

NEW SYNTHESIS OF 1,2,4-TRIAZOLIDINE-5-THIONE DERIVATIVES

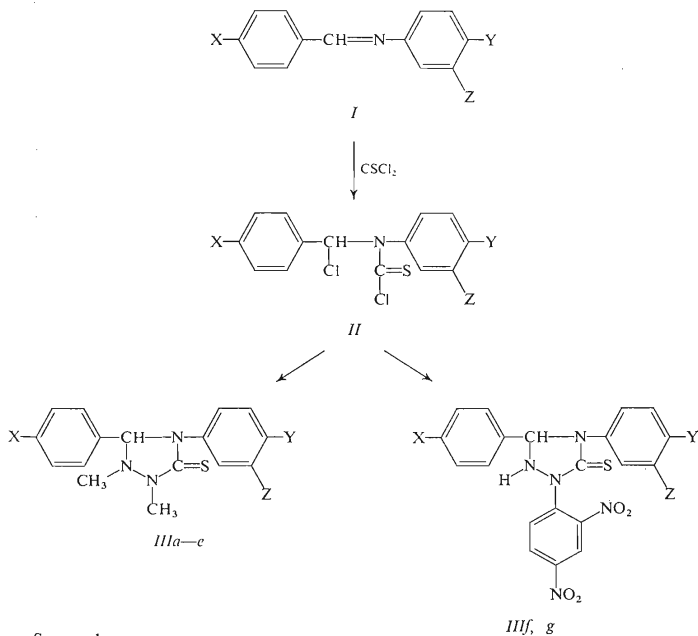
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Reaction of substituted benzylideneanilines (*I*) with thiophosgene afforded derivatives of *N*-(1-chlorobenzyl)phenylthiocarbonyl chloride (*II*) which were transformed by reaction with *N,N*-dimethylhydrazine or *N*-(2,4-dinitrophenyl)hydrazine into derivatives of 1,2,4-triazolidine-5-thione *III*. ¹H-NMR and IR spectra of the products are discussed.



SCHEME 1

Although reactions of carbamoyl chlorides with hydrazines are known¹, preparation of 1,2,4-triazolidine-5-thione derivatives by an analogous reaction of thiocarbamoyl

TABLE I
Physical Constants, Yields and Analytical Data of the Synthesised Derivatives

Com- pound	Substituent			Formula (mol.w.)	Calculated/Found			M.p., °C Yield, %
	X	Y	Z		% N	% S	% C	
<i>IIa</i>	H	H	H	C ₁₄ H ₁₁ Cl ₂ NS (296·2)	4·73 4·61	10·82 10·75	11·96 11·79	87—90 43·0
<i>IIb</i>	NO ₂	H	H	C ₁₄ H ₁₀ Cl ₂ N ₂ O ₂ S (341·2)	4·10 4·0	9·39 9·31	10·39 10·35	138—140 53·5
<i>IIc</i>	H	Cl	H	C ₁₄ H ₁₀ Cl ₃ NS (330·7)	4·23 4·20	9·69 9·62	10·72 10·68	70—73 76·0
<i>IId</i>	H	Br	H	C ₁₄ H ₁₀ BrCl ₂ NS (345·1)	4·06 4·00	9·29 9·15	10·27 10·10	90—91 62·5
<i>IIe</i>	H	H	NO ₂	C ₁₄ H ₁₀ Cl ₂ NOS (341·2)	4·10 3·92	9·39 9·26	10·39 10·21	125—128 30·0
<i>IIf</i>	CH ₃ O	H	H	C ₁₅ H ₁₃ Cl ₂ NOS (326·2)	—	—	—	decompo- sition ^a 29·5
<i>IIg</i>	NO ₂	CH ₃	H	C ₁₅ H ₁₂ Cl ₂ N ₂ O ₂ S (367·3)	3·81 3·68	8·73 8·60	9·65 9·51	122—125 70·5
<i>IIIa</i>	H	H	H	C ₁₆ H ₁₇ N ₃ S (284·6)	14·76 14·75	11·26 11·23	—	125—128 40·0
<i>IIIb</i>	NO ₂	H	H	C ₁₆ H ₁₆ N ₄ O ₂ S (328·4)	17·06 16·98	9·76 9·65	—	175—177 55·0
<i>IIIc</i>	H	Cl	H	C ₁₆ H ₁₆ ClN ₃ S (317·8)	13·22 13·15	10·08 9·92	—	118—120 60·0
<i>IIId</i>	H	Br	H	C ₁₆ H ₁₆ BrN ₃ S (362·3)	11·59 11·02	8·85 8·63	—	155 45
<i>IIIe</i>	H	H	NO ₂	C ₁₆ H ₁₆ N ₄ O ₂ S (328·4)	17·06 16·90	9·76 9·59	—	168—170 42·0
<i>IIIf</i>	H	H	H	C ₂₀ H ₁₅ N ₅ O ₄ S (421·4)	16·62 16·60	7·60 7·58	—	246—248 70
<i>IIIg</i>	NO ₂	CH ₃	H	C ₂₁ H ₁₆ N ₆ O ₆ S (480·4)	17·49 17·36	6·69 6·59	—	254—256 66·0

^a The compound was very hygroscopic and was therefore not analysed.

chlorides is hitherto not described. Since 1,2,4-triazolidine derivatives receive still increasing attention²⁻⁴, we tried to find a new method of their preparation.

Series of substituted thiocarbamoyl chlorides *Ila-g* (Table I) was prepared by reaction of thiophosgene with substituted azomethines. These compounds reacted in an anhydrous medium with *N,N*-dimethylhydrazine or *N*-(2,4-dinitrophenyl)hydrazine to give the corresponding substituted 1,2,4-triazoline-5-thiones *IIIa-g*. Best results were obtained when a solution of thiocarbamoyl chloride in benzene was added to *N,N*-dimethylhydrazine (at room temperature) or *N*-(2,4-dinitrophenyl)hydrazine (reflux) in benzene (Scheme 1). The optimum reaction time was found by following the reaction chromatographically; longer reaction times gave rise to side products.

TABLE II
Spectral Data of the Substituted 1,2,4-Triazolidine-5-thiones

Compound	$\delta(\text{CH})$ (cm^{-1})		ν skeletal (cm^{-1})			$\nu(\text{CH})$ (cm^{-1})		δ , ppm
<i>IIIa</i>	850	945	1 315	1 385		2 865		CH ₃ , 2.75, 3.22 s CH, 5.73 s H arom 7.25 m
			1 435	1 460		2 970		
			1 505	1 600		3 030		
<i>IIIb</i>	830	860	1 320	1 385	1 460	2 870	2 970	CH ₃ , 2.75, 3.15 s CH, 5.5 s H arom, 7.25 m, 7.8
		945	1 505	1 600			3 030	
<i>IIIc</i>	830	860	1 320	1 350	1 380	2 870	2 970	CH ₃ , 2.78 s, 3.68 s CH, 5.96 s H arom, 7.1 m
		945	1 460	1 505	1 600	3 030		
<i>III d</i>	830	860	1 315	1 395	1 440	2 860	2 950	CH ₃ , 2.7, 3.75 s CH, 5.6 s H arom, 7.23
		950	1 505	1 600			3 025	
<i>III e</i>	860	900	1 320	1 395	1 490	2 855	2 980	CH ₃ , 2.65, 3.80 s CH, 5.7 s H arom, 7.85 m
		950	1 585			3 020		
<i>III f</i> ^a	835	925	1 315	1 360	1 430	2 850	3 000	CH, 6.6 d H arom, 7.75, 8.24, 8.95 NH 9.75 d
			1 520	1 600			3 020	
<i>III g</i> ^b	860	945	1 325	1 375	1 460	2 850	2 920	—
						2 975		

^a $\nu(\text{NH})$ 3 320 cm^{-1} ; ^b $\nu(\text{NH})$ 3 280 cm^{-1} .

The IR and $^1\text{H-NMR}$ spectra of the products are given in Table II. The $^1\text{H-NMR}$ spectra exhibit a singlet (δ 5–6 ppm) corresponding to the proton in the position 3 of the triazolidine ring.

Triazolidines are not the only products of the studied reaction. For example, in the preparation of the compound *III d* we were able to prove benzaldehyde and 4-bromophenyl isothiocyanate in the reaction mixture. Treatment of the compound *II f* with *N,N*-dimethylhydrazine did not afford the corresponding triazolidine and the reaction mixture contained 4-methoxyphenyl isothiocyanate, benzaldehyde, benzalmethylaniline and azomethine.

EXPERIMENTAL

Thiocarbamoyl Chlorides *II a–g*

A solution of freshly distilled thiophosgene (6.0 g; 0.05 mol) in benzene (15 ml) was added in the course of 15 minutes to a stirred solution of the corresponding azomethine (0.05 mol) in benzene (25 ml). The mixture was stirred for 1 h at 35–45°C and the precipitate was filtered and crystallised from cyclohexane. Physical constants and analytical data of the prepared thiocarbamoyl chlorides are given in Table I.

Tetrasubstituted 1,2,4-Triazolidine-5-thiones *III a–e*

A solution of the corresponding thiocarbamoyl chloride (0.025 mol) in benzene (30 ml) was added dropwise at room temperature to a stirred solution of *N,N*-dimethylhydrazine (5.0 g; 0.085 mol) in benzene (100 ml) and the mixture was stirred at 40–50°C for 1 h. After cooling, the mixture was poured into water (150 ml), the benzene layer separated, dried and concentrated *in vacuo* to a small volume. The product was precipitated by addition of cyclohexane, filtered and crystallised from ethanol. Physical constants of the products and analyses are given in Table I.

Trisubstituted 1,2,4-Triazolidine-5-thiones *III f, g*

A mixture of the corresponding thiocarbamoyl chloride (0.035 mol), *N*-(2,4-dinitrophenyl)-hydrazine (0.01 mol) and benzene (80 ml) was refluxed for 4 h. After cooling, water (100 ml) was added, the benzene layer was separated, dried and concentrated to a small volume. The separated product was filtered and crystallised from acetone. For physical properties and other data see Table I.

Spectral Measurements

IR spectra were taken in the region 700–3600 cm^{-1} on a UR-20 (Zeiss, Jena) double-beam spectrophotometer. Concentration of the chloroform solutions was $4 \cdot 10^{-2}\text{M}$. The $^1\text{H-NMR}$ spectra were measured in deuteriochloroform on a Tesla BS 847 C (80 MHz) instrument, internal standard hexamethyldisiloxane, the δ values were related to tetramethylsilane. The spectral data are listed in Table II.

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