J. Org. Chem. 1987, 52, 1089–1092

case to give a mixture of 630 mg (35%) of **10b** and 400 mg (20%) of **4b**.

In an attempted thermolysis, a solution of **3b** (150 mg, 0.34 mmol) in diphenyl ether (10 mL) was refluxed for 15 h and worked up in the usual manner to give 1.45 g (96%) of the recovered starting material **3b**.

Thermolysis of 12b. A sample of **12b** (150 mg, 0.36 mmol) was heated in a sealed tube at ca. 290–295 °C for 2 h. The mixture was chromatographed over silica gel. Elution with a mixture (1:1) of benzene and petroleum ether gave 80 mg (56%) of **10b**, mmp 228–229 °C, after recrystallization from a mixture (1:9) of methylene dichloride and petroleum ether.

Attempted Thermolysis of 4a. Refluxing a solution of **4a** (100 mg, 0.188 mmol) in diphenyl ether (10 mL) for 20 h and workup in the usual manner gave 90 mg (90%) of the unchanged starting material (**4a**), mmp 139–140 °C.

In a repeat experiment, **4a** (0.5 g, 0.94 mmol) was heated at ca. 300–310 °C for 1.5 h and worked up in the usual manner to give 150 mg (30%) of the recovered starting material **4a**, mmp 139–140 °C. No other product could be isolated from this reaction.

Attempted Thermolysis of 4b. A solution of **3b** (150 mg, 0.34 mmol) in diphenyl ether (10 mL) was refluxed for 15 h and worked up in the usual manner to give 140 mg (93%) of the unchanged starting material **4b**, mmp 178–179 °C.

In a repeat experiment, **4b** (440 mg, 1 mmol) was heated in a sealed tube at ca. 295–300 °C for 1 h and worked up by chromatographing over silica gel and elution with a mixture (1:9) of ethyl acetate and benzene to give 200 mg (45%) of the unchanged starting material **4b**, mmp 178–179 °C.

Laser Flash Photolysis. For laser flash photolysis, use was made of pulsed outputs from a UV-400 Molectron nitrogen (337.1 nm, 2–3 mJ, ~8 ns) or a Quanta-Ray DCR-1 Nd-YAG (third harmonic, 355 nm, ~6 ns). The laser intensities were attenuated and kept in the range 2–10 mJ/pulse. The details of the kinetic spectrophotometer and data collecting system are described in earlier publications[30,31] from the Radiation Laboratory. For transient spectra, a flow cell was used. For kinetics, static cells (path lengths 1–3 mm) containing 1–2 mL of the solutions for photolysis were used. Unless the effect of oxygen was meant to be studied, the solutions were deaerated by saturating with high-purity argon.

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Cyclization Reactions through the $S_{RN}1$ Mechanism. Reactions of *o*-Dihaloaromatic Compounds with Dithiolate Ions

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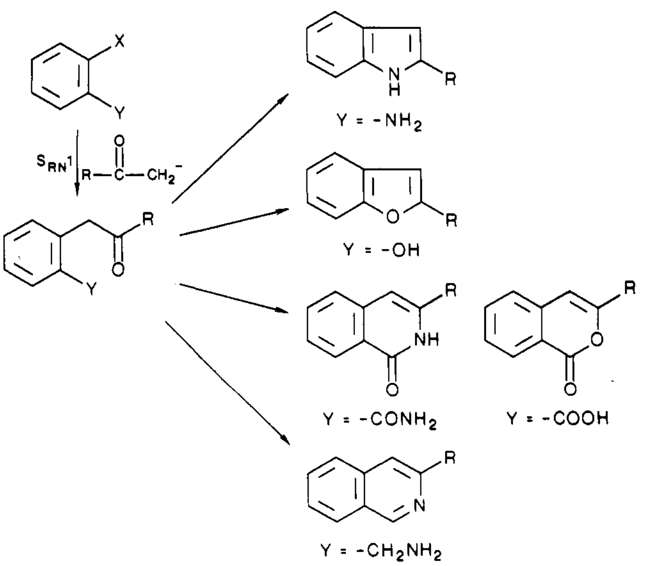
In the present paper we report the reactions of *o*-dihaloaromatic compounds with dithiolate ions as new cyclization reactions occurring by the $S_{RN}1$ mechanism. *o*-Diiodo- and *o*-bromochlorobenzene react under photostimulation with 3,4-toluenedithiolate ion to give good yields (≈60%) of the cyclic disubstituted compound 2-methylthianthrene. The reaction occurs to a lesser extent (≈20%) when the substrate was 1-bromo-2-iodonaphthalene. 2,3-Dichloroquinoxaline reacts with the same nucleophile in the dark or in the presence of radical traps to give a 100% yield of the cyclic disubstituted compound. The reaction of *o*-diiodobenzene with 1,2-ethanedithiolate gave a low yield of the cyclic compound benzo-1,4-dithiane. This decrease was explained in terms of fragmentation reactions of the proposed radical anions intermediates.

The synthetic scope of the radical nucleophilic substitution reaction ($S_{RN}1$) is broad and widely known.[1]

The fact that the mechanism produces a regiospecific substitution of the leaving group has been extensively used as a synthetic route to heterocyclic ring systems. Treatment of enolate anions derived from ketones or aldehydes with aryl halides bearing a function adjacent to the leaving group led to the $S_{RN}1$ substitution product which can undergo a spontaneous cyclization to give indoles,[2,3] azaindoles,[3,4] benzofurans,[5] isocarbostyrils,[6,7] isocumarones,[6] and isoquinolines[8] (Scheme I).

Scheme I



Another route to cyclization reactions through the $S_{RN}1$ mechanism has been the intramolecular photosubstitution

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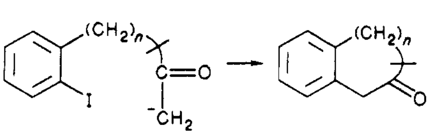
Table I. Reactions of *o*-Dihaloaromatic Compounds with Dithiolate Ions in Liquid Ammonia

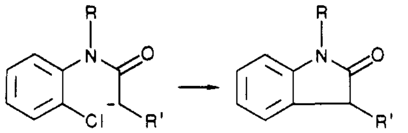
expt	starting materials (substrate)	M × 10^3	nucleophile	M × 10^3	irradiation time, min	% X^- [a]	products (% yield)[b] XArY	products (% yield)[b] product
1	**2** (BrC_6H_5)	3.0	1	6.0	180[c]	–	**2** (70)	**3** (23)[d]
2	**6** (o-$BrClC_6H_4$)	8.2	1	8.0	180[c]	–	**6** (29)	**7** (55)[e]
3	**6** (o-$BrClC_6H_4$)	6.3	1	6.3	180[c]	–	**6** (9)	**7** (55)
4	**6** (o-$BrClC_6H_4$)	6.2	1	6.2	180[f,g]	20	**6** (90)	–
5	**8** (o-$I_2C_6H_4$)	5.2	1	5.2	180[c]	–	**8** (14)	**7** (64)
6	**9** (1,2-bromoiodonaphthalene)	3.0	1	3.7	180[f]	Br^-, 37 I^-, 47	**9** (39)[h]	**10** (24)
7	**9** (1,2-bromoiodonaphthalene)	3.0	1	3.7	180[c,g]	–	**9** (82)[i]	–
8	**9** (1,2-bromoiodonaphthalene)	3.0	–	—	180	9	*j*	–
9	**11** (2,3-dichloroquinoxaline)	11.3	1	12.6	180[f]	–	–	**12** (100)[e]
10	**11** (2,3-dichloroquinoxaline)	4.5	1	4.5	180[f,g]	200	–	**12** (100)
11	**11** (2,3-dichloroquinoxaline)	6.3	1	6.3	180[f,k,g]	200	–	**12** (100)
12	**8** (*o*-$I_2C_6H_4$)	10.2	5	21.0	150[c]	–	**8** (5)	**13** (13)[l]

[a] Quantified potentiometrically based on mmol of substrate. [b] Quantified by GLC by the internal standard method. [c] Quenched with CH_3I. [d] Determined by GLC together with 6% of diphenylthiotoluene (4) assuming equal molar response. [e] Isolated by column chromatography. [f] Quenched with NH_4NO_3. [g] Dark reaction. [h] Bromonaphthalene 14%. [i] Traces of naphthalene and bromonaphthalene. [j] Bromonaphthalene 7%. [k] Di-*tert*-butyl nitroxide (10 mmol %). [l] Phenyl methyl sulfide (17%), 1-((2-iodophenyl)thio)-2-(metylthio)ethane (20%), 2-(methylthio)ethyl disulfide (2%).

of compounds bearing a good leaving group and a ketone enolate anion functionality in the same molecule[9,10] (eq 1, 2).



(1)



(2)

The cyclization reactions represented by eq 1 were successful only in those cases where the internal hydrogen atom transfer from the γ-position of the ketone was blocked.[9]

It is known that many *m*- and *p*-dihalobenzenes react with nucleophiles through the $S_{RN}1$ mechanism to give high yields of disubstitution products.[11]

The propagation cycle proposed to describe the mechanism of these reactions is outlined in Scheme II.

Scheme II

$$(XArY)\bullet^- \rightarrow XAr\bullet + Y^- \quad (3)$$

$$XAr\bullet + Nu^- \rightarrow (XArNu)\bullet^- \quad (4)$$

$$(XArNu)\bullet^- + XArY \rightarrow XArNu + (XArY)\bullet^- \quad (5)$$

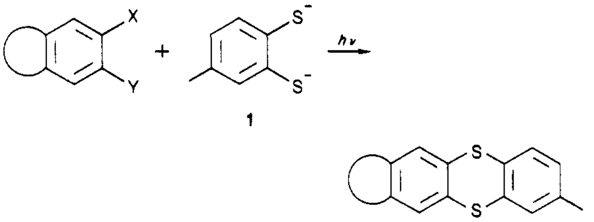
$$(XArNu)\bullet^- \rightarrow NuAr\bullet + X^- \quad (6)$$

$$NuAr\bullet + Nu^- \rightarrow (NuArNu)\bullet^- \quad (7)$$

$$(NuArNu)\bullet^- + XArY \rightarrow NuArNu + (XArY)\bullet^- \quad (8)$$

These reactions provided evidence that monosubstitution products are not intermediates in the formation of the disubstitution ones. Some dihalobenzenes react to give mainly monosubstitution products. This indicates, that in those cases step 5 in faster than step 6.

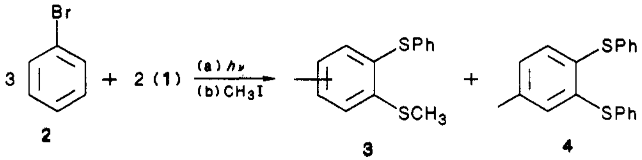
In the hope of finding another good synthetic route to heterocyclic ring systems through the $S_{RN}1$ mechanism we decided to investigate the reactions of *o*-dihalobenzenes, 1-bromo-2-iodonaphthalene, and 2,3-dichloroquinoxaline with the nucleophile 3,4-toluenedithiolate (**1**) to give 2-methylthianthrene (2-methyl-9,10-dithianthracene) type compounds (eq 9). A similar type of compounds has been



(9)

synthesized from reaction of this nucleophile with (η^6-*o*-dichlorobenzene)(η^5-cyclopentadienyl)iron hexafluorophosphate.[12]

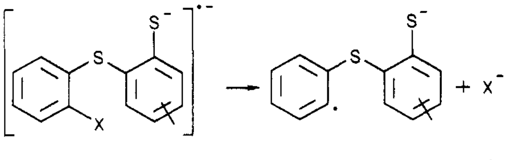
Nucleophile **1** was chosen because it reacts with bromobenzene **2** in liquid ammonia under photostimulation in a molar ratio 1:2 to give a 30% yield of substitution products. This percentage based on the bromobenzene used corresponds to the formation of mono- and disubstitution products, **3** and **4**, respectively, in a ratio 3.7:1 (eq 10) (Table I, experiment 1).



2 **3** **4**

(10)

In the reaction of *o*-dihaloaromatic compounds with nucleophile **1** the ortho-monosubstituted radical dianion formed in step 4 of the proposed mechanism could fragment to give a radical anion and an anion (step 6′). The



(6′)

radical anion thus formed could suffer an intramolecular

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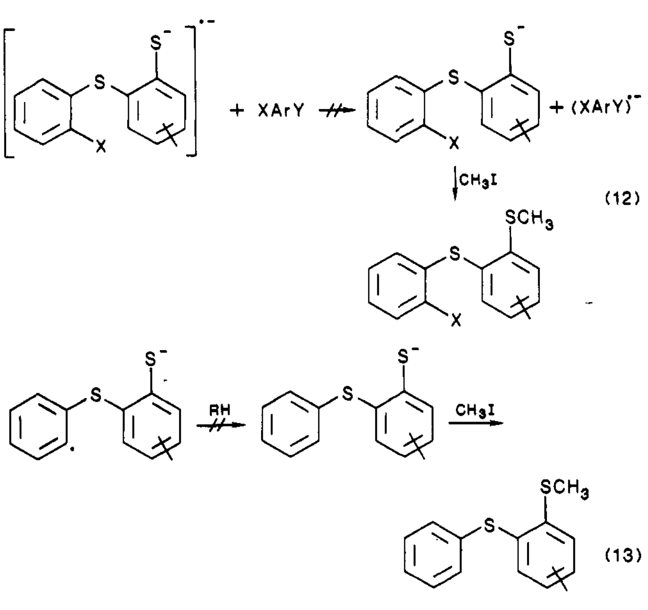
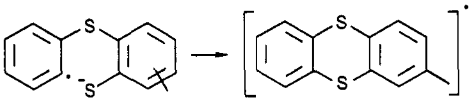
Scheme III



(12)

(13)

nucleophile–radical coupling to give a new radical anion (step 7′) with the other mechanistic steps being the same.



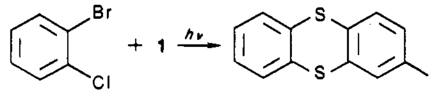
(7′)

The studies were extended to the reactions of the same dihaloaromatic substrates with the nucleophile 1,2-ethanedithiolate **5**.

Results and Discussion

All the reactions were carried out in liquid ammonia at −33 °C. The dianions **1** and **5** were formed by acid–base reaction of the respective dithiol with sodium amide and recovered in 100% yield as the dimethyl derivative after quenching with methyl iodide.

Reactions with 3,4-Toluenedithiolate Ion. The reaction of *o*-bromochlorobenzene (**6**) with **1** after 180 min of irradiation gave 55% of cyclization product 2-methylthianthrene (**7**) and 29% of unreacted **6** (eq 11) (Table I, experiment 2).

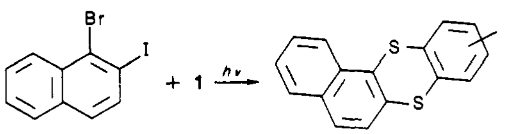


6 **7** (11)

In the reaction carried out under the same experimental conditions but with *o*-diiodobenzene (**8**) as the substrate the percentage of cyclization product **7** increased to 64% (Table I, experiment 5). This slight increase could be ascribed to an increase in the rate of initiation due to the easier reducibility of the diiodocompound as well as to the better nucleofugicity of iodine than bromine. In those cases where the reactions were quenched with methyl iodide we could not detect the formation of the methyl derivative of the monosubstitution product coming from step 5 nor the methyl derivative coming from the reduction of the ortho-substituted phenyl radical formed in step 6′ of the proposed mechanism (Scheme III) (eq 12, 13). These results indicate that for the system under study the fragmentation rate of the monosubstituted radical anion is greater than the electron transfer to the substrate as well as that the rate constant for the cyclization reaction (attack of the second nucleophilic center to the radical) is greater than the reduction rate of the intermediate.

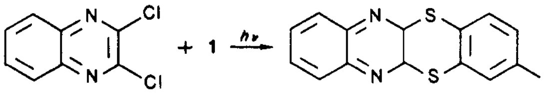
When we carried out the reaction of **6** with **1** in the dark, **6** was recovered unchanged in 90% yield. No other products were detected by GLC (Table I, experiment 4).

The photostimulated reaction of 1-bromo-2-iodonaphthalene **9** gave a 24% yield of cyclization product **10** (eq 14) (Table I, experiment 6). Unreacted 1-bromo-2-iodonaphthalene amounted to 39% while 1-bromonaphthalene was formed in 14% yield. Under the same experimental conditions but in the dark there was no reaction (Table I, experiment 7). To determine the stability of **9** under our experimental conditions we irradiated an ammonia solution of this compound for the same period of time as the reactions carried out in presence of the nucleophile. In this reaction 1-bromonaphthalene amounted to a 7% yield (Table I, experiment 8).



9 **10** (14)

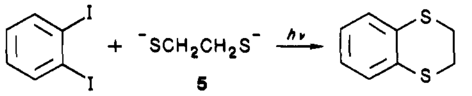
The photostimulated reaction of **1** with 2,3-dichloroquinoxaline **11** gave 100% yield of cyclization product **12** (eq 15) (Table I, experiment 9). The same result was obtained in reactions carried out either in the dark or in presence of radical traps (di-*tert*-butylnitroxide) (Table I, experiments 10, 11).



11 **12** (15)

From the present results we conclude that a $S_{RN}1$ mechanism could be in play for the reaction of nucleophile **1** with *o*-dihalobenzene and 1-bromo-2-iodonaphthalene while a classic S_NAr substitution is in play for the compound 2,3-dichloroquinoxaline although it is known that 2-chloroquinoxaline reacts with various nucleophiles by the $S_{RN}1$ mechanism.[13]

Reactions of Ethanethiolate Ion. The photostimulated reaction of this nucleophile with *o*-diiodobenzene gave a 13% yield of cyclization product **13** (eq 16) (Table I, experiment 12). The low yield of cyclization could be ascribed to fragmentation reactions of the intermediate radical anions.



8 **5** **13** (16)

Fragmentation reactions of radical anions of this type have already been reported. The phenyl radical gives only the substitution product when it reacts with benzenethiolate ions. However when it reacts with alkanethiolate ions the radical anion formed mainly fragments to give a new pair of radical and anion (eq 17). This fragmentation pattern has been observed when R = methyl, ethyl, *n*-butyl, *tert*-butyl, and benzyl.[14]

$$\mathrm{Ar\cdot} + \mathrm{RS^-} \longrightarrow (\mathrm{ArSR})^{\cdot-} \begin{cases} \xrightarrow{k_t(\mathrm{ArX})} \mathrm{ArSR} \\ \xrightarrow{k_f} \mathrm{ArS^-} + \mathrm{R\cdot} \end{cases} \qquad (17)$$

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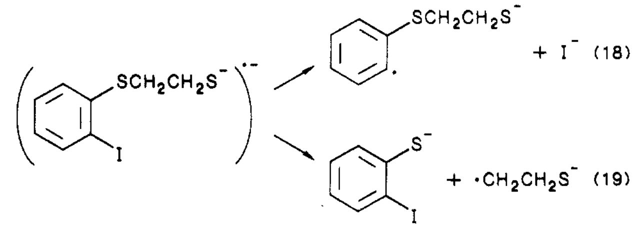
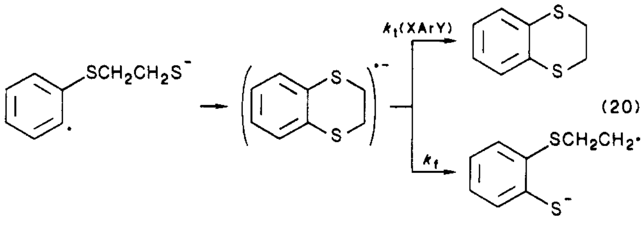
[14] Rossi, R. A.; Palacios, S. M. *J. Org. Chem.* **1981**, *46*, 5300.

Because electron transfer is a propagation step while fragmentation is a termination step, overall substitution will decrease as fragmentation increases. In our system the fragmentation possibilities are enhanced. The *o*-halo-substituted radical anion formed in step 6′ could fragment at two levels: the C–I bond to give the ortho-substituted phenyl radical or the S–CH_2 bond to give the *o*-phenyl sulfide anion (eq 18, 19). The radical anion formed in step 18 could cyclize to give a new radical anion which could transfer its extra electron to give the cyclic substitution product or could fragment to give a rearranged radical anion (eq 20).





Even though we were unable to isolated products coming from the fragmentation reactions of the proposed radical anions intermediates, the low yield of the substitution reaction and the isolation of the compounds phenyl methyl sulfide, 1-(2-iodophenyl)thio-2-methyl thioethane, and 2-(methylthio)ethyl disulfide, the last two products ascribed to the termination steps, are good evidence in favor of the fragmentation reactions proposed.

Experimental Section

General Method. NMR spectra were recorded on a Bruker 80 nuclear magnetic resonance spectrometer, and all spectra are reported in parts per million relative to Me_4Si (δ), with CCl_4 as the solvent. Mass spectral measurements were obtained with a Finningan Model 3300 mass spectrometer. Gas chromatographic analyses were performed on a Varian Aerograph Series 1400 instrument with a flame ionization detector by using a column packed with 3% SE-30 on Chromosorb P (1.5 m × 3 mm). Irradiation was conducted in a reactor equipped with four 250-W lamps emitting maximally at 350 nm (Philips Model HPT, water refrigerated). Column chromatography was performed on MN-Silica Gel 60 (70–270 mesh ASTM). Melting points are uncorrected.

Materials. 3,4-Toluenedithiolate and 1,2-ethanedithiolate ions were prepared from 2,3-toluenedithiol (Merck) and 1,2-ethanedithiol (Aldrich) by acid–base reaction with twice their amount of equivalents of sodium amide in liquid ammonia. 1-Bromo-2-iodonaphthalene was prepared from reaction of potassium iodide with 1-bromo-2-naphthyldiazonium salt as described.[15] Di-*tert*-butylnitroxide was kindly provided by Professor James F. Wolfe.

Photostimulated Reaction of *o*-Bromochlorobenzene with 3,4-Toluenedithiolate Ion. This reaction is representative. The equipment used has been previously described.[14] To 250 mL of distilled ammonia were added sodium metal (3 mmol) and a catalytic amount of $FeCl_3$ to form sodium amide, and then 3,4-toluenedithiol (1.5 mmol) was added. To the 3,4-toluenedithiolate ion thus formed *o*-bromochlorobenzene (1.5 mmol) was added and the reaction mixture irradiated for 180 min. The reaction was quenched by addition of methyl iodide in excess, the ammonia was allowed to evaporate, and the residue was extracted with diethyl ether. The ether extract was analyzed by GLC and the product 2-methylthianthrene isolated by column chromatography with petroleum ether/benzene (90:10) as eluant: mp 79.5–80.5 °C (lit.[12] 74 °C); MS, *m/e* (relative intensity) 232 (10), 231 (19), 230 (100), 215 (3), 214 (3), 199 (6), 198 (25), 197 (64), 185 (6), 184 (7), 171 (10), 165 (11), 153 (9), 152 (16), 139 (5), 121 (5), 115 (9), 108 (3), 77 (7); ^{1}H NMR δ 2.66 (s, 3 H), 7.20–8.00 (m, 7 H), identical with that previously reported.[12]

2-Methyl-5,12-dithianaphtho[2,3-*b*]quinoxaline (12). 12 was isolated by column chromatography and eluted with benzene: mp 173.4–175 °C; HNMR δ 2.40 (s, 3 H), 7.02–8.18 (m, 7 H); MS, *m/e* (relative intensity) 283 (13), 282 (20), 281 (100), 267 (7), 251 (4), 250 (20), 249 (46), 239 (4), 238 (17), 237 (13), 155 (7), 154 (15), 153 (48), 121 (26), 110 (13), 108 (9), 97 (7), 77 (9).

Anal. Calcd for $C_{15}H_{10}N_2S_2$: C, 63.80; H, 3.56; N, 9.92; S, 22.71. Found: C, 63.67; H, 3.78; N, 9.93; S, 22.86.

9(and/or 10)-Methylbenzo[*a*]thianthrene (10). Liquid was isolated by column chromatography and eluted with petroleum ether: H NMR δ 2.23 (s, 3 H), 6.67–7.80 (m, 9 H); MS, *m/e* (relative intensity) 282 (12), 281 (20) 280 (100), 266 (1), 265 (3), 264 (5), 250 (2), 249 (6), 248 (34), 247 (31), 215 (4), 158 (1), 139 (6), 122 (4).

Anal. Calcd for $C_{17}H_{12}S_2$: C, 72.82; H, 4.31; S, 22.87; Found: C, 72.67; H, 4.30; S, 22.82.

Benzo-1,4-dithiane (13). Liquid was isolated by column chromatography and eluted with petroleum ether/benzene (90:10); H NMR δ 3.17 (s, 4 H), 6.83–7.16 (d, 4 H); identical with that of an authentic sample prepared by a literature procedure;[16] MS, *m/e* (relative intensity) 170 (6), 171 (7), 168 (62), 155 (7), 154 (9), 153 (100), 152 (11), 140 (41), 135 (7), 134 (12), 122 (4), 121 (13), 109 (5), 108 (8), 98 (4), 97 (7), 96 (49), 91 (10), 77 (18), 76 (5), 75 (22), 69 (19), 45 (18).

Anal. Calcd for $C_8H_8S_2$: C, 57.10; H, 4.79; S, 38.10. Found: C, 56.98; H, 4.99; S, 38.3.

3(or 4)-(Methylthio)-4(or 3)-(phenylthio)toluene (3). 3 was isolated by column chromatography (petroleum ether) as a colorless oil which was shown by GLC–MS to consist of 3 and 3,4-bis(phenylthio)toluene (4) in a ratio 90:10–.

MS, *m/e* (relative intensity) for compound 3: 248 (2), 247 (3), 246 (24), 231 (3), 216 (7), 100 (2), 199 (10), 198 (23), 197 (15), 185 (4), 184 (24), 183 (14), 169 (4), 168 (6), 167 (12), 155 (3), 154 (7), 153 (15), 139 (4), 123 (7), 122 (11), 121 (49), 107 (3), 106 (3), 105 (24), 93 (11), 92 (12), 91 (63), 78 (40), 77 (100), 65 (53), 51 (87), 45 (79).

MS, *m/e* (relative intensity) for compound 4: 308 (90), 231 (7), 216 (5), 199 (30), 184 (50).

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Registry No. 1, 26083-09-0; 2, 108-86-1; 3, 106139-98-4; 4, 106139-96-2; 5, 52724-23-9; 6, 694-80-4; 7, 53691-97-7; 8, 615-42-9; 9, 90948-03-1; 10, 106139-99-5; 11, 2213-63-0; 12, 106161-11-9; 13, 6247-55-8; CH_3I, 74-88-4; $HSCH_2CH_2SH$, 540-63-6; PhSMe, 100-68-5; 3,4-toluenedithiol, 496-74-2; bromonaphthalene, 27497-51-4; 1-((2-iodophenyl)thio)-2-(methylthio)ethane, 106139-97-3; 2-(methylthio)ethyl disulfide, 56160-67-9.

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