

Isothiocyanates. XLVIII. Preparation and mass spectra of 1,2,3-thiadiazoles

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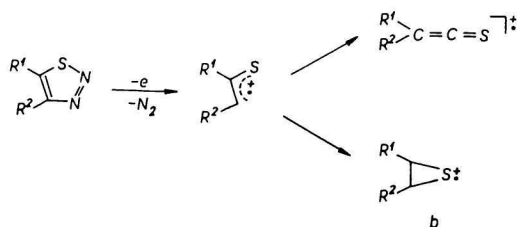
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The preparation of 4-methyl-5-(R-amino)-1,2,3-thiadiazoles from the appropriate isothiocyanates and an ethereal solution of diazoethane is described and mass spectra of the synthesized thiadiazoles are interpreted.

Описывается приготовление 4-метил-5-(R-амино)-1,2,3-тиадиазолов реакцией изотиоцианатов с эфирным раствором диазоэтана и обсуждаются масс-спектры синтезированных тиадиазолов.

The reaction of substituted phenyl isothiocyanates with diazoethane has already been reported [1], as well as that of acyl isothiocyanates with the same reagent [2]. 4-Methyl-5-phenylamino-1,2,3-thiadiazole has been synthesized to study the mass spectral fragmentation [3].

In this part we report the preparation of 4-methyl-5-(R-amino)-1,2,3-thiadiazoles from 4-substituted phenyl isothiocyanates, or 2-naphthyl isothiocyanate and diazoethane. The yields of the synthesized thiadiazoles (Table 1) indicate similar reactivities of diazoethane and diazomethane in reactions with aromatic isothiocyanates [4].



Scheme 1

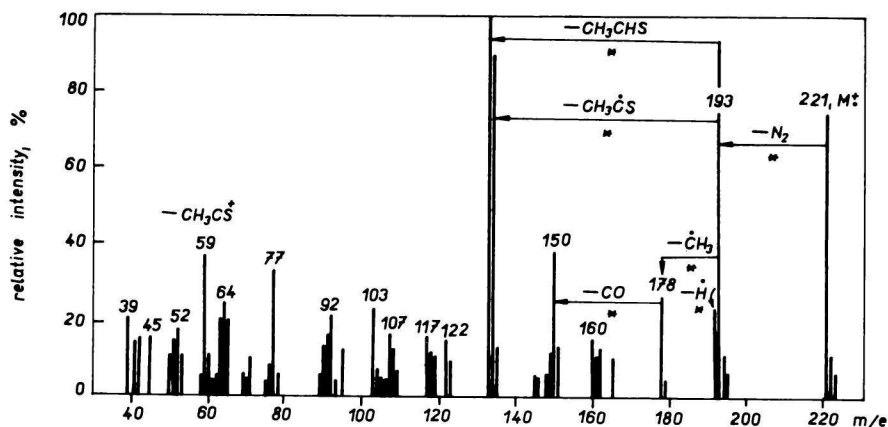


Fig. 1. Mass spectrum of 4-methyl-5-(4-methoxyphenyl)amino-1,2,3-thiadiazole.

The ultraviolet spectra of 4-methyl-5-(R-amino)-1,2,3-thiadiazoles are characterized by two absorption maxima and a shoulder in the 278–292 nm region (Table 1).

The mass spectra revealed relatively intense molecular ion peaks (Figs. 1–5). The principal fragmentation pathway of 1,2,3-thiadiazoles involved the fission of a nitrogen molecule to form $[M-N_2]^+$ ions [5]. Depending on substituents either a thioketal [6] *a*, or a cyclic structure *b* [3] was presumed for this radical ion (Scheme 1).

Structure *b* could explain the elimination of the CH_3CS radical from the species $[M-N_2]^+$ of 4-methyl-5-phenylamino-1,2,3-thiadiazole [3]; this possibility was examined with derivatives of 4-methyl-5-(R-amino)-1,2,3-thiadiazoles. The fragmentation of 4-methyl-5-(4-methoxyphenyl)amino-1,2,3-thiadiazole is shown in Schemes 2 and 3. The composition of the more important peaks was obtained from high resolution measurements

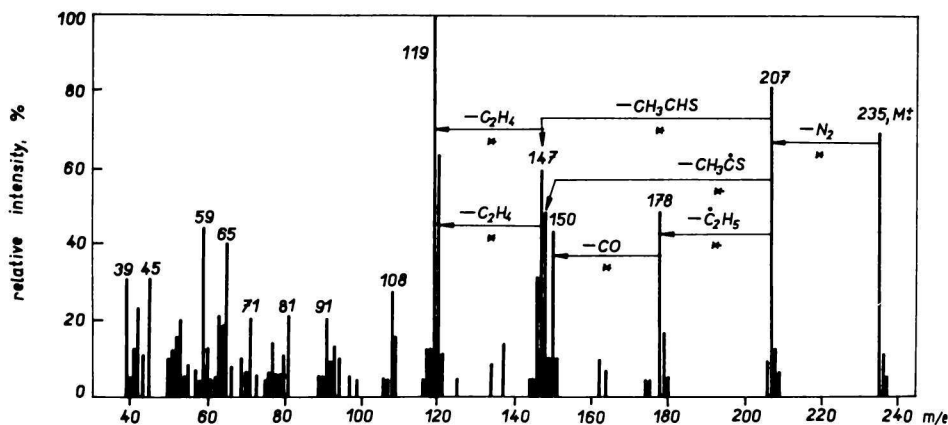


Fig. 2. Mass spectrum of 4-methyl-5-(4-ethoxyphenyl)amino-1,2,3-thiadiazole.

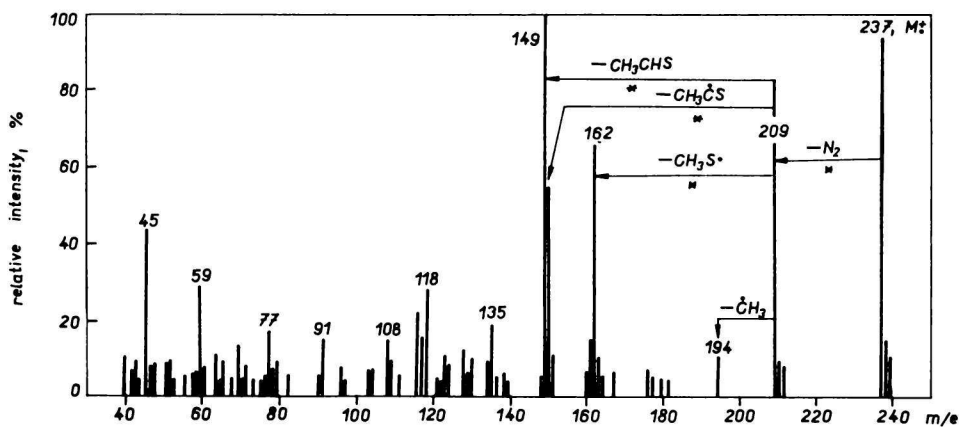


Fig. 3. Mass spectrum of 4-methyl-5-(4-methylthiophenyl)amino-1,2,3-thiadiazole.

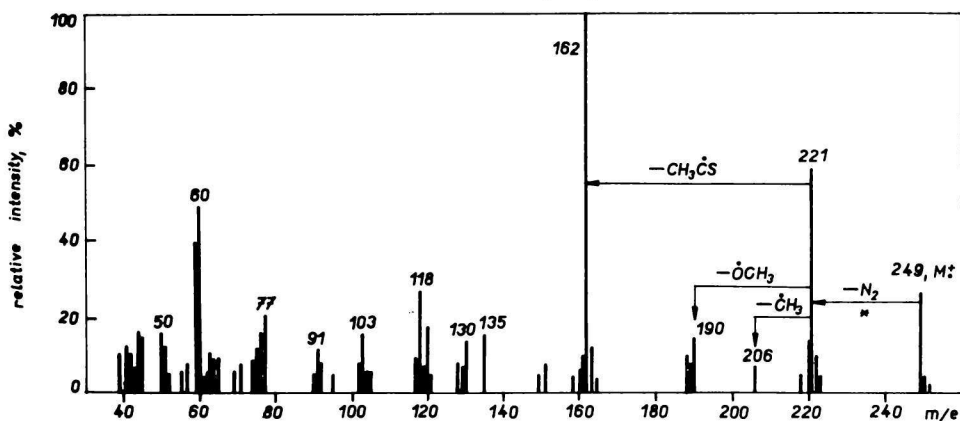


Fig. 4. Mass spectrum of 4-methyl-5-(4-carbomethoxyphenyl)amino-1,2,3-thiadiazole.

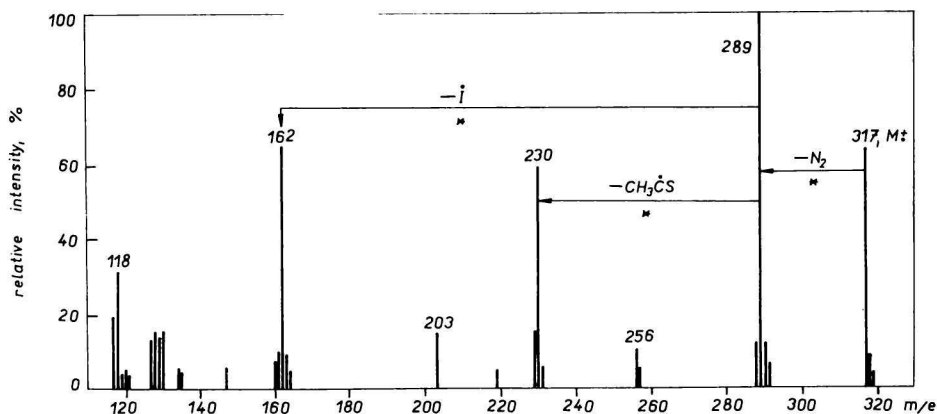


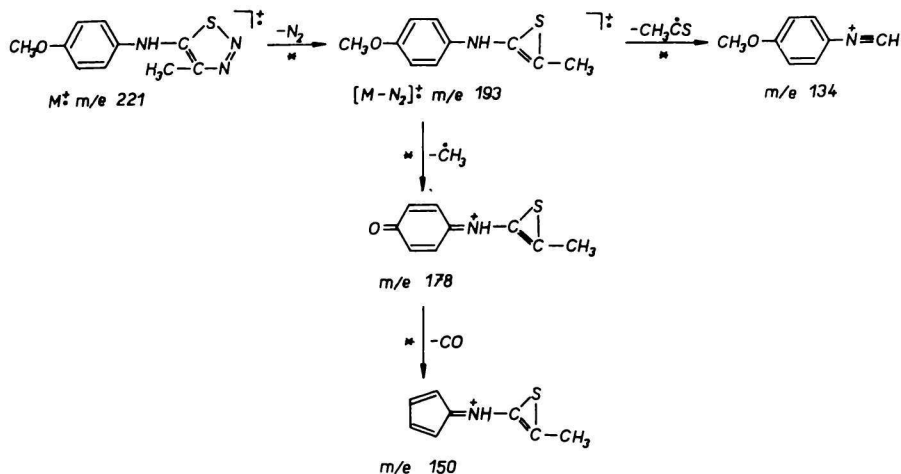
Fig. 5. Mass spectrum of 4-methyl-5-(4-iodophenyl)amino-1,2,3-thiadiazole.

Table 1

Characteristic data of 4-methyl-5-(R-amino)-1,2,3-thiadiazoles

R	Formula	M	Calculated/found		Yield %	M.p. °C	$\lambda_{\max I}$, nm log ϵ	$\lambda_{\max II}$, nm log ϵ
			% N	% S				
Phenyl	C ₉ H ₉ N ₃ S	191.3	—	—	42.2	187—188 ^a	249, 282 sh 3.90	326 4.18
4-Methoxyphenyl	C ₁₀ H ₁₁ N ₃ OS	221.3	—	—	33.2	168—170	249, 284 sh 3.95	326 4.08
4-Ethoxyphenyl	C ₁₁ H ₁₃ N ₃ OS	235.3	—	—	30.5	176—177	250, 281 sh 3.94	328 4.07
4-Carbomethoxyphenyl	C ₁₁ H ₁₁ N ₃ O ₂ S	249.3	16.86 16.99	12.86 12.60	45.2	173—174	274, 292 sh 3.98	339 4.38
4-Chlorophenyl	C ₉ H ₈ ClN ₃ S	225.7	—	—	52.6	171—172	253, 286 sh 3.79	327 3.99
4-Iodophenyl	C ₉ H ₈ IN ₃ S	317.1	13.25 13.30	—	50.1	199—201	256, 285 sh 4.11	330 4.26
4-Methylthiophenyl	C ₁₀ H ₁₁ N ₃ S ₂	237.3	17.70 17.53	27.02 26.89	32.3	191—193	266 4.16	335 4.22
2-Naphthyl	C ₁₃ H ₁₁ N ₃ S	241.3	17.41 17.37	13.29 13.18	33.4	194—195	250, 278, 286 sh 4.44	339 4.23

a) According to [3] the m.p. is 180—181°C, yield 45% ; sh — shoulder.



(Table 2). The metastable transitions in the first-field free region were in cases $m/e\ 193 \rightarrow m/e\ 134$ and $m/e\ 193 \rightarrow m/e\ 133$ verified by high-voltage scan technique [7]. The fission of CH_3CHS from the $[\text{M}-\text{N}_2]^+$ radical ion could be rationalized by a hydrogen migration due to a possible equilibrium of the two contributing structures of this ion (Scheme 3).

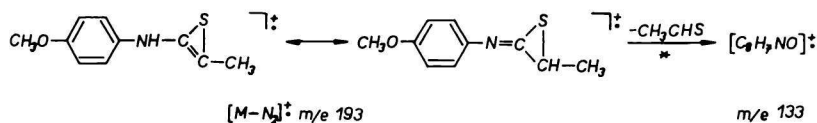


Table 2

Composition of some ions in the mass spectrum of 4-methyl-5-(4-methoxyphenyl)amino-1,2,3-thiadiazole

Ion (<i>m/e</i>)	Mass		Composition	Ion (<i>m/e</i>)	Mass		Composition
	found	calculated			found	calculated	
193	193.0557	193.0561	$\text{C}_{10}\text{H}_{11}\text{NOS}$	103	103.0414	103.0422	$\text{C}_7\text{H}_5\text{N}$
192	192.0476	192.0483	$\text{C}_{10}\text{H}_{10}\text{NOS}$	95	95.0504	95.0497	$\text{C}_6\text{H}_2\text{O}$
178	178.0326	178.0324	$\text{C}_9\text{H}_8\text{NOS}$	92	92.0279	92.0262	$\text{C}_6\text{H}_4\text{O}$
150	150.0383	150.0377	$\text{C}_8\text{H}_8\text{NS}$	77	77.0380	77.0391	C_6H_5
134	134.0605	134.0606	$\text{C}_8\text{H}_8\text{NO}$	64	64.0319	64.0313	C_5H_4
133	133.0528	133.0528	$\text{C}_8\text{H}_7\text{NO}$	59	58.9966	58.9955	$\text{C}_2\text{H}_3\text{S}$
122	122.0605	122.0606	$\text{C}_7\text{H}_8\text{NO}$	45	44.9802	44.9799	CHS

The fragmentation of further 1,2,3-thiadiazole derivatives resembled that of 4-methyl-5-(4-methoxyphenyl)amino-1,2,3-thiadiazole. It has been found that $\text{CH}_3\dot{\text{C}}\text{S}$ or $\text{CH}_3\dot{\text{C}}\text{HS}$ were eliminated from radical ions $[\text{M}-\text{N}_2]^{\cdot+}$, so that the structure *b* of the $[\text{M}-\text{N}_2]^{\cdot+}$ radical ion is reasonable [3].

The p.m.r. spectrum of 4-methyl-5-phenylamino-1,2,3-thiadiazole measured in deuteriochloroform and hexadeuteriodimethyl sulfoxide mixture evidenced the structure proposed for this compound.

Experimental

Phenyl isothiocyanate is commercially available; 4-substituted phenyl isothiocyanates were prepared according to [8], 2-naphthyl isothiocyanate according to [9] and the ethereal solution of diazoethane according to [10].

The ultraviolet spectra of the synthesized derivatives were measured with a UV VIS (Zeiss, Jena) spectrophotometer in 10 mm cells in the 200–350 nm region; concentration 3 to 5×10^{-5} M. The mass spectra were taken with an MS 902 S (AEI Manchester) spectrometer with a direct inlet system at a ionizing electron energy 70 eV, trap current 100 μA at a constant temperature of the ionizing chamber varying between 70 and 110°C with respect to the volatility of the sample. The p.m.r. spectrum was recorded with a BS 847 C (Tesla) apparatus at 25°C.

4-Methyl-5-(*R*-amino)-1,2,3-thiadiazoles

An ethereal solution of diazoethane containing 0.01 mole of the reagent was dropwise added to a solution of the respective isothiocyanate (0.01 mole) in ether (25 ml). The reaction mixture was allowed to stand for 3–4 days in a well closed flask at room temperature. In course of the reaction the colour of the reaction mixture underwent changes and possibly a crystalline product was formed. Crystals were filtered off by suction and the filtrates were concentrated using a vacuum evaporator. The final products were crystallized from ethanol, chloroform or acetone. Characteristic data of compounds synthesized are listed in Table 1.

The p.m.r. spectrum of 4-methyl-5-phenylamino-1,2,3-thiadiazoles revealed following signals on the δ scale in p.p.m.: 2.61 (3H, s, CH_3), 6.9–7.5 (5H, m, aromat, H), 9.07 (H, s, NH).

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