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REACTION OF AROYL ISOTHIOCYANATE WITH ACTIVE METHYLENE COMPOUNDS

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nitrile, ethyl acetoacetate, and cyanothioacetamide and with the possible utility of the resultant compounds in the synthesis of functionalized heterocyclic systems.

When aroyl isothiocyanates **1** were allowed to react with malononitrile in a 1:1 ratio thioamides **2** were obtained via the addition of the methylene function of malononitrile to the isothiocyanate function of the aroyl isothiocyanate. Cyclization of thioamides **2** into oxazine **3** was achieved in basic medium. The conversion of **2** into **3** may proceed via the addition of enolate anion to the cyano group to yield the imino form **3** which tautomerizes to the more stable enamino compound **4**. Acetic acid cyclization of **2** afforded oxazine **4**. ^1H NMR of **4a** revealed amino signal at δ 6.2. Reaction of benzoyl isothiocyanate with ethyl acetoacetate gave

TABLE I

Cmpd	M.P $^{\circ}\text{C}$	Formula (MW)	Analysis Calc. / Found %				
			C	H	N	S	Cl
<u>2a</u>	168-70	$\text{C}_{11}\text{H}_7\text{N}_3\text{OS}$ (229.25)	57.63	3.08	18.33	13.98	
			57.60	3.00	18.40	13.90	
<u>2b</u>	158-60	$\text{C}_{11}\text{H}_6\text{N}_3\text{OSCl}$ (263.7)	50.10	2.29	15.93	12.16	13.44
			50.00	2.20	15.90	12.20	13.50
<u>4a</u>	208-10	$\text{C}_{11}\text{H}_7\text{N}_3\text{OS}$ (229.25)	57.63	3.08	18.33	13.98	
			57.70	3.00	18.30	14.30	
<u>4b</u>	200-02	$\text{C}_{11}\text{H}_6\text{N}_3\text{OSCl}$ (263.7)	50.10	2.29	15.43	12.16	13.44
			50.00	2.30	16.00	12.20	13.40
<u>5</u>	161-64	$\text{C}_{14}\text{H}_{15}\text{NO}_4\text{S}$ (293.34)	57.32	5.15	4.77	10.93	
			57.00	5.20	4.80	11.00	
<u>6</u>	122-24	$\text{C}_{20}\text{H}_{18}\text{N}_2\text{O}_2\text{S}$ (350.38)	68.55	5.18	7.99	9.15	
			68.50	5.20	8.00	9.10	
<u>7</u>	180-82	$\text{C}_{18}\text{H}_{14}\text{N}_2\text{O}_2\text{S}$ (322.38)	67.06	4.38	8.69	9.94	
			67.00	4.40	8.60	9.90	
<u>9a</u>	163-65	$\text{C}_{11}\text{H}_7\text{N}_3\text{S}_2$ (245.32)	53.86	2.88	17.13	26.14	
			53.80	2.90	17.20	26.20	
<u>9b</u>	193-95	$\text{C}_{11}\text{H}_6\text{ClN}_3\text{S}_2$ (291.32)	49.48	2.08	14.42	22.01	12.01
			49.50	2.00	14.40	22.00	12.30
<u>9c</u>	190-91	$\text{C}_{12}\text{H}_9\text{N}_3\text{OS}_2$ (275.34)	52.35	3.29	15.26	23.29	
			52.40	3.30	15.20	23.20	

thionamide 5. Aminolysis of thioamide 5 using aniline yielded ethyl pyrimidine-4-carboxylate 6 and 4-acetyl-pyrimidine 7. Aroyl isothiocyanate was reacted with cyanothioacetamide to yield pyrimidines 9a-c presumably via the thiourea intermediate 8.

EXPERIMENTAL

Melting points are all uncorrected. IR spectra (KBr) were recorded on a Pye-Unicam Sp-1100 spectrophotometer. ^1H NMR were recorded on a Varian (EM 390 L). Microanalyses were carried out by Microanalytical Centre Cairo University.

TABLE II

Compound	IR (Cm^{-1}) Selected bands
<u>2a</u>	3400 - 3300 (NH), 2225 (CN), 1200 (C=S)
<u>2b</u>	3400 - 3250 (NH), 2220 (CN), 1190 (C=S)
<u>4a</u>	3350 - 3250 (NH), 2215 (CN), 1190 (C=S)
<u>4b</u>	3400 - 3250 (NH), 2220 (CN), 1190 (C=S)
<u>5</u>	3400 - 3300 (NH), 1670, 1665 (CO), 1185 (C=S)
<u>6</u>	1660 (C=O), 1200 (C=S)
<u>7</u>	1665, 1650 (CO)
<u>9a</u>	3400 - 3000 (NH), 2220 (CN), 1200 (C=S)
<u>9b</u>	3400 - 3300 (NH), 2220 (CN), 1195 (C=S)
<u>9c</u>	3400 - 2225 (NH), 2225 (CN), 1195 (C=S)

TABLE III

Compound	^1H NMR (δ , CDCl_3)
<u>4a</u>	6.2 (s, 2H, NH_2), 6.9 - 7.4 (m, 5H, ArH's);
<u>4b</u>	6.4 (s, 2H, NH_2), 6.65 - 6.98, 7.2 - 7.4 (m, 4H, ArH's)
<u>7</u>	2.3 (s, 3H, CH_3), 6.2 - 7.5 (m, 10H, ArH's), 9.1 (s, 1H, SH),
<u>9a</u>	7.2 - 8.0 (m, 5H, ArH's), 9.3 (s, 1H, SH), 9.9 (s, 1H, SH)
<u>9c</u>	3.2 (s, 3H, OCH_3), 6.4, 7.4 (m, 4H, ArH's), 9.7 (s, 1H, SH), 10.4 (s, 1H, SH).

Aroylamino-thiocarbonylmalonodinitrile (2)

To a stirred solution of aroyl isothiocyanate 1 [prepared by addition of appropriate aroyl chloride (0.01 mol) to a stirred ammonium thiocyanate (0.015 mol) in acetone (20 ml) dropwise over 10 minutes, stirring continued for 1/2 hour] malononitrile was added over 10 minutes. Stirring continued for 1/2 hour, poured onto ice-water (20 ml), the solids that separated, collected by filtration and recrystallized from methanol to produce yellow crystals of 2 (Table I) in 80% yield.

2-Aryl-5-cyano-6-amino-1,3-oxazine-4-thione 4a,b

a) A mixture of compound 2 (0.01 mol) and sodium ethoxide (0.01 mol) in ethanol (20 ml) was heated under reflux for 1/2 hour. The solids obtained were collected by filtration, recrystallized from methanol to give orange crystals of 4 (Table I) yield 50%.

b) A solution of 2 (0.01 mole) and conc. hydrochloric acid (3 drops) in acetic acid (15 ml) was heated under reflux for 1/2 hour. The solid that was obtained upon dilution with water (20 ml) was collected by filtration and recrystallized from methanol to give orange crystals of 4 (Table I) in 45% yield.

Thioamide 5

To a stirred solution of benzoyl isothiocyanate 1 (0.01 mol) was added ethyl acetoacetate (0.01 mol) over 20 minutes. After stirring 1/2 hour, the mixture was poured onto ice-water (30 ml). The solid that separated was collected by filtration and recrystallized from aqueous methanol to afford yellow crystals of 5 (Table I) in 70% yield.

Pyrimidine-4-carboxylate 6 and 4-acetylpyrimidine 7

A mixture of 4 (0.01 mol) and aniline (0.01 mol) was fused at (160°C) for 1/2 hour. The solids obtained upon addition of ethanol (10 ml) were collected by filtration, recrystallized from ethanol to give colorless crystals of 6 (yield 50%). The filtrate diluted with water (20 ml), filtered, crystallized from dilute methanol into yellow crystals of 7 (10% yield).

Pyrimidines dithione 9a-c

A mixture of 1a-c (0.01 mol) and cyanothioacetamide (0.01 mol) in ethanol (20 ml) was heated under reflux for one hour. The orange solids obtained upon cooling were collected by filtration and crystallized from ethanol to give orange crystals of 9a-c (Table I) yield 70-75%.

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