REACTIONS OF ARENECARBONYL ISOTHIOCYANATES WITH HYDRAZINE HYDRATE AND ARYLHYDRAZINES

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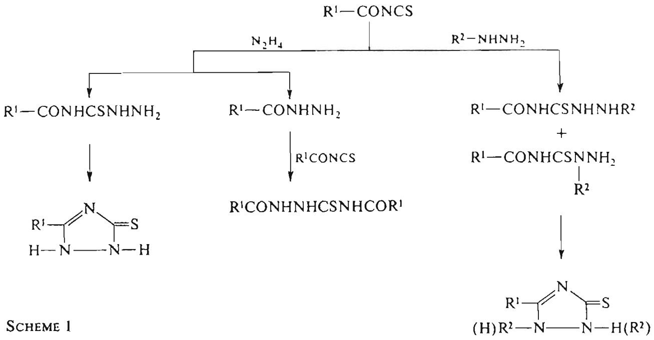
Received November 8th, 1979

This paper describes the preparation of 1,2,4-triazoline-5-thiones from arenecarbonyl isothiocyanates and hydrazine hydrate or arylhydrazines. The IR, UV and mass spectra are commented.

Benzoyl isothiocyanate affords with an excess of hydrazine under conditions of Einhorn–Brunnes reaction[1] a mixture of triazolinethione and benzoylhydrazine, whilst at an equimolar ratio dibenzoylthiosemicarbamide was obtained[2]. Dixon[3] described the reaction of benzoyl isothiocyanate with phenylhydrazine for the first time; he presumed the formation of 4-benzoyl-1-phenylthiosemicarbazide. Reactions with aliphatic hydrazines were studied by Durant[4]. Preparation of triazolinethione from benzoyl isothiocyanates and phenylhydrazines was already reported[5].

In continuation of our study concerning the reactions of benzoyl isothiocyanates leading to heterocyclic compounds[6], we examined the reactions of unsubstituted and substituted benzoyl and furoyl isothiocyanates with hydrazine hydrate and arylhydrazines (Scheme 1).



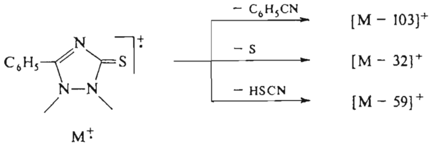
SCHEME 1

5-Nitrofuroyl isothiocyanate was without isolation used for the preparation of substituted thioureas[7]; its characteristic data are reported in this paper. The reaction of benzoyl isothiocyanate with an excess of hydrazine hydrate proceeded in one or two steps, with other isothiocyanates in one step only. In addition of 1,2,4-triazoline-5-thione also benzoyl and furoylhydrazines were isolated from the reaction mixture *via* neutralization of the filtrate and extraction with chloroform. Another product of this reaction was 1,4-dibenzoylthiosemicarbazide, the subsequent cyclization of which was not observed. The reaction of arenecarbonyl isothiocyanates with arylhydrazines afforded 1-phenyl-4-benzoyl and 2-phenyl-4-benzoylthiosemicarbazides, which cyclized in an alkaline medium to give two types of 1,2,4-triazoline-5-thiones (Scheme 1).

The UV spectra of the prepared substances revealed bands in the 224 – 242, 254 to 268 and 288 – 345 nm regions. The replacement of phenyl for furyl in compounds *I* – *IV* (Table I) was of no practical effect on the position of λ_{max}; nonetheless a hypochromic shift (log ε 4·34 → 3·97) was observed. Spectra of *V* and *XI* considerably differed, what indicated that substituents R^2 were not attached to the same nitrogen atom[4,8,9]. The absorption band at the longest wavelength of derivatives *VII*, *IX* and *XI* had virtually the same position as *I* (Table I), *i.e.* it revealed no substituent effect, what means that R^2 was bound to N^2. Due to a steric hindrance the mesomeric interaction of the lone electron pair at nitrogen with π-electrons of the aromatic ring could not come into effect and therefore, these compounds absorb in the UV light as unsubstituted derivatives. Spectra of *V*, *VI*, *VIII* and *X* displayed a notable bathochromic shift of the band at the longest wavelength when compared with that of *I*. In these cases one is entitled to anticipate that R^2 was attached to N^1 adjacent to the C=S group.

The IR spectra were characteristic of intense bands of aromatic C—H bonds δ(CH) at 753 – 859, of a $\rangle N{-}\underset{|}{C}{=}S$ grouping at 1230 – 1319, of two to three bands ν(C=C) and ν(C=N) in the 1500 to 1632 cm^{-1} regions, of ν(C—H) of aromatic rings at 3010 to 3095, of weak bands ν(N—H) at ~3130 (derivatives *V*, *VI*, *VIII* and *X* and of two strong bands ν(N—H) at about 3280 and 3400 cm^{-1}; bands ν(C=C) were overlapped by ν(C=N).

Mass spectra of compounds under investigation showed peaks, the most intensive of which belonged to molecular ions. Fragmentation of a 1,2,4-triazoline-5-thione ring could be outlined as follows

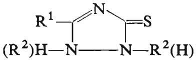


EXPERIMENTAL

Isothiocyanates employed in this paper were prepared according to[10]. 5-Nitrofuroyl isothiocyanate, m.p. 39—41°C, 51%, ν(C=O) 1 708, ν_{as}(NCS) 1 940 and 1 975 cm^{-1} in $CHCl_3$. 4-Chloro- and 4-methoxyphenylhydrazines were prepared according to[9]. The UV spectra of 3—5 . 10^{-5}M

TABLE I

1,2,4-Triazoline-5-thiones



Compound	R^1 R^2	Formula (M.w.)	M.p., °C (yield, %)	Calculated/Found		λ_{max}, nm (log ε)	
				% N	% S		
I	C_6H_5 H—	$C_8H_7N_3S$ (177·2)	258[a] (27)	—	—	224 (4·26)	256 (4·34)
II	4-NO_2—C_6H_4 H—	$C_8H_6N_4O_2S$ (222·2)	260[a] (35)	—	—	229 (4·13)	322 (4·16)
III	4-CH_3—C_6H_4 H—	$C_9H_9N_3S$ (191·2)	269—271[a] (23)	—	—	—	263 (4·19)
IV	2-Furyl- H—	$C_6H_5N_3OS$ (167·2)	271—274[b] (33)	—	—	255 (3·97)	313 (4·20)
V	C_6H_5 C_6H_5	$C_{14}H_{11}N_3S$ (253·3)	238—239[c] (53)	—	—	233 (4·44)	291 (4·20)
VI	C_6H_5 4-Cl—C_6H_4	$C_{14}H_{10}ClN_3S$ (287·8)	218—220 (67)	14·60 14·42	11·14[d] 11·02	232 (4·45)	290[e]
VII	C_6H_5 4-CH_3O—C_6H_4	$C_{15}H_{13}N_3OS$ (283·3)	223—225 (55)	14·83 14·62	11·32 11·15	256 (4·40)	—
VIII	C_6H_5 4-NO_2—C_6H_5	($C_{14}H_{10}N_4O_2S$ (298·3)	197—200 (30)	18·78 18·48	10·75 10·36	242 (4·18)	288 (3·90)
IX	4-NO_2—C_6H_5 4-CH_3O—C_6H_4	$C_{15}H_{12}N_4O_3S$ (328·3)	214—217 (51)	17·06 17·12	9·77 9·15	256 (4·48)	—
X	2-Furyl- 4-Cl—C_6H_4	$C_{12}H_8ClN_3OS$ (277·7)	207—209 (48)	15·13 14·99	11·55[f] 11·31	268 (4·36)	345 (4·10)
XI	2-Furyl 4-CH_3O—C_6H_4	$C_{13}H_{11}N_3O_2S$ (273·3)	220—223 (43)	15·37 15·15	11·73 11·48	254 (4·35)	—

[a] M.p. of *I* 269°C, *II* 258—258·5°C, *III* 268—270°C (ref.[5]); [b] m.p. 272—273°C (ref.[11]); [c] m.p. 239—240°C (ref.[12]); [d] calculated: 12·32% Cl; found: 12·06% Cl; [e] shoulder; in 1 mol cm^{-1}; [f] calculated: 12·77% Cl, found: 12·58% Cl.

methanolic solutions were recorded with a UV VIS (Zeiss) spectrophotometer in 10 mm-cells, the IR spectra were measured with a UR-20 (Zeiss) apparatus (2 mg/1 g KBr), mass spectra were taken with an AEI MS-902 S instrument using a direct inlet system at an ionization chamber temperature 150—200°C, ionizing electrons energy 70 eV, trap current 100 μA.

Reactions of Arenecarbonyl Isothiocyanates with Hydrazine Hydrate

A) A solution of hydrazine hydrate (50%, 0·5 mol) was dropwise added to a solution of benzoyl isothiocyanate (0·1 mol) in ethanol (60 ml) at room temperature. Yellow crystals, separated after cooling, were suction-filtered and crystallized from ethanol. Yield of 4-benzoylthiosemicarbazide 85%, m.p. 151—152°C.

4-Benzoylthiosemicarbazide (20 mmol) dissolved in NaOH (5 g in 100 ml of water) was refluxed for 3 h, cooled and neutralized with dilute HCl. The crude product was filtered off, washed with water and crystallized from ethanol. Yield of *I* 60%, m.p. 258—259°C.

B) The 4-substituted thiosemicarbazide, obtained by mixing solutions of hydrazine hydrate (85%, 1·1 g, 35 mmol) in water (10 ml) and the respective isothiocyanate (7 mmol) in ethanol (5 ml), was refluxed with HCl (15%, 100 ml) for 5 h; the product was filtered off and crystallized from ethanol. In this way products *I*—*IV* (Table I) were obtained.

Reactions of Arenecarbonyl Isothiocyanates with Arylhydrazines

The appropriate isothiocyanate (7 mmol) was either directly or in benzene solution added to a solution of arylhydrazine (7 mmol) in benzene (20—50 ml, 4-nitrophenylhydrazine in 60—70 ml of boiling xylene) and the 1,4-disubstituted thiosemicarbazide formed was filtered off and refluxed in NaOH (10%, 100 ml) for 4 h. Products obtained after cooling, neutralization and filtration were crystallized (Table I, derivatives *V*—*XI*).

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Translated by Z. Votický.