

# Reactions of 2-naphthoyl isothiocyanate and $\beta$ -(1-naphthyl)acryloyl isothiocyanate with enamines, phenylhydrazine, and sodium hydrogen sulfide

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Received 2 November 1976

The reactions of 2-naphthoyl and  $\beta$ -(1-naphthyl)acryloyl isothiocyanates with enamines, phenylhydrazine, and sodium hydrogen sulfide were studied. 2,5-Disubstituted 4-thioxo-6-methylpyrimidines, 3-substituted 2-phenyl-5-thioxo-1,2,4-triazoles, and 6-(1-naphthyl)-2-thioxo-4-oxoperhydro-1,3-thiazine were obtained as resulting products. The structures of the synthesized compounds were proved by i.r. and  $^1\text{H-n.m.r.}$  spectroscopy.

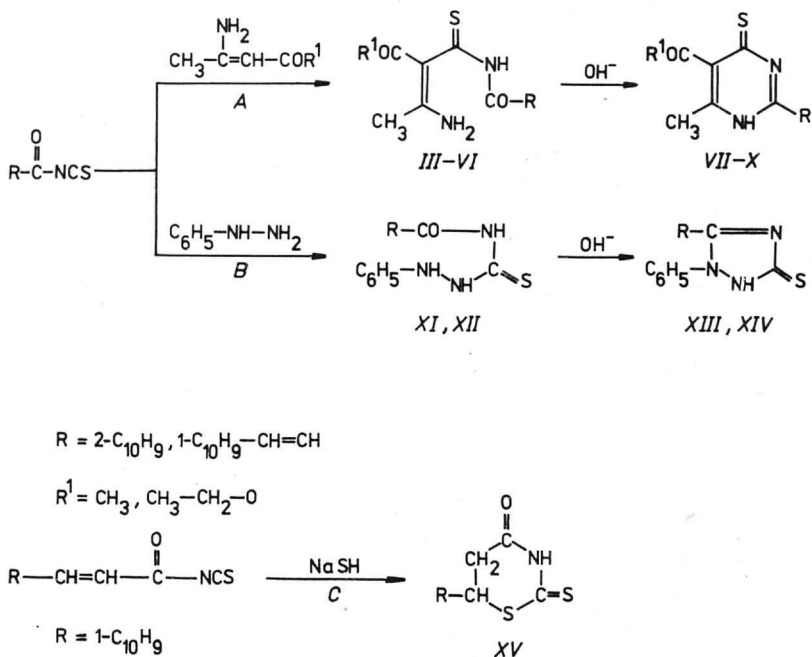
Изучались реакции 2-нафтоилизотиоцианата и  $\beta$ -(1-нафтил)акрилоил-изотиоцианата с энаминами, фенилгидразином и гидросульфидом натрия. В качестве продуктов реакции получены 2,5-дизамещенные-4-тиоксо-6-метил-пиримидины, 3-замещенные-2-фенил-5-тиоксо-1,2,4-триазолы и 6-(1-нафтил)-2-тиоксо-4-оксопергидро-1,3-тиазин. Структура синтезированных продуктов была подтверждена инфракрасными и ЯМР спектрами.

There are several reports in the literature dealing with the reactions of acyl isothiocyanates affording heterocyclic compounds [1, 2]. In our previous papers we studied the reactions of cinnamoyl isothiocyanates with enamines [3] and sodium hydrogen sulfide [4]. Other authors [5, 6] described the reaction of benzoyl isothiocyanates with phenylhydrazines which resulted in the formation of appropriate 1,3,4- and 1,2,4-triazoles.

The present paper deals with the reactions of acyl isothiocyanates of the naphthalene type with enamines, phenylhydrazine, and sodium hydrogen sulfide. The aim of this study was to obtain new knowledge about the properties of the synthesized compounds.

2-Naphthoyl isothiocyanate (*I*) and  $\beta$ -(1-naphthyl)acryloyl isothiocyanate (*II*) were prepared from the appropriate acyl chlorides [7] by treating with lead thiocyanate in benzene [8, 9].

The course of the individual reactions with the mentioned isothiocyanates is given in Scheme 1.



Scheme 1

The isothiocyanates *I*, *II* with enamines gave in the first step the appropriate *N*-substituted thio-crotonamides *III*–*VI* (Scheme 1A) which were formed easier from enamines containing ketone group (products *III*, *V*). By cyclization of *III*–*VI* in alkali medium at laboratory temperature pyrimidines *VII*–*X* were formed.

Depending on the reaction conditions, phenylhydrazine can react with isothiocyanates under the formation of 1,3- or 1,4-substituted thiosemicarbazides. When the reactions were accomplished in benzene and ethanol, the compounds *I* and *II* gave 1,4-substituted thiosemicarbazides *XI* and *XII* which in alkali medium cyclized to the derivatives of 1,2,4-triazole *XIII* and *XIV* (Scheme 1B). The structures of the obtained 1,4-substituted thiosemicarbazides were proved by negative results of their condensation with benzaldehyde as well as by i.r. spectra. The reaction of *II* with sodium hydrogen sulfide in methanol proceeded as an addition-cyclization reaction resulting in the formation of 6-(1-naphthyl)-2-thioxo-4-oxoperhydro-1,3-thiazine *XV* (Scheme 1C).

The structures of the synthesized compounds were proved by i.r. and <sup>1</sup>H-n.m.r. spectroscopy.

Table 1

## Characterization of the prepared compounds

Compound	Formula	M	Calculated/found			Yield %	M.p., °C Solvent
			% C	% H	% N		
III	C <sub>17</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> S	312.2	65.39	5.12	8.97	78	102—103
			65.56	5.43	8.98		Chloroform—light petroleum
IV	C <sub>18</sub> H <sub>18</sub> N <sub>2</sub> O <sub>3</sub> S	342.2	63.17	5.26	8.18	74	105—107
			63.48	5.30	8.02		Acetone—light petroleum
V	C <sub>19</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub> S	338.4	61.43	5.36	8.27	83	132—133
			61.69	5.30	8.08		Acetone—light petroleum
VI	C <sub>20</sub> H <sub>20</sub> N <sub>2</sub> O <sub>3</sub> S	368.5	66.27	5.56	7.72	80	108—110
			66.16	5.60	7.83		Acetone—light petroleum
VII	C <sub>17</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub> S	294.2	69.39	4.76	9.52	50	194—196
			69.12	4.73	9.25		Ethanol
VIII	C <sub>18</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> S	324.2	66.67	4.93	8.64	89	181—182
			66.92	4.90	8.22		Ethanol
IX	C <sub>19</sub> H <sub>16</sub> N <sub>2</sub> OS	320.4	71.22	5.03	8.74	73	205—207
			71.49	5.11	8.39		<i>n</i> -Butanol
X	C <sub>20</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub> S	350.2	68.54	5.17	7.99	83	196—198
			68.88	5.28	7.60		Ethanol
XI	C <sub>18</sub> H <sub>15</sub> N <sub>3</sub> OS	321.4	67.26	4.70	13.07	65	233—235
			67.11	4.57	12.90		Ethanol
XII	C <sub>20</sub> H <sub>17</sub> N <sub>3</sub> OS	347.2	69.14	4.93	12.09	60	185—186
			69.43	4.51	12.51		Ethanol

XIII	C <sub>18</sub> H <sub>13</sub> N <sub>3</sub> S	303.4	71.26	4.32	13.85	76	255
			71.17	4.63	13.63		Ethanol
XIV	C <sub>20</sub> H <sub>15</sub> N <sub>3</sub> S	329.4	72.92	4.50	12.75	67	235—236
			72.63	4.48	12.94		Ethanol
XV	C <sub>14</sub> H <sub>11</sub> NOS <sub>2</sub>	273.3	61.53	4.03	5.12	68	173—174
			61.84	3.85	4.88		Chloroform—light petroleum

Table 2

Infrared and <sup>1</sup>H-n.m.r. spectra of the prepared compounds

Compound	$\bar{\nu}$ , cm <sup>-1</sup>						$\delta$ , p.p.m.					
	$\nu(\text{C}=\text{O})_{\text{carb}}$	$\nu(\text{C}=\text{O})_{\text{est}}$	$\nu(\text{NHCS})$	$\nu(\text{C}=\text{C})$	$\nu(\text{NCS})$	$\nu(\text{NH})$	$\delta(\text{NH})$	$\delta(\text{NH}_2)$	$\delta(\text{CH}_2)$	$\delta(\text{CH}_3)$	$\delta(\text{CH}=\text{CH})$	$\delta(\text{CH})$
III	1695	—	1324	—	—	—	10.56	8.78	—	2.27; 2.30	—	—
IV	1690	1669	1328, 1515	—	—	—	11.82	8.75	4.08	2.47; 1.15	—	—
V	1688	—	1316, 1498	1618	—	—	12.51	10.57	—	2.22; 2.17	8.65; 7.32	—
VI	1702	1677	1345, 1558	1628	—	—	11.85	9.81	4.16	2.37; 1.23	8.57; 7.20	—
VII	1693	—	—	—	1349	—	8.87	—	—	2.77; 2.43	—	—
VIII	—	1723	—	—	1284	—	8.86	—	4.51	2.50; 1.51	—	—
IX	1696	—	—	1632	1353	—	14.47	—	—	2.72; 2.42	8.92; 7.35	—
X	—	1727	—	1635	1271	—	—	—	4.60	2.47; 1.53	8.92; 7.32	—
XI	1689	—	1215, 1532	—	—	3423	—	—	—	—	—	—
XII	1694	—	1186, 1536	1629	—	3421	—	—	—	—	—	—
XIII	—	—	1493	—	—	3436	—	—	—	—	—	—
XIV	—	—	1489	1648	—	3435	—	—	—	—	—	—
XV	1716	—	1071, 1293, 1438	—	—	3348	—	—	3.73	—	—	5.85

## Experimental

2-Naphthoyl isothiocyanate (*I*) was prepared according to [8].  $\beta$ -(1-Naphthyl)acryloyl isothiocyanate (*II*) was synthesized according to the method described in [9]; yield 78%, m.p. after crystallization from cyclohexane 120°C (decomposition).

For  $C_{14}H_9NOS$  (239.3) calculated: 70.26% C, 3.79% H, 5.85% N; found: 70.38% C, 3.84% H, 5.96% N.

Infrared spectra of the synthesized compounds were measured on a UR-20 Zeiss spectrophotometer in the region of 800—3500  $cm^{-1}$  in chloroform and KBr pellets. The apparatus was calibrated with a polystyrene foil.

The  $^1H$ -n.m.r. spectra were measured on a Tesla BS 487 instrument at 80 MHz in deuterated chloroform and dimethyl sulfoxide. Hexamethyldisiloxane was used as an internal standard.

### $\alpha,\beta$ -Disubstituted thiocrotonamides III—IV

To isothiocyanates *I* and *II*, respectively (0.013 mole) dissolved in anhydrous ether (10—15 ml), enamine (0.013 mole) was added dropwise under stirring at 5—10°C. After 30 min stirring, an orange and a red, respectively very fine precipitates were formed. Stirring was continued for another 1 h and the obtained precipitate was filtered and dissolved in a small amount of polar solvent. Addition of petroleum ether to turbidity resulted in crystallization of the appropriate  $\alpha,\beta$ -disubstituted thiocrotonamides. Characterization and i.r. and  $^1H$ -n.m.r. spectra of *N*-( $\beta$ -amino- $\alpha$ -acetylthiocrotonoyl)-2-naphthamide (*III*), *N*-( $\beta$ -amino- $\alpha$ -ethoxycarbonylthiocrotonoyl)-2-naphthamide (*IV*), *N*-( $\beta$ -amino- $\alpha$ -acetylthiocrotonoyl)- $\beta$ -(1-naphthyl)acrylamide (*V*), and *N*-( $\beta$ -amino- $\alpha$ -ethoxycarbonylthiocrotonoyl)- $\beta$ -(1-naphthyl)acrylamide (*VI*) are in Tables 1 and 2.

### 2,5-Disubstituted 4-thioxo-6-methylpyrimidines VII—X

To the appropriate  $\alpha,\beta$ -disubstituted *N*-thiocrotonamides *III*—*VI* (0.01 mole) dissolved in a smallest amount of methanol, 1 M sodium hydroxide was added dropwise until the red colour of the solution became yellow. The solution was filtered and neutralized by 1 M hydrochloric acid. The immediately formed yellow precipitate of the appropriate pyrimidine was sucked and crystallized from a suitable solvent. Characterization and i.r. and  $^1H$ -n.m.r. spectra of 2-(2-naphthyl)-4-thioxo-5-acetyl-6-methylpyrimidine (*VII*), 2-(2-naphthyl)-4-thioxo-5-ethoxycarbonyl-6-methylpyrimidine (*VIII*), 2-[ $\beta$ -(1-naphthyl)vinyl]-4-thioxo-5-acetyl-6-methylpyrimidine (*IX*), and 2-[ $\beta$ -(1-naphthyl)vinyl]-4-thioxo-5-ethoxycarbonyl-6-methylpyrimidine (*X*) are in Tables 1 and 2.

### 1-Substituted 4-phenylthiosemicarbazides XI, XII

Into isothiocyanates *I* and *II*, respectively (0.011 mole) dissolved in a small amount of benzene, phenylhydrazine (0.01 mole) dissolved in benzene was added dropwise. The

immediately formed precipitate was sucked and crystallized from ethanol. Characterization and i.r. and  $^1\text{H}$ -m.r. spectra of 1-(2-naphthoyl)-4-phenylthiosemicarbazide (XI) and 1- $[\beta$ -(1-naphthyl)acryloyl]-4-phenylthiosemicarbazide (XII) are in Tables 1 and 2.

### 3-Substituted 2-phenyl-5-thioxo-1,2,4-triazoles XIII, XIV

4-Phenylthiosemicarbazides XI and XII, respectively (0.005 mole) were dissolved in 2 M sodium hydroxide (10 ml) at heating. After cooling the solution, 2 M hydrochloric acid was added dropwise until total precipitation. The precipitate was sucked, washed with cold water, and crystallized from a suitable solvent. Characterization and i.r. and  $^1\text{H}$ -n.m.r. spectra of 2-phenyl-3-(2-naphthyl)-5-thioxo-1,2,4-triazole (XIII) and 2-phenyl-3- $[\beta$ -(1-naphthyl)vinyl]-5-thioxo-1,2,4-triazole (XIV) are in Tables 1 and 2.

### 6-(1-Naphthyl)-2-thioxo-4-oxoperhydro-1,3-thiazine XV

To methanolic solution (30 ml) of sodium hydrogen sulfide (0.014 mole), small portions of the compound II (0.007 mole) were added at cooling with cold water and vigorous stirring. After addition of water a precipitate was formed which was filtered, washed with water, dried, and crystallized from the mixture of chloroform and petroleum ether.

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Translated by A. Kardošová