Syntheses of Polycyclic-1,4-dithiines and Related Heterocycles

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Received August 19, 1991

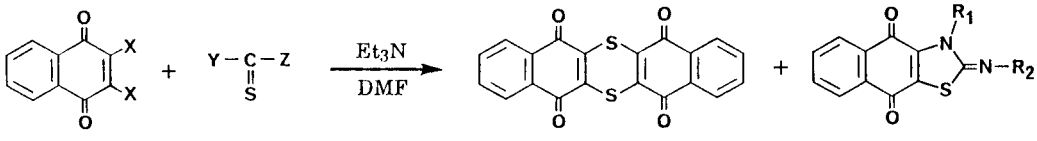
Reactions of dihalogenoquinones or dihalogenoquinoxalines with thioamides gave the corresponding 1,4-dithiines in high yields. Many of polycyclic 1,4-dithiin derivatives can be synthesized by the reactions of dihalogenoheterocycles with thioamides, and they are useful as pigments and functional materials for electro-optical applications. Some of heteroaromatic-1,4-dithiins formed an intermolecular charge-transfer (CT) complex with a π-acceptor such as TCNQ, and they are useful as π-donors for CT complex.

J. Heterocyclic Chem., **29**, 439 (1992).

Polyheterocyclic compounds are of current interest as functional materials for electronic, opto-electronic and photonic devices [1]. They have been used as a charge-generation material for organic photoconductors and an electron donating molecule for organic superconductors. Some of the dye chromophores such as tetraaminoanthraquinone act as a new electron donating molecules for the intermolecular CT complexes with high electric conductivity [2]. In our previous paper [3], we reported the new syntheses of dibenzo[*b,i*]thianthrene-5,7,12,14-tetrone (**3**) by the reaction of 2,3-dihalogeno-1,4-naphthoquinone (**1**) with dithiooxamide (**2a**) which gave **3** in 90% yield but not 2,2'-bis(naphtho[2,3-*d*]thiazole-4,9-dione) (**4**) as previously reported [4]. This reaction can be applied to the synthesis of wide varieties of 1,4-dithiin derivatives. The reaction of dihalogenonaphthoquinone (**1**) with thioamides **2** were studied and the results are summarized in Table 1 and Scheme 1.

The reaction of **1** with **2** gave **3** as the main product but in the cases of alkylthiourea as a reagent, 2-imino-4,9-dioxonaphtho[2,3-*d*]thiazoles **5** were obtained. The increase of the nucleophilicity of the amino group in **2** by the alkyl substitution promotes the ring closure reaction to give thiazoles **5** (Runs 3-5), but tetramethylthiourea (**2e**) no longer gave thiazole but **3** in 33% yield (Run 6). The nucleophilic attack of the thiocarbonyl group first occurred and **3** was obtained in 95% yield by the reaction of **1a** with thioacetoamide (**2f**) (Run 7), and none of the corresponding thiazole **6b** was obtained. The reaction of dibromonaphthoquinone (**1b**) with **2f** also gave **3** in 96% yield (Run 8). The isolation of **5a** and **5b** were very difficult from the complex reaction mixtures and they were detected by mass spectroscopy of the products (Runs 3 and 4). While in the case of the reaction of **1a** with **2d**, **5c** was obtained in 57%

Scheme 1



1

a, X=Cl
b, X=Br

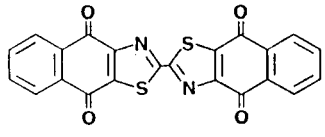
2

	Y	Z
a,	NH_2	$C(S)NH_2$
b,	NH_2	NH_2
c,	NH_2	$NHCH_3$
d,	$NHCH_3$	$NHCH_3$
e,	$N(CH_3)_2$	$N(CH_3)_2$
f,	CH_3	NH_2

3

5

	R_1	R_2
a,	H	H
b,	CH_3 (H)	$H(CH_3)$
c,	CH_3	CH_3



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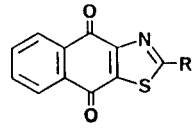

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a, R=NH_2
b, R=CH_3

Table 1

Reaction Products from 2,3-Dihalogeno-1,4-naphthoquinones and Thioamides [a]

Run	Reactant	Thioamide	Molar ratio	Time hours	Temperature °C	Product (%) 3	5
1	**1a**	**2a**	2:1	10	50	90	0
2	**1b**	**2a**	2:1	10	50	74	0
3	**1a**	**2b**	1:1	5	50	39	**5a** [b]
4	**1a**	**2c**	1:1	10	50	[c]	**5b** [d]
5	**1a**	**2d**	1:1	10	50	[b]	**5c** (57)
6	**1a**	**2e**	1:1	10	50	33	0
7	**1a**	**2f**	1:1	10	50	95	0
8	**1b**	**2f**	1:1	10	50	96	0

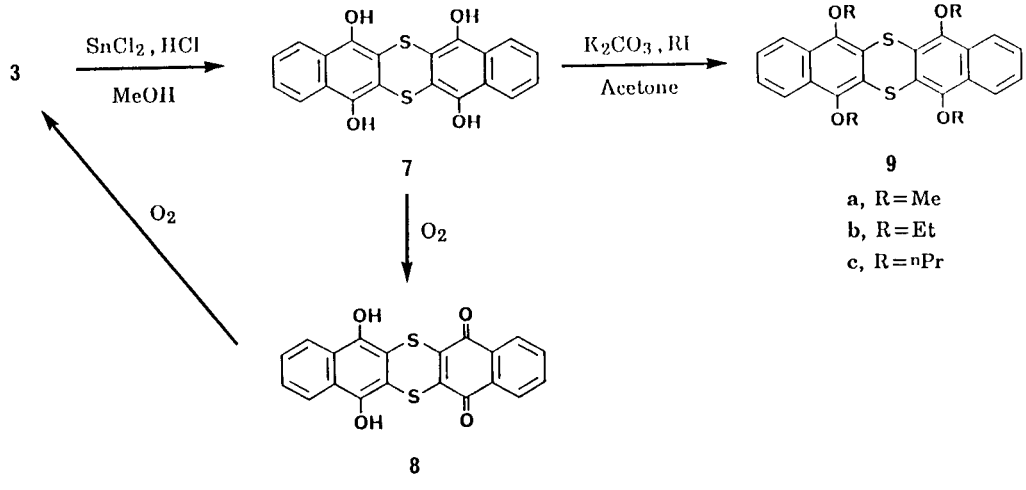
[a] The mixture of **1** and **2** in DMF was stirred in the presence of triethylamine. [b] Trace amounts. [c] Minor product in low yields. [d] Major product in low yields.

yield as a main product and **3** was obtained in trace amounts (Run 5).

The reduction of **3** with tin(II) chloride gave 5,7,12,14-tetrahydroxydibenzo[*b,i*]thianthrene (**7**) which was spontaneously oxidized by atmospheric oxygen to 7,12-dihydroxydibenzo[*b,i*]thianthrene-5,14-dione (**8**) and then was further oxidized to **3**. The oxidation of **7** to **8** can be followed by the nmr spectra in dimethyl sulfoxide-d_6. The aromatic protons of **7** were observed at 8.12 (m, 4H) and 7.50 (m, 4H), while in **8**, those were observed at 8.00 (m, 2H), 7.95 (m, 2H), 7.84 (m, 2H) and 7.45 ppm (m, 2H), respectively. An increase in the aromatic signals of **8** and decrease in those of **7** were observed during the nmr measurement. The isolation of **8** failed but the formation of **8** from **7** was also observed by the increase of the absorbance at 530 nm and decrease of it at 359 nm. The isosbestic point was observed at 390 nm in dimethylformamide solution. Compound **7** can be stabilized by alkylation. The reaction of **7** with alkyl iodide in the presence of potassium carbonate in acetone gave the corresponding alkoxy derivatives **9a-9c** (Scheme 2).

Compound **9** has a planar structure along with the five ring-systems from the observation of the CPK molecular model. Compound **9** has strong donor moieties of the alkoxy groups and the sulfide linkage and thus is proposed to act as a strong electron donating molecule to form the intermolecular charge-transfer (CT) complex. The mixture of **9a** with tetracyanoquinodimethane (TCNQ) as an acceptor in acetonitrile gave the CT complex **10** which is obtained as a quite big black colored single crystals in size of 5.2 x 1.3 x 1.0 mm^3. Compounds **9b** and **9c** did not give a CT complex because of their steric hindrance of the longer alkyl groups. The partial electron transfer from **9a** to TCNQ was confirmed from by the absorption spectra at 700-900 nm region caused by the TCNQ anion radical in dimethylformamide solution [5]. The absorption spectra of the TCNQ anion radical was also observed from the combinations of **7** and **8** with TCNQ, respectively, but none of

Scheme 2



the CT complexes were isolated from the solution because of spontaneous oxidation of **7** and **8** by air. The X-ray structure analysis of the CT complex **10** is now under investigation.

We recently reported [3] that the reaction of 3,4-dichloro-*N*-phenylmaleimide (**11**) with dithiooxamide (**2a**) gave 2,6-diphenyl-2,3,6,7-tetrahydro-1*H*,5*H*-[1,4]dithiino[2,3-*c*:5,6-*c'*]dipyrrole (**12**) but not formerly reported bisthiazole

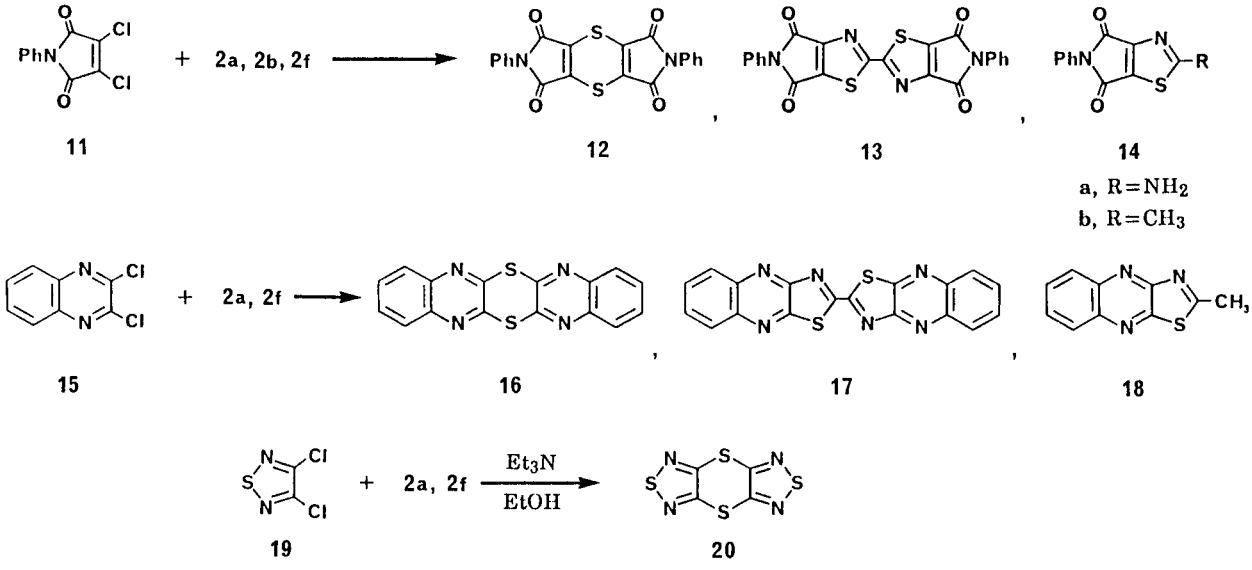
Table 2

Comparison of the reaction Products from Dichloroheterocycles **1**,**11** and **15** and Thioamides

Run	Reactant	Thioamide	Molar ratio	Reaction conditions [a]	Product Yield (%)	Ref [b]
1	**1a**	**2a**	2:1	A	**3** (90)	[3]
2	**1a**	**2a**	2:1	A	**4** (57)	[4]
3	**1a**	**2b**	1:1	B	**3** (39)	[3]
4	**1a**	**2b**	1:1	E	**3** (49)	a
5	**1a**	**2b**	1:1	F	**3** (22)	a
6	**1a**	**2b**	1:1	E	**6a** (45)	[6]
7	**1a**	**2f**	1:1	A	**3** (95)	a
8	**1a**	**2f**	1:1	E	**3** (89)	a
9	**1a**	**2f**	1:1	E	**6b** (62)	[6]
10	**11**	**2a**	2:1	C	**12** (80)	[3]
11	**11**	**2a**	2:1	C	**13** (70)	[4]
12	**11**	**2b**	1:1	A	**12** (77)	a
13	**11**	**2b**	1:1	E	**12** (27)	a
14	**11**	**2b**	1:1	F	**12** (40)	a
15	**11**	**2b**	1:1	E	**14a** (59)	[6]
16	**11**	**2f**	1:1	E	**12** (85)	a
17	**11**	**2f**	1:1	E	**14b** (58)	[6]
18	**15**	**2a**	1:1	D	**16** (77)	a
19	**15**	**2a**	2:1	E	**16** (24)	a
20	**15**	**2a**	2:1	E	**17** (42)	[6]
21	**15**	**2f**	1:2	D	**16** (51)	a
22	**15**	**2f**	1:1	E	**16** (9)	a
23	**15**	**2f**	1:1	E	**18** (49)	[6]

[a] Reactant and thioamide in solvent were heated in the presence of base. A: DMF, 50°C x 10 hours, Et_3N; B: DMF, 50°C x 5 hours, Et_3N; C: DMF, 60°C x 10 hours, Et_3N; D: DMF, 100°C x 5 hours, Et_3N; E: DMSO, 120°C x 5 hours, DABCO; F DMSO, 20°C x 5 hours, DABCO; DMF: *N*,*N*-Dimethylformamide; DMSO: Dimethyl sulfoxide. DABCO: 1,4-Diazabicyclo[2.2.2]octane. [b] a: This work.

Scheme 3



13 [4]. Furthermore, the reaction of 2,3-dichloroquinoxaline (**15**) with **2a** also gave [1,4]dithiino[2,3-*b*:5,6-*b'*]diquinoxaline (**16**) but not formerly reported 2,2'-bisthiazolo-[4,5-*b*]quinoxaline (**17**) [6]. Reexaminations of the reactions between **1, 11** and **15** with other thioamides gave completely different products from the formerly reported thiazole derivatives **6, 14** and **18**, respectively. These results are summarized in Table 2 and Scheme 3. As reported previously [3], reactions of **1a** with **2a** (Runs 1 and 2) gave the 1,4-dithiin derivative **3** but not the formerly reported thiazoles **4** under the same conditions. Katritzsky *et al.* reported that the reaction of **1a** with thiourea **2b** gave 2-aminonaphtho[2,3-*d*]thiazole-4,9-dione (**6a**) in 45% yield (Run 6) [6], but the same reaction did not give **6a** but gave **3** in 49% yield (Run 4). A similar reaction of **1a** with **2b** at 20° gave **3** in 22% yield (Run 5). The reaction of **1a** with **2b** in dimethylformamide in the presence of triethylamine as a base also gave **3** in 39% yield but none of **6a** was obtained (Run 3). In the case of **1a** with **2f**, previously reported 2-methylnaphtho[2,3-*d*]thiazole-4,9-dione (**6b**) was not obtained (Run 9), but **3** was obtained in high yield under the same (Run 8) and similar conditions (Run 7). The reaction of **11** and **2a** also gave the different products **12** in 80% yield (Run 10) but not **13** in 70% yield as reported (Run 11) [4] under the same conditions. The reaction of **11** and **2b** gave **12** under various conditions (Runs 12-14) but the reported **14a** (Run 15) was not obtained. Similar reaction of **11** with **2f** also gave **12** in 85% yield (Run 16) but not the thiazole **14b** (Run 17) as reported [6]. On the other hand, the reaction of 2,3-dichloroquinoxaline (**15**) with **2a** gave **16** in 77% yield (Run 18) but not **17** as reported (Run 20). The same reaction of **15** with **2a** gave **16** in 24% yield (Run 19). Similar reaction of **15** with **2f** gave **16** in 9% yield (Run 22) but not **18** as reported (Run 23), and higher yield of **16** in 51% yield was obtained under the improved conditions (Run 21) but none of the thiazole **18** was obtained.

Furthermore, the reaction of 3,4-dichloro-1,2,5-thiadiazole (**19**) with **2a** gave [1,4]dithiino[2,3-*c*:5,6-*c'*]bis[1,2,5]-thiadiazole (**20**) in 26% yield. Similar reactions of **19** with **2f** also gave **20** in 23% yield.

From the results, we can conclude that the reaction of reactive *ortho*-dihalogenoheterocycles with thioamides gave the coupling product from 1,4-dithiin ring but not the thiazole derivatives as previously reported [4 and 6].

EXPERIMENTAL

The ^{1}H nmr spectra were taken on a JEOL JNM-GX 270 (270 MHz) spectrometer. The ir spectra were recorded with a Shimadzu IR-420 instrument. The ms spectra were recorded on a Finnigan MAT TSQ-70 spectrometer. The visible spectra were measured on a Shimadzu UV-265FS spectraphotometer. Melting points were determined on a Yanaco MP-500D apparatus without correction. Elemental analyses were conducted with a Yanaco CHN MT-3 recorder.

2,3-Dichloro-1,4-naphthoquinone (**1a**), thioamides **2a-2f**, 2,3-dichloroquinoxaline (**15**) and 3,4-dichloro-1,2,5-thiadiazole (**19**) are reagent grade and were used without further purification. 2,3-Dibromo-1,4-naphthoquinone (**1b**) and 3,4-dichloro-*N*-phenylmaleimide (**11**) were synthesized and identified by the usual methods. Compounds **3,7** and **12** were identified previously [3].

2-Methylimino-3-methyl-4,9-dioxonaphtho[2,3-*d*]thiazole (**5c**).

2,3-Dichloro-1,4-naphthoquinone (**1a**, 8.8 mmoles) and 1,3-dimethylthiourea (**2d**, 8.8 mmoles) were dissolved in dimethylformamide (30 ml), and then triethylamine (1.8 g) was added to the solution with stirring and the reaction mixture was heated at 50° for 10 hours. The purplish-black product precipitated out during the reaction. After cooling, the product was collected by filtration, washed with water and then ethanol, and recrystallized from ethanol to give **5c**, yield 57%, mp 230-232°; ^{1}H nmr (DMSO-d_6): 8.04 (m, 1H), 7.98 (m, 1H), 7.84 (m, 2H), 3.69 (s, 3H), 3.04 (s, 3H); ir (potassium bromide): 1680, 1650, 1340, 1280, 720 cm^{-1}; ms: (m/z) 258 (M$^+$, 100%); uv/vis (ethanol): λ max 283 (24000) and 516 nm (ε 2000).

Anal. Calcd. for $C_{13}H_{10}N_2O_2S$: C, 60.45; H, 3.90; N, 10.85. Found: C, 60.62; H, 3.51; N, 10.73.

5,7,12,14-Tetraalkoxydibenzo[*b,i*]thianthrenes **9a-9c**.

A suspension of 5,7,12,14-tetrahydroxydibenzo[*b,i*]thianthrene (**7**, 3 mmoles) and potassium carbonate (3.5 g) in dry acetone (50 ml) was refluxed for 30 minutes under an argon atmosphere. Alkyl iodide (2 ml) was added to the mixture and heated for 15 hours. After cooling, the reaction mixture was poured into water (200 ml) and the precipitate was collected by filtration, washed with water, then dried *in vacuo*. The product was isolated by column chromatography on alumina, and then recrystallized from acetonitrile to give **9a-9c**.

5,7,12,14-Tetramethoxydibenzo[*b,i*]thianthrene (**9a**).

The yield was 42%, mp 194-195°; ^{1}H nmr (deuteriochloroform): 8.06 (m, 4H), 7.51 (m, 4H), 4.08 (s, 12H); ir (potassium bromide): 2970, 1460, 1360, 1080, 1000, 760 cm^{-1}; ms: (m/z) 436 (M$^+$, 100%); uv/vis (chloroform): λ max 298 nm (ε 57600).

Anal. Calcd. for $C_{24}H_{20}O_4S_2$: C, 66.03; H, 4.62. Found: C, 65.68; H, 4.44.

5,7,12,14-Tetraethoxydibenzo[*b,i*]thianthrene (**9b**).

The yield was 40%, mp 217-218°; ^{1}H nmr (deuteriochloroform): 8.04 (m, 4H), 7.45 (m, 4H), 4.23 (q, 8H, J = 7), 1.65 (t, 12H, J = 7); ir (potassium bromide): 3000, 1480, 1360, 1350, 1080, 1020, 940, 770 cm^{-1}; ms: (m/z) 492 (M$^+$, 100%); uv/vis (chloroform): λ max 297 nm (ε 59200).

Anal. Calcd. for $C_{28}H_{28}O_4S_2$: C, 68.26; H, 5.73. Found: C, 67.88; H, 5.65.

5,7,12,14-Tetra-*n*-propoxydibenzo[*b,i*]thianthrene (**9c**).

The yield was 21%, mp 205-206°; ^{1}H nmr (deuteriochloroform): 8.04 (m, 4H), 7.47 (m, 4H), 4.11 (t, 8H, J = 7), 2.07 (q, 8H, J = 7), 1.24 (t, 12H, J = 7); ir (potassium bromide): 3000, 1360, 1080, 960, 770 cm^{-1}; ms: (m/z) 548 (M$^+$, 100%); uv/vis (chloroform): λ max 298 nm (ε 57800).

Anal. Calcd. for $C_{32}H_{36}O_4S_2$: C, 70.04; H, 6.61. Found: C, 69.69; H, 6.58.

[1,4]Dithiino[2,3-*b*:5,6-*b'*]diquinoxaline (**16**).

2,3-Dichloroquinoxaline (**15**, 5 mmoles) and dithiooxamide (**2a**, 5 mmoles) were dissolved in dimethylformamide (30 ml), and triethylamine (1.0 g) was added with stirring. The reaction mixture was heated at 100° for 5 hours. The yellowish-brown product precipitated out during the reaction. After cooling, the product was collected by filtration, washed with water and then ethanol to give **16**, yield 77%, mp 350°, sublimed over 360°; ^{1}H nmr (deuteriochloroform): 7.94 (m, 4H), 7.71 (m, 4H); ir (potassium bromide): 1325, 1255, 1180, 1110, 1045, 755, 600 cm^{-1}; ms: (m/z) 320 (M^+, 100%); uv/vis (chloroform): λ max 281 (22400) and 390 nm (ε 19000).

Anal. Calcd. for $C_{16}H_8N_4S_2$: C, 59.98; H, 2.52; N, 17.49. Found: C, 59.79; H, 2.22; N, 17.67.

[1,4]Dithiino[2,3-*c*:5,6-*c'*]bis[1,2,5]thiadiazole (**20**).

3,4-Dichloro-1,2,5-thiadiazole (**19**, 10 mmoles) and dithiooxamide (**2a**, 10 mmoles) were dissolved in ethanol (30 ml), and triethylamine (3 ml) was added with stirring. The reaction mixture was refluxed for 5 hours. After cooling, the precipitate was collected by filtration, washed with ethanol, then dried *in vacuo*. The product were isolated by column chromatography on silica gel to give **20**, yield 26%, mp 182-183°; ^{13}C nmr (deuteriochloroform): 148.4; ir (potassium bromide): 1300, 1240, 1050, 820 cm^{-1}; ms: (m/z) 232 (M^+, 100%); uv/vis (chloroform): λ max 328 nm (ε 13500).

Anal. Calcd. for $C_4N_4S_4$: C, 20.68; N, 24.12. Found: C, 20.74; N, 24.34.

CT Complex of **9a**-TCNQ (**10**).

5,7,12,14-Tetramethoxydibenzo[*b,i*]thianthrene (**9a**, 100 mg, 0.23 mmole) was dissolved in acetonitrile (100 ml) at 80°. The solution was added to the solution of tetracyanoquinodimethane (TCNQ, 47 mg, 0.23 mmole) in acetonitrile (50 ml) with stirring at 80°. The single crystal of the CT complex was grown after 75 days at room temperature as a black colored columns in a yield of 42% (64 mg).

Anal. Calcd. for $C_{38}H_{27}N_5O_4S_2$ (**9a**:TCNQ:CH_3CN = 1:1:1): C, 66.94; H, 3.99; N, 10.27. Found: C, 66.77; H, 3.74; N, 10.58.

The X-ray analysis of the CT complex **10** has been conducted and the structure will be shortly reported in this journal.

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