was directly crystallised). The thus-obtained compounds *II* (yields, 70—80%) were purified by crystallisation (for solvents see Table I) for purposes of elemental analysis and spectral measurements.

Substituted Methanesulfonylthioureas

The procedure was analogous to the preceding paragraph except for the use of methanesulfonamide instead of chloromethanesulfonamide. When the reaction was complete, the mixtures were diluted with water (200 ml) and adjusted to pH 3 with hydrochloric acid. The thus-obtained substituted methanesulfonylthioureas were collected with suction, washed with water, dried, and (if required) purified by crystallisation. The following compounds were prepared in this manner:

N-*Phenyl*-N′-*methanesulfonylthiourea*[3]. M.p. 165—167°C.

N-(2-*Methoxyphenyl*)-N′-*methanesulfonylthiourea*. M.p. 169—171°C (ethanol). For $C_9H_{12}N_2O_3S_2$ (260·3) calculated: 41·52% C, 4·65% H, 10·76% N, 24·63% S; found: 41·68% C, 4·67% H, 10·61% N, 24·34% S.

N-(4-*Methoxyphenyl*)-N′-*methanesulfonylthiourea*. M.p. 144—146°C (ethanol). For $C_9H_{12}N_2O_3S_2$ (260·3) calculated: 41·52% C, 4·65% H, 10·76% N, 24·64% S; found: 41·47% C, 4·44% H, 10·52% N, 24·41% S.

N-(2-*Chlorophenyl*)-N′-*methanesulfonylthiourea*. M.p. 179—180°C (1,1,2,2-tetrachloroethane). For $C_8H_9ClN_2O_2S_2$ (264·8) calculated: 36·29% C, 3·43% H, 13·39% Cl, 10·58% N, 24·22% S, found: 36·40% C, 3·55% H, 13·46% Cl, 10·53% N, 24·10% S.

4-Methyl-5-phenylimino-1,3,4-dithiazolidine 3,3-Dioxide (*III*)

A. A mixture of compound *IIa* (11·4 g; 0·05 mol), 1M methanolic sodium methoxide (55·0 ml), methyl iodide (7·8 g; 0·55 mol), and methanol (100 ml) was refluxed for 2 h (drop of alkalinity) and evaporated under diminished pressure. The residue was washed with water, dried, and the solid (11·45 g; 94·5%) crystallised from acetone to afford 9·9 g (81·6%) of compound *III*, m.p. 180—181°C. For $C_9H_{10}N_2O_2S_2$ (242·3) calculated: 44·61% C, 4·16% H, 11·56% N, 24·46% S, found: 44·53% C, 4·31% H, 11·80% N, 24·20% S.

B. Ethereal diazomethane was added in 5 ml portions at 20°C to a solution of compound *IIa* (2·28 g; 0·01 mol) in methanol (50 ml) as long as nitrogen was evolved and until the yellow-green colour of the solution persisted for 3 h. The solution was evaporated and the residue recrystallised from tetrachloromethane. Yield, 95·5% of compound *III*, m.p. 180—181°C, identical (IR spectrum, m.p.) with the specimen obtained in the preceding paragraph.

Bromination of Compound *IIa*

Bromine (9·6 g; 0·06 gramatom) and iodine (0·1 g) was added to a solution of compound *IIa* (4·56 g; 0·02 mol) in tetrachloromethane (100 ml) and the whole kept at 20°C for 60 h. The mixture was then shaken with aqueous sodium thiosulfate, the solid collected with suction, and the tetrachloromethane filtrate evaporated. The residue was combined with the above solid (total

5·6 g; m.p. 256—258°C) and crystallised from acetone to afford compound *IIk*, m.p. 260—262°C, identical (IR spectrum, m.p.) with the specimen obtained by a direct synthesis.

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