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## A CONVENIENT PROCEDURE TO PREPARE 1, 4- DITHIOAROYL PIPERAZINES

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**ABSTRACT** A simple, convenient and high-yield synthetic method for 1,4-dithioaroyl piperazines is reported. Aromatic aldehydes, anhydrous piperazine and elementary sulfur were used as starting synthetic materials. The reaction condition was mild.

Derivatives of piperazines have wide biological activities. However, only a few 1,4-dithioaroyl piperazines were prepared<sup>[1]</sup>, some compounds exhibited antisecretory and antiulcer activities<sup>[2]</sup>. They were synthesized from corresponding 1,4-dibenzoyl piperazines<sup>[3]</sup>, but the operation was difficult and the yield was unsatisfactory.

We were interested in the kind of compounds as medicines and corrosion inhibitors, and also as ligands possessing both hard and soft donor atoms. In connection with our before work<sup>[4]</sup>, we now report a convenient and highly efficient synthesis of 1,4-dithioaroyl piperazines.

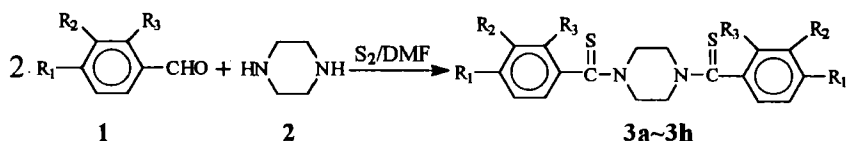
The synthetic route is outlined as Scheme 1. Aromatic aldehydes, anhydrous piperazines and elementary sulfur were used as starting synthetic materials. The anhydrous piperazine was obtained from hexahydrate piperazine by dehydrating with dried benzene. The reactions were carried out at 70-90°C for 2-3 h. The target compounds were easily obtained in 63-91% yield. The

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reaction conditions were listed in Table 1. The structures of all target products were confirmed by IR,  $^1\text{H}$ NMR and elementary analysis (Table 2). The IR spectra of all products showed C=S absorption at  $1202\sim 1232\text{ cm}^{-1}$ .

Thus, We provide a simple, convenient synthetic method for 1,4-dithioaroyl piperazines. The biological activities of the products are to be tested.



**Scheme 1** Synthetic route of 1,4-dithioaroyl piperazines

General procedure for preparation of 1,4-dithioaroyl piperazines: The aromatic aldehyde (10 mmol), anhydrous piperazine (5 mmol), elementary sulfur (5 mmol) and DMF (10 ml) were placed in a flask fitted a reflux condenser and magnetic stirrer. The mixture was stirred at the temperature indicated in Table 1, and the reaction was monitored by TLC. After cooled to room temperature, the crude product was filtered, washed with several drops of DMF and dried. The pure product was obtained after the crude product was refluxed in  $\text{CS}_2$  for 30 min, cooled and filtered.

**Table 1** Preparation of 1,4-dithioaroyl piperazines

Product	$\text{R}_1, \text{R}_2, \text{R}_3$	Reaction Time/Temp	yield (%)
3a	$\text{R}_1=\text{R}_2=\text{R}_3=\text{H}$	2h/80°C	86
3b	$\text{R}_1, \text{R}_2=\text{OCH}_2\text{O}, \text{R}_3=\text{H}$	3h/70°C	79
3c	$\text{R}_1=\text{OCH}_3, \text{R}_2=\text{R}_3=\text{H}$	2h/80°C	86
3d	$\text{R}_1=\text{R}_2=\text{OCH}_3, \text{R}_3=\text{H}$	3h/80°C	90
3e	$\text{R}_1=\text{OH}, \text{R}_2=\text{R}_3=\text{H}$	2h/80°C	88
3f	$\text{R}_1=\text{OH}, \text{R}_2=\text{OCH}_3, \text{R}_3=\text{H}$	2h/80°C	91
3g	$\text{R}_1=\text{NO}_2, \text{R}_2=\text{R}_3=\text{H}$	2h/90°C	77
3h	$\text{R}_1=\text{R}_3=\text{NO}_2, \text{R}_2=\text{H}$	3h/90°C	63

Table 2 Physical and Chemical data of Compound 3a~3h

Comp.	mp (°C)	molecular formula	Analysis(%)			IR(KBr) ν(cm <sup>-1</sup> )	<sup>1</sup> HNMR (DMSO/TMS) δ(ppm)	
			Calcd.	Found				
			C	H	N			
3a	276~278	C <sub>18</sub> H <sub>18</sub> N <sub>2</sub> S <sub>2</sub>	66.22	5.56	8.58	1500	1490	3.66, 3.88, 4.24, 4.49 (m,
			(66.34)	(5.43)	(8.39)	1300	1220	8H, 4CH <sub>2</sub> N), 7.29~7.44 (m,
						760	700	10H, Ar-H)
3b	302~304	C <sub>20</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub> S <sub>2</sub>	57.95	4.38	6.76	1492	1438	3.72, 3.91, 4.19, 4.40 (m, 8H,
			(57.98)	(4.53)	(6.34)	1300	1214	4CH <sub>2</sub> N), 5.97, 6.09(s, 4H,
						864	814	2OCH <sub>2</sub> O), 6.86~6.97(m, 6H,
								Ar-H)
3c	272~274	C <sub>20</sub> H <sub>22</sub> N <sub>2</sub> O <sub>2</sub> S <sub>2</sub>	62.14	5.74	7.25	1600	1480	3.73, 3.93, 4.21, 4.44 (m, 8H,
			(62.24)	(5.58)	(7.23)	1300	1218	4CH <sub>2</sub> N), 3.77, 3.80(s, 6H,
						814		2OCH <sub>3</sub> ), 6.90~7.38(m, 8H,
								Ar-H)
3d	260~262	C <sub>22</sub> H <sub>26</sub> N <sub>2</sub> O <sub>4</sub> S <sub>2</sub>	59.17	5.87	6.27	1600	1519	3.72, 3.75, 3.78, 3.82 (s, 12H,
			(59.50)	(5.88)	(6.12)	1478	1290	4OCH <sub>3</sub> ), 3.84, 3.93, 4.21,
						1232	820	4.42 (m, 8H, 4CH <sub>2</sub> N), 6.93~
								6.97 (m, 6H, Ar-H)

(continued)

Table 2 Continued

Comp.	mp (°C)	molecular formula	Analysis(%)			IR(KBr) ν(cm <sup>-1</sup> )	<sup>1</sup> HNMR (DMSO/TMS) δ(ppm)
			Calcd.	Found			
			C	H	N		
3e	321~323	C <sub>18</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub> S <sub>2</sub>	60.31	5.06	7.82	3218	1608
			(60.45)	(5.12)	(7.43)	1480	1300
						1202	831
							3.74, 3.93, 4.19, 4.40 (m, 8H, 4CH <sub>2</sub> N), 6.72~6.74 (m, 4H, Ar-H), 7.23~7.24(m, 4H, Ar-H), 9.96 (s, 2H, 2OH)
3f	334~336	C <sub>20</sub> H <sub>22</sub> N <sub>2</sub> O <sub>4</sub> S <sub>2</sub>	57.39	5.30	6.70	3394	1602
			(57.53)	(5.12)	(6.89)	1483	1308
						1210	809
							3.76, 3.80 (s, 6H, 2OCH <sub>3</sub> ), 3.82, 3.95, 4.20, 4.41 (m, 8H, 4CH <sub>2</sub> N), 6.75~6.96 (m, 6H, Ar-H)
3g	133~135	C <sub>18</sub> H <sub>16</sub> N <sub>4</sub> O <sub>4</sub> S <sub>2</sub>	51.92	3.87	13.46	3420	1598
			(51.68)	(3.94)	(13.64)	1408	1350
						1212	854
							3.12~4.51 (m, 8H, 4CH <sub>2</sub> N), 7.53~7.64 (m, 4H, Ar-H), 8.22~8.31(m, 4H, Ar-H)
3h	200~202	C <sub>18</sub> H <sub>14</sub> N <sub>6</sub> O <sub>8</sub> S <sub>2</sub>	42.68	2.79	16.60	3422	1627
			(42.95)	(2.63)	(16.31)	1522	1349
						820	739
							2.66~4.10 (m, 8H, 4CH <sub>2</sub> N), 7.22~8.84 (m, 6H, Ar-H)

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