

Isothiocyanates. XLVII.

Reaction of substituted benzyl isothiocyanates with diazomethane

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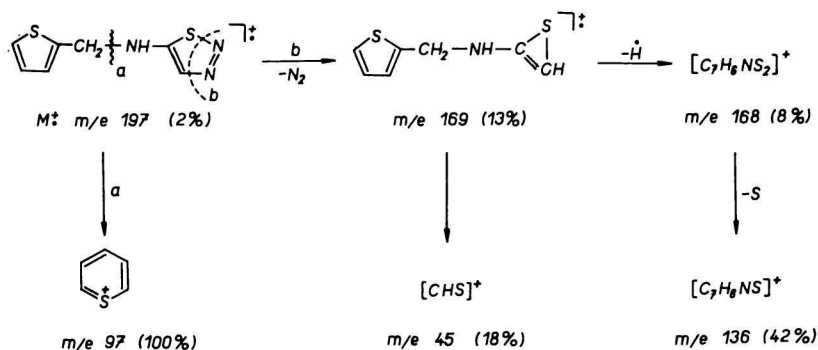
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Received 27 May 1975

The reaction of isothiocyanates of general formula $R-CH_2-NCS$, where R = phenyl-, 3- and 4-nitrophenyl-, 2-furyl-, 5-nitro-2-furyl- and 2-thienyl, with diazomethane is described. The ultraviolet and mass spectra of 1,2,3-thiadiazoles thus prepared are interpreted.

Описывается реакция изотиоцианатов общей формулы $R-CH_2-NCS$, где R = π -фенил-, 3- и 4-нитрофенил-, 2-фурил-, 5-нитро-2-фурил- и 2-тиенил с диазометаном. Обсуждаются ультрафиолетовые и масс-спектры.

Our previous paper dealt with the reaction of aromatic isothiocyanates with diazomethane [1]. In this part we wish to discuss the reaction of less reactive isothiocyanates of general formula $R-CH_2-NCS$, where R = phenyl-, 3- and 4-nitrophenyl-, 2-furyl-, 5-nitro-2-furyl- and 2-thienyl, with an ethereal solution of diazomethane, for only one paper dealing with the preparation of 5-benzylamino-1,2,3-thiadiazole has been published as yet [2].



Scheme 1

R		m.p.	Calcd.		M.p.	log ϵ	log ϵ	
			Found					
			N	S				
Benzyl	$C_9H_9N_3S$	191.2	—	—	9.0	94—95 ^a	232	302
							3.68	4.17
4-Nitrobenzyl	$C_9H_8N_4O_2S$	236.2	23.71	13.57	19.5	153—155	267	301
			23.50	13.39			4.22	4.01
3-Nitrobenzyl	$C_9H_8N_4O_2S$	236.2	23.71	13.57	15.5	125—128	265	300
			23.58	13.67			3.29	3.28
2-Furfuryl	$C_7H_7N_3OS$	181.2	23.15	17.70	14.2	145—147	252	301
			22.91	17.79			3.95	3.78
5-Nitro-2-furfuryl	$C_7H_6N_4O_3S$	226.2	24.77	14.17	21.2	196—199 (decomp.)	230	305
			25.00	13.99			3.82	4.29
2-Thienyl	$C_7H_7N_3S_2$	197.2	21.30	32.50	15.1	84—85	235	302
			21.38	32.55			4.05	4.08

a) Ref. [2] reports the m.p. and yield to be 93—95°C and 7.3%, respectively.

The starting isothiocyanates were prepared by the thiophosgene method excepting 2-thenyl isothiocyanate, which was synthesized also *via* thiocyanate; 2-furfuryl isothiocyanate could alternatively be obtained by isomerization of 2-furfuryl thiocyanate, it has been reported that up to 20% of the corresponding thiocyanate remained unchanged in the reaction mixture [3].

4-Nitrobenzyl isothiocyanate was reacted with diazomethane for 2 days at room temperature, other isothiocyanates for 10 days. Ether was removed from the reaction mixture upon standing in an open flask and the residue was crystallized from ethanol and chloroform. The relatively low yields of the thiadiazoles prepared (Table 1) indicate the low reactivity of the isothiocyanates under study.

The ultraviolet spectra of substituted 5-amino-1,2,3-thiadiazoles revealed two maxima in the 230—267 and 300—305 nm ranges (Table 1). The absorption maximum at higher wavelengths might be due to a conjugated system in the 1,2,3-thiadiazole ring.

It has been found that the mass spectra of some derivatives of 1,2,3-thiadiazoles contained the characteristic species $[M-N_2]^+$ [4]. Further fragmentation depends both on the structure of the molecule and substituents.

The base peak of 5-(2-thenyl)amino-1,2,3-thiadiazole at m/e 97 belonged to the thiopyrylium ion [5], the formation of which is in this case more favoured than the fission of molecular nitrogen from the thiadiazole ring. The fragmentation pattern is shown in Scheme 1.

Experimental

Benzyl-, 4-nitro- and 3-nitrobenzyl isothiocyanates were prepared by the thiophosgene method according to [6], 2-furfuryl isothiocyanates according to [7]. 5-Nitro-2-furfuryl isothiocyanate was synthesized from furfuryl alcohol: nitration afforded 5-nitrofurfuryl nitrate which, upon reaction with metal halides, furnished the corresponding halide; this was without isolation reacted with hexamethylenetetramine to form the complex salt, which was decomposed in the reaction medium with a stream of dry hydrogen chloride to yield 5-nitrofurfurylammonium chloride. The latter furnished the corresponding isothiocyanate [8]. 2-Thenyl isothiocyanate was obtained both by the thiophosgene and thiocyanate methods according to [9]. The ethereal solution of diazomethane was prepared by an alkaline decomposition of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (commercially available Diazald) [10].

The ultraviolet spectra of thiadiazoles prepared were recorded with a UV VIS (Zeiss, Jena) spectrophotometer in the 200—350 nm region in 10 mm cells as methanolic solutions at a 3×10^{-5} M concentration.

The mass spectra of selected compounds were measured with an MS 902 S (AEI Manchester) spectrometer with an direct inlet system at 70 eV, trap current 100 μ A. The temperature of the ionizing chamber was between 70 to 110°C, depending on the volatility of each compound.

5-(R-Amino)-1,2,3-thiadiazoles

An ethereal solution of diazomethane (0.01 mole) was added dropwise to the solution of the respective isothiocyanates (0.01 mole) in ether (20 ml). The reaction mixture was kept thoroughly closed at room temperature for 10 days. The solution was then poured into a crystallization dish and the solvent was allowed to evaporate. The crystals obtained were crystallized from ethanol or ether; their characteristic data are given in Table 1.

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Translated by Z. Votický