

REACTIONS OF SULFONYLISOTHIOCYANATES WITH SOME 1,3-DIPOLES

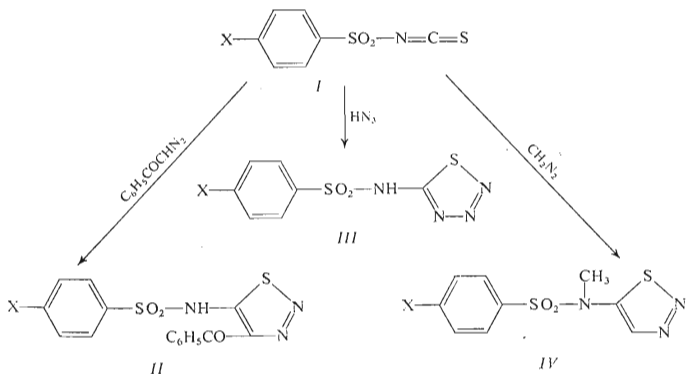
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Received March 26th, 1976

In this study the reaction of some phenylsulfonyl isothiocyanates (*I*) with ω -diazoacetophenone azoimide and diazomethane are discussed. On the basis of IR, $^1\text{H-NMR}$ and mass spectra the structures of the cycloaddition products obtained is discussed, *i.e.* of 4-benzoyl-5-phenyl-sulfonylamino-1,2,3-thiadiazoles (*II*), 5-phenylsulfonylamino-1,2,3,4-thiadiazoles (*III*) and *N*-methyl-5-phenylsulfonylamino-1,2,3-thiadiazoles (*IV*).

In our papers^{1,2}, as well as in the papers of some other authors³⁻⁷ cycloaddition reactions of isothiocyanates of various types with numerous 1,3-dipoles have been investigated. The course of these reactions is considerably influenced by substituents R in R-NCS . It is known³ that isothiocyanates are less reactive in these reactions than isocyanates, in consequence of the lower polarity of the $\text{C}=\text{S}$ bond in the NCS

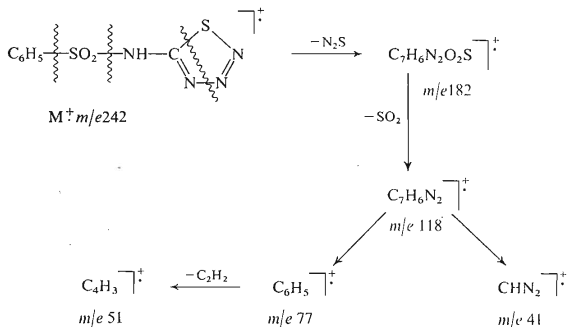


SCHEME 1

group. Therefore we endeavoured to introduce the SO_2 group between the aromatic nucleus and the NCS group and so to increase its reactivity with common 1,3-dipolar reagents. Simultaneously we wanted to reinvestigate the course of the cycloaddition from the point of view of the existence of two possible reaction centres, *i.e.* $\text{C}=\text{N}$ resp. $\text{C}=\text{S}$ bonds in the NCS group.

The phenylsulfonyl isothiocyanates employed in the reaction were prepared by reacting corresponding phenylsulfonylamides with CS_2 and KOH , under formation of potassium salts of corresponding benzenesulfonyldithiocarbamic acids. According to ref.^{7,8}, these afford corresponding phenylsulfonyl isothiocyanates under the effect of SOCl_2 , in good yields. The prepared isothiocyanates were not isolated in pure state from the reaction medium, because they polymerize and decompose easily. They were identified by means of IR spectra and their concentration was determined by hydrolysis to sulfonamides, which takes place quantitatively⁷.

The cycloaddition reactions (Scheme 1) were carried out by mixing ethereal solutions of isothiocyanates with ethereal solutions of ω -diazooacetophenone or diazomethane. In the case of azoimide benzene solutions were used. The reaction of sulfonyl isothiocyanates with diazomethane took place instantaneously under formation of a precipitation and liberation of N_2 . The precipitation of the solid in the reaction with azoimide took place after 4–8 h. The reaction with ω -diazooacetophenone was slowest, it took place 24 h.



SCHEME 2

The structure of the cycloadducts obtained (Table I) was confirmed by means of IR, $^1\text{H-NMR}$ and mass spectra. Absorption bands in the 3200 cm^{-1} region could be observed in the infrared absorption spectra of the compounds *IIa-c* or *IIIa-c* prepared (Table II), belonging to $\nu(\text{N-H})$ vibrations, which indicates that the ad-

dition of ω -diazoacetophenone and azoimide took place at the C=S bond of the NCS group. This assumption is also confirmed by the fragmentation (in the mass spectrum) of compounds *II* and *III*, a part of which – for derivative *IIIa* – is represented in Scheme 2.

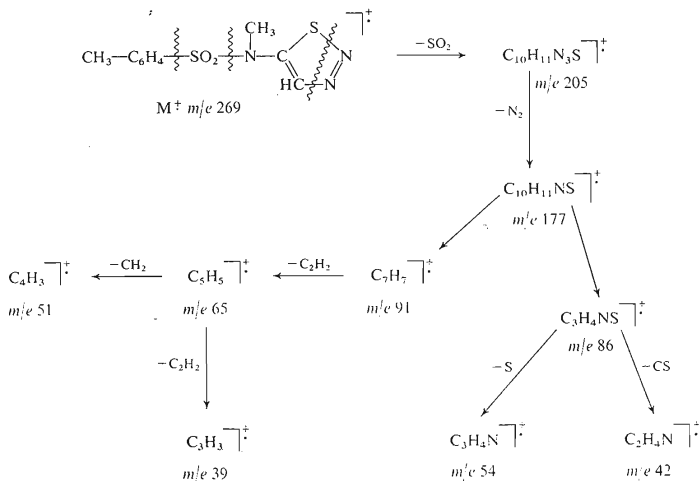
In the infrared spectra of compounds *IVa–c* the vibrations in the 3200 cm^{-1} ($\gamma(\text{N—H})$) region were absent, but in the $^1\text{H-NMR}$ spectra of all compounds *IVa–c* a singlet due to the CH_3 group protons ($\delta_1 = 3.25$ ppm) was observed. In the case of compound *IVb*, i.e. 4-tolyl derivative, two singlets were observed ($\delta_1 = 3.25$ ppm and $\delta_2 = 2.33$ ppm). On the basis of this observation we assume that in the case of the reaction of phenylsulfonyl isothiocyanates with diazomethane methylation of the secondary amino group with diazomethane takes place simultaneously with the cyclization, because a molar excess of diazomethane was always used. This assump-

TABLE I
List of Synthesized Compounds

Compound	Substituent X	Formula (m.w.)	Calculated/Found		M.p., °C (yield, %)
			% N	% S	
<i>Ila</i>	H	$\text{C}_{15}\text{H}_{11}\text{N}_3\text{O}_3\text{S}_2$ (354.4)	12.50 12.40	18.60 18.74	142–144 (40)
<i>Ilb</i>	CH_3	$\text{C}_{16}\text{H}_{13}\text{N}_3\text{O}_3\text{S}_2$ (359.4)	11.70 12.80	17.80 18.06	167–168 (75)
<i>Ilc</i>	Cl	$\text{C}_{15}\text{H}_{10}\text{ClN}_3\text{O}_3\text{S}_2$ (379.8)	11.10 11.25	16.90 17.09	182–183 (34)
<i>IIIa</i> ^a	H	$\text{C}_7\text{H}_6\text{N}_4\text{O}_2\text{S}_2$ (242.0)	23.10 23.50	26.50 26.62	132–133 (80)
<i>IIIb</i> ^a	CH_3	$\text{C}_8\text{H}_8\text{N}_4\text{O}_2\text{S}_2$ (256.3)	21.70 21.66	24.95 24.84	138–139 (85)
<i>IIIc</i> ^a	Cl	$\text{C}_7\text{H}_5\text{ClN}_4\text{O}_2\text{S}_2$ (276.7)	20.40 20.60	23.30 23.46	133–135 (82)
<i>IVa</i>	H	$\text{C}_9\text{H}_9\text{N}_3\text{O}_2\text{S}_2$ (255.3)	16.50 16.38	25.20 25.16	131–132 (65)
<i>IVb</i>	CH_3	$\text{C}_{10}\text{H}_{11}\text{N}_3\text{O}_2\text{S}_2$ (269.0)	15.60 15.67	23.90 23.98	142–144 (78)
<i>IVc</i>	Cl	$\text{C}_9\text{H}_8\text{ClN}_3\text{O}_2\text{S}_2$ (289.8)	14.50 14.48	22.20 22.33	127–128 (58)

^a Lit.⁶ *IIIa* yield 88%, m.p. 132°C; *IIIb* yield 87%, m.p. 138°C; *IIIc* yield 82%, m.p. 133°C.

tion is also confirmed by the fragmentation observed in the mass spectra of compounds *IVd-c*. In Scheme 3 a part of the fragmentation of derivative *IVb* is shown.



SCHEME 3

TABLE II

Characteristic Vibrations in the Absorption Spectra of the Compounds Prepared (cm^{-1})

Compound	ν Skeleton	$\nu(\text{SO}_2)_s$	$\nu(\text{SO}_2)_{as}$	$\delta(\text{CH})$	$\nu(\text{NH})$	$\nu(\text{C}=\text{O})$
<i>Ila</i>	1 310, 1 520, 1 590	1 175	1 380	3 060	3 200	1 645
<i>Ilb</i>	1 310, 1 470, 1 525, 1 580	1 175	1 380	3 076	3 200	1 650
<i>Ilc</i>	1 310, 1 475, 1 522, 1 590	1 175	1 390	3 065	3 200	1 648
<i>IIIa</i>	1 305, 1 420, 1 520, 1 590	1 170	1 370	3 085	3 195	—
<i>IIIb</i>	1 305, 1 420, 1 525, 1 590	1 170	1 370	3 090	3 190	—
<i>IIIc</i>	1 305, 1 420, 1 530, 1 585	1 170	1 370	3 085	3 200	—
<i>IVa</i>	1 300, 1 485, 1 520, 1 585	1 175	1 365	3 060	—	—
<i>IVb</i>	1 330, 1 490, 1 520, 1 580	1 175	1 370	3 095	—	—
<i>IVc</i>	1 300, 1 485, 1 530, 1 570	1 170	1 365	3 100	—	—

On the basis of the results obtained it can be stated that cycloaddition reaction of phenylsulfonyl isothiocyanates with diazoacetophenone, azoimide and diazomethane has a similar course as in the case of other isothiocyanates investigated, *i.e.* on the C=S bond, but more rapidly and in higher yields.

EXPERIMENTAL

The phenylsulfonyl isothiocyanates used were prepared according to Hartke⁹. The infrared absorption spectra of the compounds studied were measured with a UR 20, Zeiss, Jena spectrophotometer, using KBr technique. The ¹H-NMR spectra were obtained on a Tesla BS-847C spectrophotometer, in deuteriochloroform or hexadeuteriodimethyl sulfoxide as solvents and hexamethyldisilane oxide as a reference. The mass spectra were obtained with a MS-902-S spectrometer of AEI Manchester. The energy of ionizing electrons was 70 eV, in a 100 μA current of electrons and at a temperature of 80 to 150°C in the ionization chamber. The reaction of phenylsulfonyl isothiocyanates with azoimide was carried out according to a procedure given in ref.⁶. The derivatives *IIIa-c* obtained are listed in Table I.

Reaction of Phenylsulfonylisothiocyanates with ω-Diazoacetophenone

An ethereal solution of ω-diazoacetophenone (0.01 mol; 19.3 ml) was added to 10 ml of an ethereal solution containing 0.01 mol of the corresponding sulfonyl isothiocyanate and the mixture was allowed to stand at room temperature for 48 hours. The mixture obtained was separated and crystallized from ethanol. Characteristic data of the 4-benzoyl-5-phenylsulfonylamino-1,2,3-thiadiazoles *IIa-c* obtained are given in Table I.

Reaction of Phenylsulfonylisothiocyanates with Diazomethane

An ethereal solution (10 ml) of corresponding phenylsulfonylisothiocyanate (0.01 mol) was added gradually to 25 ml of an ethereal solution containing 0.02 mol of diazomethane. A solid substance already began to precipitate during the addition. After 4 h standing at room temperature the solid material was separated by filtration and crystallized from ethanol. Characteristic data of the N-methyl-5-phenylsulfonylamino-1,2,3-thiadiazoles *IVa-c* prepared are listed in Table I.

REFERENCES

1. Uher M., Rybár A., Martvoň A., Leško J.: This Journal *41*, 1182 (1976).
2. Uher M., Rybár A., Martvoň A., Leško J.: Chem. Zvesti, in press.
3. Huisgen R.: Angew. Chem. *75*, 604 (1963).
4. Van Loock, Vandesavel J. M., L'Abbe G., Smets G.: J. Org. Chem. *38*, 2916 (1973).
5. McFarland J. W., Houser R. W.: J. Org. Chem. *33*, 340 (1968).
6. Neidlein R., Salzmann K.: Synthesis *1975*, 52.
7. Schaumann E., Sieviking S., Walter W.: Tetrahedron *30*, 4147 (1974).
8. Reid W., Beck B. M.: Justus Liebigs Ann. Chem. *673*, 128 (1964).
9. Hartke K.: Arch. Pharm. *299*, 174 (1966).

Translated by Ž. Procházka.