# Reactions of arenecarbonyl isothiocyanates with hydrazones

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By the reaction of benzoyl and 2-furoyl isothiocyanates, respectively, with acetone phenylhydrazone 5-benzoylimino- and 5-(2-furoylimino)-2,2-dimethyl-4-phenyl-1,3,4-thiadiazolines, respectively, were formed. The reaction with benzaldehyde phenylhydrazone resulted in benzaldehyde 2-phenyl-4-acylthiosemicarbazones, while that with acetophenone and benzophenone phenylhydrazones, respectively, did not proceed at all. The u.v., i.r., mass, <sup>1</sup>H-n.m.r., and <sup>13</sup>C-n.m.r. spectra are discussed.

Реакцией бензоил- и 2-фуроилизотиоцианатов с ацетонфенилгидразоном образуются 5-бензоилимино- или 5-(2-фуроилимино)-2,2-диметил-4-фенил-1,3,4-тиадиазолины; реакцией с бензальдегидфенилгидразоном образуются бензальдегид-2-фенил-4-ацилтиосемикарбазоны, пока что реакция с ацетофенонфенил- и бензофенонфенилгидразонами вообще не протекает. Обсуждаются УФ, ИК, масс-, <sup>1</sup>Н-ЯМР и <sup>13</sup>С-ЯМР спектры.

The possibility of a 7-membered ring formation in the reaction of benzoyl isothiocyanate with acetone phenylhydrazones was first described by Durant [1]. Yamamoto and coworkers [2] studied this reaction expecting the formation of compounds with 7-membered ring on the basis of spectroscopic data (i.r., <sup>1</sup>H-n.m.r., and mass spectra). Later, on the basis of X-ray analyses, the formed products were proved to be derivatives of 1,3,4-thiadiazoline [3, 4]. The reactions of substituted benzoyl isothiocyanates with N,N-disubstituted hydrazones were studied by Goerdeler and Bishoff [5] who expected the formation of unstable 1,3,5-oxadiazine-4-thiones.

In the previous works we described the reactions of arenecarbonyl isothiocyanates with azomethines [6], hydrazine hydrate and arylhydrazines [7], cyclic enamines [4], and phenyl-substituted tetrazoles [8]. In order to examine the possibility of utilization of carbonyl isothiocyanates for the synthesis of different heterocyclic compounds, in the present work we deal with the reactions of unsubstituted and substituted benzoyl and 2-furoyl isothiocyanates, respectively, with hydrazones, namely, benzaldehyde, acetone, acetophenone and benzophenone phenylhydrazones.

### Experimental

The starting hydrazones were prepared after [9, 10] and isothiocyanates after [11, 12]. The studied derivatives are characterized in Table 1.

Ultraviolet spectra were measured on a UV VIS (Zeiss, Jena) spectrometer in cells of 10 nm thickness; concentration  $3-5 \times 10^{-5}$  mol dm<sup>-3</sup> in methanol. Infrared spectra were recorded on a UR-20 (Zeiss, Jena) spectrophotometer in KBr pellets (2 mg/g KBr). Mass spectra were measured with an AEI MS-902 S apparatus at ionization temperature 150-200°C (direct inlet system), 70 eV, and 100  $\mu$ A. <sup>1</sup>H-N.m.r. and <sup>13</sup>C-n.m.r. spectra were taken with a Jeol FX-100 apparatus in DMSO-d<sub>6</sub> using TMS as internal standard.

5-Benzoylimino- and 5-(2-furoylimino)-2,2-dimethyl--4-phenyl-1,3,4-thiadiazolines (I-V)

The appropriate isothiocyanate (0.007 mol) was added directly or after dissolution in benzene  $(20 \text{ cm}^3)$  into the solution of acetone phenylhydrazone (1.0 g; 0.007 mol) in benzene  $(10 \text{ cm}^3)$ . After one day staying, crystalline products were obtained; these were further crystallized from benzene.

## Benzaldehyde 2-phenyl-4-acylthiosemicarbazones (VI---IX)

Into the solution of benzaldehyde phenylhydrazone (1.37 g; 0.007 mol) in ethyl acetate  $(15-20 \text{ cm}^3)$ , the appropriate isothiocyanates (0.007 mol) were added. After 2 h staying at room temperature the derivatives crystallized and were further purified by crystallization from benzene.

The reactions with acetophenone and benzophenone phenylhydrazones, respectively, were carried out similarly. The purity of the prepared compounds was checked by t.l.c. on silufol and determined by gas chromatography on a Hewlett—Packard 7620 A chromatograph with flame ionization detector and nitrogen as carrier gas.

### **Results and discussion**

By the reaction of acetone phenylhydrazone with benzoyl and 2-furoyl isothiocyanates, respectively, in benzene at room temperature the appropriate 1,3,4-thiadiazolines were obtained in very good yields (67–96%), while the reactions with benzaldehyde phenylhydrazone carried out in ethyl acetate at room temperature resulted in 4-substituted 2-phenylthiosemicarbazones (Table 1). The reactions with acetophenone and benzophenone phenylhydrazones, respectively, gave the starting compounds only even after prolonged reaction time (Scheme 1).

Characterization of the synthesized derivatives							
Compound	Acyl	Formula	М	Calculated/found		37:-14	N.
				% N	% S	%	м.р. °С
		5-Acylimino-2,2	-dimethyl-4-p	henyl-1,3,4-thia	adiazolines		
П	5-(4-Nitrobenzoyl)	$C_{17}H_{16}N_4O_3S$	356	15.74	9.01 8.88	92	182—183
III	5-(4-Methylbenzoyl)	$C_{18}H_{19}N_3OS$	325	12.93 12.75	9.87 9.62	67	282—283
IV	5-(5-Nitro-2-furoyl)	$C_{15}H_{14}N_4O_4S$	346	16.19 16.02	9.27 9.06	76	197—200
v	5-(2-Furoyl)	$C_{15}H_{15}N_3O_2S$	301	13.96 13.75	10.65 10.46	96	240—242
		Benzaldehyde	e 2-phenyl-4-a	acylthiosemicarb	pazones		
VII	4-Nitrobenzoyl	$C_{21}H_{16}N_4O_3S$	404	13.87 13.59	7.94 7.78	88	157—159
VIII	4-Methylbenzoyl	$C_{22}H_{19}N_3OS$	373	11.27	8.60 8.52	53	150—152
IX	2-Furoyl	C19H15N3OS	349	12.04 11.88	9.19 8.95	61	210-213

Table 1

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For I and VI (Acyl=benzoyl) Ref. [2] gives m.p. 131 and 136°C, respectively.



Scheme 1

The u.v. spectra of the prepared derivatives I-V revealed bands in the region of 238–240, 280–289, and 317–374 nm. Significant bathochromic shift of the band at the highest wavelength was observed with the derivatives II-IV, which is evidently connected with the nature of the substituents on benzene and furan rings, respectively. In the u.v. spectra of the compounds VI-IX, three bands were observed at wavelengths lower by about 10 nm (Table 2).

In the i.r. spectra of the compounds I-V bands belonging to v(C=O) were observed at relatively low wavenumbers 1600-1637 cm<sup>-1</sup> due to the interaction of the lone electron pair on the oxygen atom of the carbonyl group with sulfur [13]. With the derivatives VI-IX intense bands belonging to v(C=O) were observed at 1700-1730 cm<sup>-1</sup>.

In the decoupled <sup>13</sup>C{<sup>1</sup>H}-n.m.r. spectrum of the compound *I* the following signals of carbons  $\delta$ [p.p.m.] were observed: 175.8, 169.7, 140.3, 136.0, 129.7, 128.3, 128.0, 125.7, 123.0, 69.4, and 26.8. The signal at 175.8 p.p.m. belongs to carbon of the C=O group and that at 169.7 p.p.m. to carbon of the C=N group. In the case of the presence of C=S group, the signal of the carbon atom of this group would be observed at higher p.p.m. values. The signals in the region of 140—123 p.p.m. belong to carbons of the benzene rings, the signal at 69.4 p.p.m. to the quaternary carbon C(CH<sub>3</sub>)<sub>2</sub>, and that at 26.8 p.p.m. to the carbon atoms of the CH<sub>3</sub> groups.

Infrared and ultraviolet spectral data of the prepared compounds

Table 2

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In the <sup>1</sup>H-n.m.r. spectrum of the compound I a singlet of the N—H protons (5.05 p.p.m.), a multiplet of the aromatic protons at 7.5—8.0 p.p.m., and a signal of the CH<sub>3</sub> protons at 1.65 p.p.m. were observed.

The mass spectra of the prepared compounds I-V revealed besides peaks of molecular ions also peaks of fragment ions formed by the following fragmentation



The peaks belonging to  $R-CO^{+}$  were very intense. In the spectra of the compounds *I*-*III* they were shown to be the base peaks, while in the spectra of the compounds *IV* and *V* the base peaks belonged to  $C_6H_5N^{+}$ . The presence of these peaks proves that the investigated compounds contained five-membered rings.

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