TRANSFORMATION OF 1,2,3-THIADIAZOLES INTO 1,2,3-TRIAZOLES

M.UHER[a], A.RYBÁR[b], A.MARTVOŇ[a] and J.LEŠKO[c]

[a] *Department of Organic Chemistry, Slovak Institute of Technology, 880 37 Bratislava*
[b] *Research Institute of Medicaments, 801 00 Bratislava and*
[c] *Laboratory of Mass Spectrometry, Slovak Institute of Technology, 880 37 Bratislava*

Received July 7th, 1975

5-(Substituted)amino-1,2,3-thiadiazoles were transformed into 1-substituted 5-mercapto-1,2,3--triazoles which were desulphurised to 1-substituted 1,2,3-triazoles. The IR, UV and mass spectra of the prepared compounds are discussed.

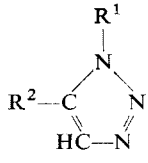
Rearrangement of 5-(substituted)amino-1,2,3-thiadiazoles represents one of the possible ways to 1-substituted 1,2,3-triazoles. Kindt-Larsen and Pedersen[1] transformed 5-anilino-1,2,3-thiadiazole into 1-phenyl-5-mercapto-1,2,3-triazole by treatment with alkali. Methylation of the mercapto group followed by desulphurisation afforded 1-phenyl-1,2,3-triazole. The authors assumed that the rearrangement proceeds probably *via* diazothioacetanilide which was assumed by Sheehan and Izzo[2] to be an intermediate in the formation of 5-anilino-1,2,3-thiadiazole from phenyl isothiocyanate and diazomethane. A similar rearrangement was observed by Goerdeler and Gnad[3] in the case of 4-substituted 5-amino-1,2,3-thiadiazoles. Also the Dimroth rearrangement of 4-acyl-5-arylamino-1,2,3-thiadiazoles to the corresponding mercaptotriazoles was reported[4,5].

In the present communication we describe the transformation of 5-(substituted)-amino-1,2,3-thiadiazoles into 1-substituted 5-mercapto-1,2,3-triazoles and their desulphurisation by the action of Raney nickel. The selected 5-(substituted)amino--1,2,3-thiazoles were prepared by reaction of the corresponding isothiocyanates with diazomethane[6,7]. The rearrangement was accomplished by heating of the corresponding 1,2,3-thiadiazole with 1M-NaOH to 90°C. Acidification of the formed salt with dilute hydrochloric acid afforded 1-substituted 5-mercapto-1,2,3-triazole. Its sodium salt reacted with methyl iodide to give 5-methylmercapto derivative which was desulphurised by activated Raney nickel to 1-substituted 1,2,3-triazole (Table I). A direct desulphurisation of the mercapto derivatives was unsuccessful because of their instability towards the desulphurisation agent. In the case of 1-benzyl-1,2,3-triazole the rearrangement and desulphurisation was accomplished directly in the reaction mixture without isolating the formed mercapto and methylmercapto

derivatives. 1-Substituted 1,2,3-triazoles were obtained in a 38–43% yield and thus isothiocyanates could be used as starting material for their synthesis.

In order to prove the structure of the synthesised derivatives we measured their IR, UV and mass spectra and prepared 1-(4-methylphenyl)-1,2,3-triazole by refluxing the corresponding azide with sodium ethoxide for several hours[8]. The IR

TABLE I

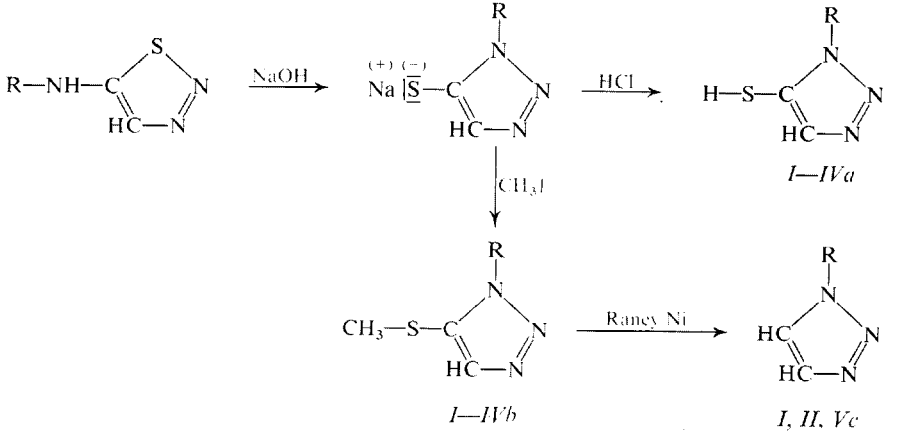
The Synthesised 1- and 5-Substituted 1,2,3-Triazoles 

Compound	R^1 R^2	Formula (mol.w.)	M.p., °C (solvent)	Yield %	Calculated/Found % N	Calculated/Found % S	λ_{max}, nm (log ε)
Ia	4-Methylphenyl SH	$C_9H_9N_3S$ (191·3)	83–84 (ether)	85	22·19 22·06	16·75 16·59	257 (3·95)
Ib	4-Methylphenyl SCH_3	$C_{10}H_{11}N_3S$ (205·3)	56·5–57·5 (methanol)	61	20·47 20·22	15·62 15·41	238 (4·04)
Ic	4-Methylphenyl H	$C_9H_9N_3$ (159·2)	86–87[a] (ether–n-hexane)	38	26·39 26·48	— —	250 (4·12)
IIa	4-Ethoxyphenyl SH	$C_{10}H_{11}N_3OS$ (221·3)	105–107 (ether–n-hexane)	86	19·40 19·39	14·49 14·36	270 (3·96)
IIb	4-Ethoxyphenyl SCH_3	$C_{11}H_{13}N_3OS$ (235·3)	83–85 (methanol)	69	17·85 17·84	13·63 13·86	248 (4·15)
IIc	4-Ethoxyphenyl H	$C_{10}H_{11}N_3O$ (189·2)	77–78 (ether–n-hexane)	42	22·20 22·28	— —	257 (4·12)
IIIa	4-Acetylphenyl SH	$C_{10}H_9N_3OS$ (219·3)	87–89 (ether–n-hexane)	55	19·17 18·95	14·67 14·48	260 (4·15)
IIIb	4-Acetylphenyl SCH_3	$C_{11}H_{11}N_3OS$ (233·3)	152·5–153·5 (ether–n-hexane)	65	18·02 18·20	13·74 13·91	258 (4·26)
IVa	4-Bromophenyl SH	$C_8H_6BrN_3S$ (256·1)	129–131 (ether)	75	16·40 16·27	12·50[b] 12·69	255 (3·98)
IVb	4-Bromophenyl SCH_3	$C_9H_8BrN_3S$ (270·1)	108 (methanol)	77	15·56 15·67	11·87[c] 11·68	242 (4·12)
Vc	Benzyl H	$C_9H_9N_3$ (159·2)	58 (ether–n-hexane)	43	26·39 26·35	— —	210 (4·09)

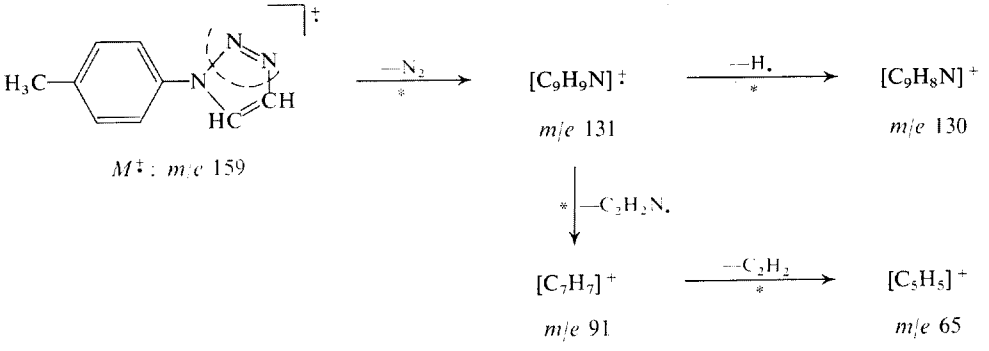
[a] Ref.[8] reports m.p. 88°C; [b] calculated: 31·17% Br; found: 31·29% Br; [c] calculated: 29·58% Br; found: 29·78% Br.

spectra of the prepared compounds display medium absorption bands at ~1600 cm^{-1} due to C=C and C=N stretching vibrations. Bands due to skeletal vibrations in the region 1260–1520 cm^{-1} are strong or very strong, particularly the band at 1470 cm^{-1} which was present in all the derivatives. The absorption bands due to bending vibrations of CH bonds are in the regions 820–846, 950–990, ~1050, 1090–1108 and 1125 ± 5 cm^{-1}.

The UV absorption spectra of 1- and 5-substituted 1,2,3-triazoles exhibit one maximum in the region 240–270 nm (except the derivative *Vc*, Table I). There is a marked hypsochromic shift in comparison with the spectra of 1,2,3-thiadiazoles[6]. The triazole ring is more electronegative than the thiadiazole one and therefore a higher energy is required for the excitation of electrons of its molecular orbital.



It can be inferred from mass spectra that the main direction of fission of molecular ions is the elimination of a neutral nitrogen molecule, similarly as in the case of 1,2,3-thiadiazoles[6,9,10]. The mass spectrum of 1-(4-methylphenyl)-1,2,3-triazole is shown in Fig. 1*a* and formation of the most important fragment ions is described in Scheme 1. The mass spectrum of 1-benzyl-1,2,3-triazole (Fig. 1*b*) is similar to the spectrum of the isomeric 1-(4-methylphenyl)-1,2,3-triazole and the spectra differ only in the relative intensities of the particular ions. However, formation of the ion $[C_7H_7]^+$, *m/e* 91, is different; in this case the ion is formed by fission of the C—N bond in the β-position to the aromatic nucleus. The mass spectrum of 1-(4-methylphenyl)-5-methylmercapto-1,2,3-triazole (Fig. 1*c*) exhibits a base peak of *m/e* 118. Formation of this and other fragment ions is described in Scheme 2.



SCHEME 1

EXPERIMENTAL

5-(Substituted)amino-1,2,3-thiadiazoles were prepared according to ref.[6,7]. The IR spectra were measured in Nujol on a double-beam UR-20 (Zeiss, Jena) spectrophotometer in KBr cells. Before the measurements, the instrument was calibrated with polystyrene foil (thickness 25 μm). The UV spectra were taken on a recording spectrophotometer UV VIS Specord (Zeiss, Jena) in the region 200—800 nm; concentration $3-5 \cdot 10^{-5}$M, dioxane, cell thickness 10 mm. Mass

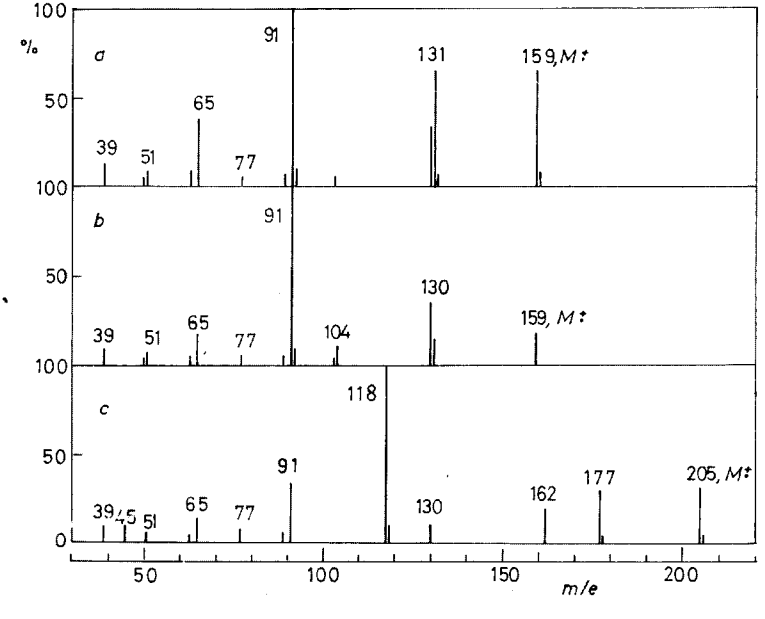
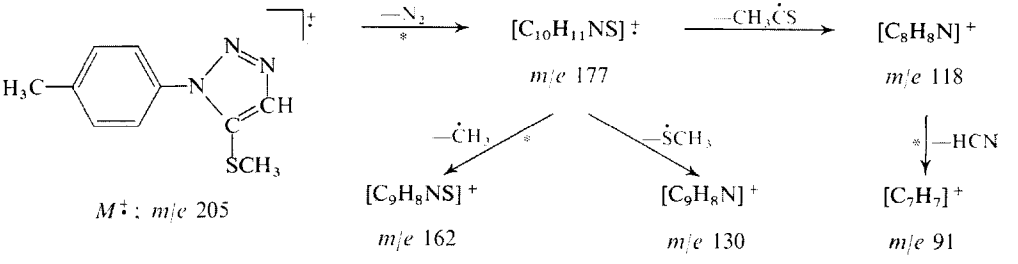


FIG. 1

Mass Spectra of *a* 1-(4-Methylphenyl)-1,2,3-triazole, *b* 1-Benzyl-1,2,3-triazole, *c* 1-(4-Methylphenyl)-5-methylmercapto-1,2,3-triazole



SCHEME 2

spectra were measured on a MS 902 S (AEI Manchester) spectrometer using a direct inlet system, 70 eV, trap current 100 μA, ionisation chamber temperature 80—150°C, according to the volatility of the sample.

1-(Substituted phenyl)-5-mercapto-1,2,3-triazoles

A suspension of 5-(substituted phenyl)amino-1,2,3-thiadiazole (0·02 mol) in 1M-NaOH (25 ml) was heated to 90°C for several minutes till the thiadiazole dissolved completely. The solution was treated with charcoal, filtered and the filtrate was acidified with dilute hydrochloric acid. The precipitated 1-(substituted phenyl)-5-mercapto-1,2,3-triazole was filtered and crystallised from ether or ether–n-hexane.

1-(Substituted phenyl)-5-methylmercapto-1,2,3-triazoles

A suspension of 5-(substituted phenyl)amino-1,2,3-thiadiazole (0·05 mol) in 1M-NaOH (150 ml) was heated to 90°C for several minutes till the compound dissolved. The solution was treated with charcoal, filtered and cooled. Methyl iodide (20 ml) was added to the cold solution and the mixture was stirred for 2 hours at room temperature. The methyl iodide was then removed by bubbling air through the mixture and the residue was extracted with ether. The ethereal extract was washed with water, dried over magnesium sulphate and taken down *in vacuo*. The residue was crystallised from methanol or ether–n-hexane.

1-(Substituted phenyl)-1,2,3-triazoles

Activated Raney nickel[11] (5 g) was added to a solution of 1-(substituted phenyl)-5-methylmercapto-1,2,3-triazole (0·005 mol) in ethanol (20 ml) and the mixture was refluxed for 8 hours. The nickel was filtered off and washed twice with hot ethanol. The ethanol was driven off *in vacuo* and the residue was dissolved in ether, treated with charcoal and filtered. n-Hexane was added to the hot solution and the mixture was allowed to deposit crystals. 1-Benzyl-1,2,3-triazole was prepared directly from the corresponding thiadiazole without isolating the intermediates. The prepared 1- and 5-substituted 1,2,3-triazoles are listed in Table I.

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Translated by M. Tichý.