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### The Chemistry of 2-Alkoxy-1,3-Benzodithioles and 1,3-Benzodithiolium Salts. Reactions and Synthetic Applications

Juzo Nakayama<sup>a</sup>

<sup>a</sup> Department of Chemistry, Faculty of Science, Saitama University, Urawa, Saitama, Japan

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# THE CHEMISTRY OF 2-ALKOXY-1,3-BENZODITHIOLES AND 1,3-BENZODITHOLIUM SALTS. REACTIONS AND SYNTHETIC APPLICATIONS

JUZO NAKAYAMA

*Department of Chemistry, Faculty of Science, Saitama University,  
Urawa, Saitama 338, Japan*

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2-Alkoxy-1,3-benzodithioles have recently become readily obtainable. 1,3-Benzodithiolium salts are easily derived from the former compounds. The chemistry of these compounds is described, emphasis being placed on synthetic aspects. The preparation of 2-alkoxy-1,3-benzodithioles and 1,3-benzodithiolium salts is first described and then synthetic applications of these reagents are shown. This review cites 79 references.

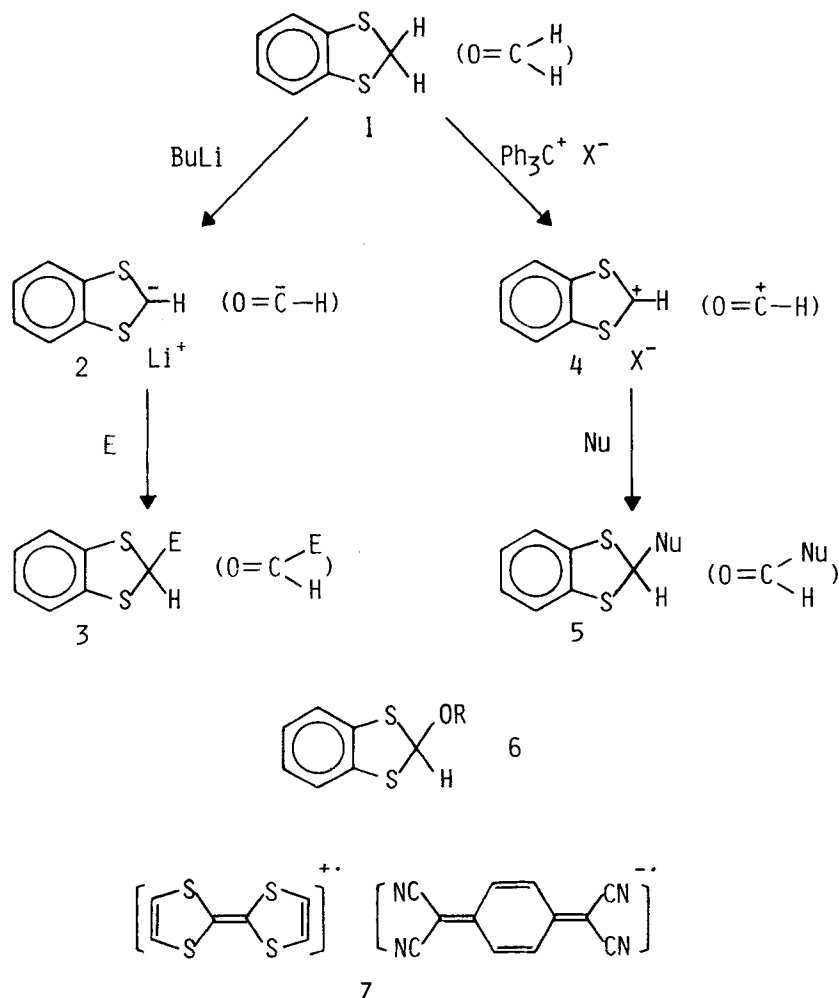
## INTRODUCTION

The methylene hydrogen atoms of 1,3-benzodithiole (**1**) are acidic enough to allow the formation of the stable carbanion **2** upon treatment with butyllithium. The carbanion **2** is capable of reacting as a nucleophilic formyl group with an electrophile (E) leading to 2-substituted derivative (**3**). In addition **1** can undergo a hydrogen-exchange reaction with trityl salts to produce the stable carbonium ion **4**. The carbonium ion **4** is able to react as a masked formyl cation with nucleophiles (Nu) to form 2-substituted derivatives (**5**). In this way, **1** can react with both an electrophile and a nucleophile. The resulting **3** and **5** are both converted to the corresponding formyl derivatives by conventional methods. Conversion of **3** and **5** to the corresponding methylene compounds is also possible. This is the very property that makes this heterocycle synthetically very versatile.

Notwithstanding this outstanding property of **1**, the use of **1** and related derivatives in organic synthesis had scarcely been mentioned in the literature until the author developed a simple one-pot preparation of 2-alkoxy-1,3-benzodithioles (**6**) in 1975 and their application to organic synthesis.<sup>1,2</sup> After that, stimulated by this finding, several groups started studies on the synthetic use of this heterocycle.

The discovery of the unusually high solid-state conductivity of the charge-transfer salt of tetrathiafulvalene (TTF) with tetracyanoquinodimethane (TCNQ) (**7**) in 1972 undoubtedly plays a significant role in the development of the chemistry of this heterocycle. With this discovery, studies focused on the preparation of 1,3-dithiolium and related ions which function as precursor compounds of TTF and its derivatives became very active.<sup>3</sup> The 1,3-benzodithiolium ion **4** is the benzo analog of the 1,3-dithiolium ion which is the most important precursor of TTF.

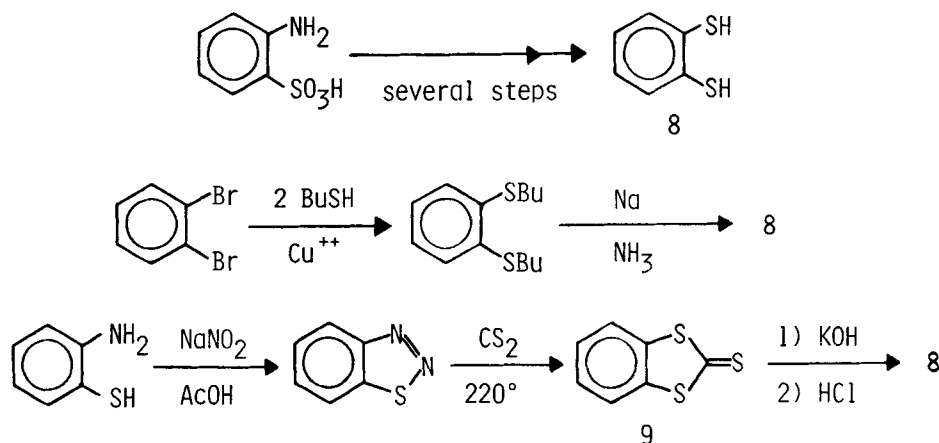
Currently all of the 1,3-benzodithiole derivatives can be prepared from the dithioles **6** as the starting material. This article describes the chemistry of the dithioles **6** and the dithiolium salts **4**, the latter compounds being easily derived from the former. Emphasis will be placed on organic synthesis with these reagents. References after 1975 are mainly covered and therefore most studies on 1,3-benzodithioles and related compounds in the early stages of development are omitted.



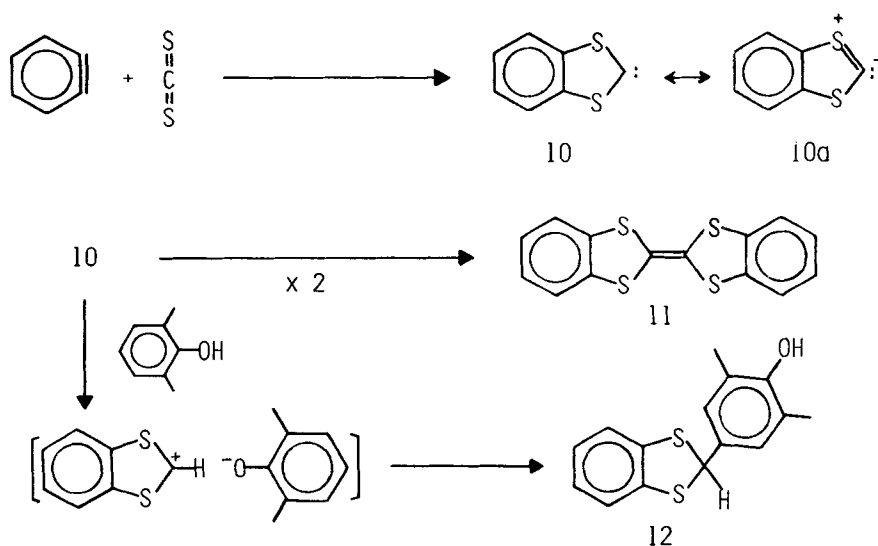
### PREPARATION OF 2-ALKOXY-1,3-BENZODITHIOLES, 1,3-BENZODITHIOLIUM SALTS, AND RELATED COMPOUNDS

1,3-Benzodithioles had been mostly prepared from 1,2-benzenedithiol (**8**) as the starting material. The preparation of **8** was, however, tedious. The classical method starting from 2-aminobenzenesulfonic acid is lengthy.<sup>1a</sup> The method described in Organic Syntheses requires the expensive 1,2-dibromobenzene as starting material and is useful only on a limited scale (1.6–2.4 g).<sup>4</sup> The method developed by Hünig

requires drastic conditions for preparing 2-thioxo-1,3-benzodithiole (**9**), though it allows to obtain **8** in large quantity.<sup>5</sup>



In 1974 the author established that the reaction of carbon disulfide with benzyne (generated from diverse sources in solution) produces the 1,3-benzodithiol-2-ylidene carbene (**10**) in a 1,3-dipolar cycloaddition.<sup>6-8</sup> The carbene **10**, possessing an iso- $\pi$ -electronic structure with 1,3,5-cycloheptatrienyliene, constitutes a typical heteroaromatic carbene. The contribution of canonical structures such as **10a** makes the ground state of the carbene singlet and nucleophilic in reactivity. Thus, for example, heating benzenediazonium-2-carboxylate with carbon disulfide in refluxing dichloromethane gives dibenzotetrathiafulvalene (**11**) by dimerization of **10**. In the presence of 2,6-dimethylphenol, compound (**12**) is produced by the initial formation of an ion pair followed by an aromatic electrophilic substitution. Methanol adds to **10** to give 2-methoxy-1,3-benzodithiole (**6**,  $\text{R} = \text{Me}$ ).



A one-pot preparation of 2-alkoxy-1,3-benzodithioles (**6**) was devised in 1975 on the basis of the above results.<sup>9</sup> The new procedure consists of four reaction sequences; a) aprotic diazotization of anthranilic acid by an alkyl nitrite, b) thermal decomposition of the resulting benzenediazonium-2-carboxylate producing benzyne, c) the formation of the carbene **10** by reaction of benzyne with carbon disulfide, and d) addition of an alcohol (added prior to the reaction or formed by step b) to **10** yielding the final product **6**. Results of the preparation of **6** by this procedure are summarized in Table 1.

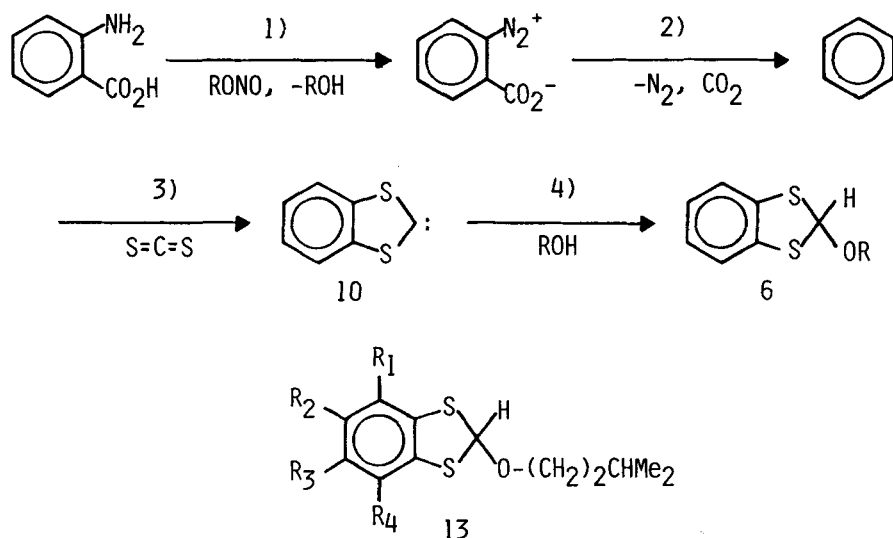


TABLE 1

Preparation of 2-Alkoxy-1,3-benzodithioles (**6**)

R	yield (%)	bp (°C/mmHg)
n-C <sub>3</sub> H <sub>7</sub>	33	104-106/0.1
n-C <sub>4</sub> H <sub>9</sub>	45	116-118/0.1
CH <sub>2</sub> CH <sub>2</sub> CHMe <sub>2</sub>	51	122-125/0.1
n-C <sub>6</sub> H <sub>13</sub>	51	125-127/0.02

The following procedure is typical.<sup>9</sup> To a stirred and mildly refluxing solution of isoamyl nitrite (42.1 g, 0.36 mol), isoamyl alcohol (52.8 g, 0.60 mol), and carbon disulfide (150 ml) in 1,2-dichloroethane (800 ml) is added a solution of anthranilic acid (41.1 g, 0.30 mol) in dioxane (100 ml) over a period of 1.5 h. The mixture is refluxed for 0.5 h, cooled, washed with water and then with aqueous sodium carbonate solution. The organic layer is, after drying, evaporated to remove the solvent and excess reagents. The resulting residue is distilled to give 37.0 g (51 %) of 2-isopentyloxy-1,3-benzodithiole (**6**, R = isopentyl), bp 122–125 °C/0.1 mmHg.

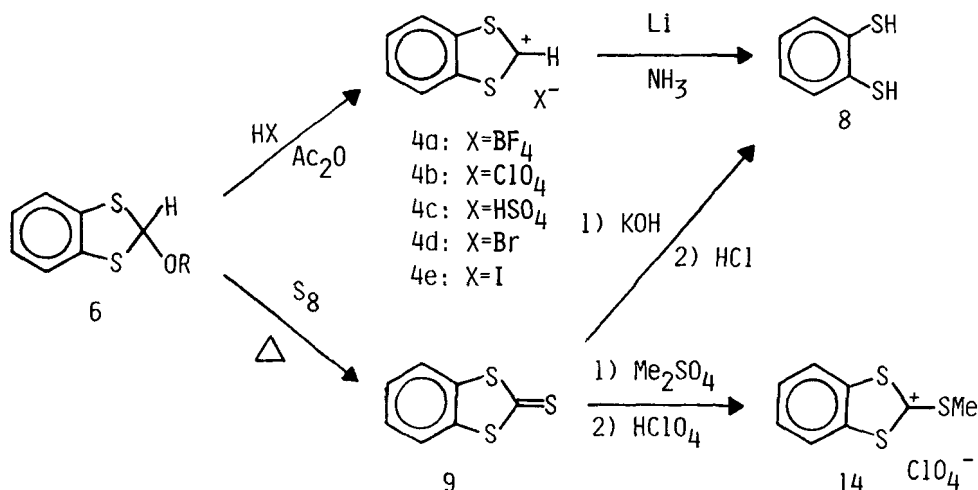
The use of anthranilic acids with substituent(s) on the benzene ring allows the

preparation of a variety of 2-isopentyloxy-1,3-benzodithioles (**13**).<sup>10</sup> Preparations of **13** are summarized in Table 2.

**TABLE 2**  
Preparation of 2-Isopentyloxy-1,3-benzodithioles (**13**)

R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	yield (%)	bp (°C/mmHg) or mp (°C)
Me	H	H	H	65	129/0.1
H	Me	H	H	35.5	131/0.1
H	Cl	H	H	34	135/0.5
H	I	H	H	49	50-51
H	NO <sub>2</sub>	H	H	46	62-64
H	-CH=CH-CH=CH-	H	H	24	86-87
Cl	Cl	Cl	Cl	73	91-92
Br	Br	Br	Br	57	92-92.5

All of the synthetically important 1,3-benzodithiole derivatives dealt within this article are currently derived from **6** (hereafter **6** stands for 2-isopentyloxy-1,3-benzodithiole unless otherwise stated). Treatment of **6** with tetrafluoroboric acid in acetic anhydride yields 1,3-benzodithiolium tetrafluoroborate (**4a**) in 96 % yield.<sup>10-13</sup> The use of perchloric, sulfuric, hydrobromic, and hydriodic acids affords the corresponding perchlorate, hydrosulfate, bromide, and iodide salts (**4b**, **4c**, **4d**, and **4e**), respectively. Birch reduction of **4a** gives a good yield of 1,2-benzenedithiol **8**.<sup>13</sup> Heating **6** with elemental sulfur in refluxing *o*-dichlorobenzene gives 2-thioxo-1,3-benzodithiole **9** in good yield.<sup>14</sup> The reaction proceeds via the carbene **10** thermally generated from **6** with loss of isoamyl alcohol. This carbene formation is the reverse of the preparation of **6**. Treatment of **9** with dimethyl sulfate followed by addition of perchloric acid yields the synthetically important 2-methylthio-1,3-benzodithiolium perchlorate (**14**).<sup>15</sup> Hydrolysis of **9** provides **8** in good yield.<sup>5</sup>

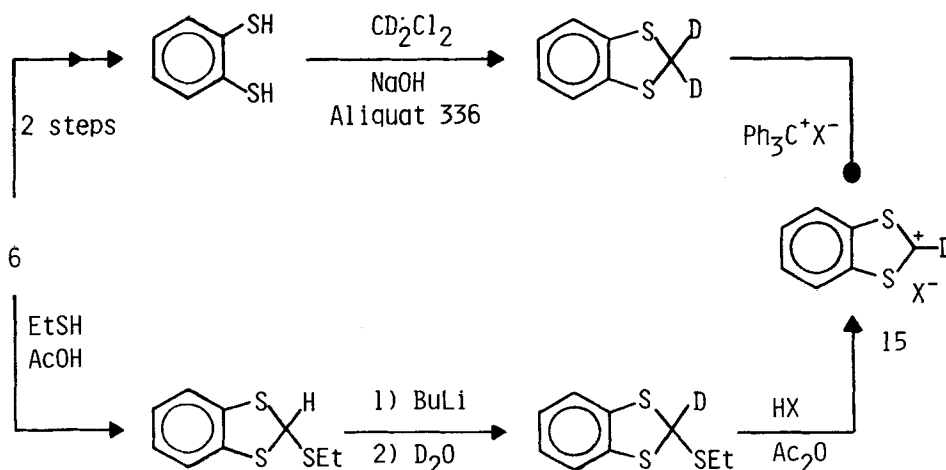


The following are procedures for the preparation of **4a** and **9**.

To a stirred and ice-cooled solution of **6** (24.0 g, 0.1 mol) in acetic anhydride (300 ml) is added 42 % tetrafluoroboric acid (42.0 g, 0.2 mol) over a period of 0.5 h while the temperature is maintained below 10 °C. Toward the end of the addition, crystals of **4a** begin to separate. After having been stirred for 0.5 h at 0 °C, the mixture is diluted with ether (400 ml). The resulting crystals are collected, washed with anhydrous ether (150 ml), and dried to give 23.0 g (96 %) of 1,3-benzodithiolium tetrafluoroborate **4a**, mp 149–150 °C (dec), as near-white crystals.<sup>12</sup>

A mixture of **6** (72 g, 0.3 mol) and elemental sulfur (9.9 g) in *o*-dichlorobenzene (900 ml) is refluxed for 4 h. The mixture is concentrated to ca. 300 ml. The resulting crystals are collected and washed with carbon tetrachloride (50 ml) to give 44.2 g (80 %) of **9**, which is sufficiently pure for most purposes.<sup>14</sup>

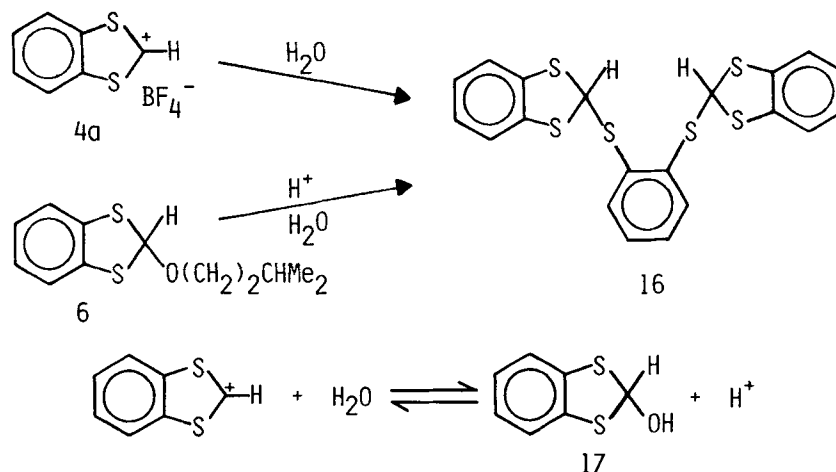
2-Deuterio-1,3-benzodithiolium salts (**15**) are useful synthons for the preparation of one-carbon homologated 1-deuterio aldehydes. They were first prepared starting from **6** in four steps.<sup>16</sup> The compounds are now prepared from **6** in three steps and more economically.<sup>17</sup> 2-Ethylthio-1,3-benzodithiole, readily obtainable from **6** and ethanethiol,<sup>18</sup> is deuterated. The resulting 2-deuterio-2-ethylthio-1,3-benzodithiole is converted to **15** by treatment with tetrafluoroboric acid or trityl salts.



Some properties of the title compounds **4** and **6** deserve mention. Although 1,3-benzodithiolium salts with a variety of different counter anions are available, the use of the tetrafluoroborate salt **4a** is recommended for synthetic purposes.<sup>19</sup> It is thermally stable and can be stored for a long period of time in a refrigerator if free from moisture and protected from light. The compound is slightly hygroscopic and is hydrolyzed in a wet solvent to give compound (**16**).<sup>12</sup> It is soluble in polar solvents such as acetonitrile, dimethyl sulfoxide, and nitromethane, and is scarcely soluble in ether and tetrahydrofuran. The perchlorate salt **4b** seems to be best for synthetic purposes, but is unfortunately **explosive**.<sup>12, 20, 21</sup> Special care should be taken in the handling of this compound.

The rates and equilibrium constants of hydration of the 1,3-benzodithiolium ion

have been determined at 30 °C in aqueous acidic solutions.<sup>22</sup> The hydrate **17** is stable below pH 5 and  $pK_R^+$  value of  $-0.40$  has been determined.



$^1H$  and  $^{13}C$  NMR data of 1,3-benzodithiolium and related ions are summarized in Table 3. The  $^{13}C$  NMR data are considered as reflecting the charge densities at the carbon atoms and proving the aromatic character of the system. The C-2 signal in 1,3-dithiolium ions appears at higher field than in the 1,3-dithiolanylium ion, though the C-4 signal appears at much lower field. This suggests that the positive charge is

TABLE 3

 **$^1H$  and  $^{13}C$  NMR Data of 1,3-Benzodithiolium and Related Ions**

	$^{13}C$ NMR Data <sup>a)</sup>			$^1H$ NMR Data <sup>b)</sup>		
	2-C	4-C	Other Aromatic C's	2-H	4-H	Aromatic H's
	179.5	146.2		11.40	9.39	(J=1.9)
	182.4	146.0	128.1 133.5	11.49		8.17 <sup>c)</sup> 8.78
	187.1	139.6 (or 135.4)	128.8 129.7 132.7 135.4 (or 139.6)	11.60		7.99 <sup>c)</sup> 8.28 <sup>c)</sup> 9.29
	221.2	46.4		11.36 <sup>d)</sup>	4.50 <sup>d)</sup>	

<sup>a)</sup> Determined at 27 °C with  $CF_3CO_2D$  as solvent.

<sup>b)</sup> Determined at 34 °C with  $CF_3CO_2D$  as solvent.

<sup>c)</sup> These signals are of AA'BB' type.

<sup>d)</sup> These signals are broad due to long range coupling.



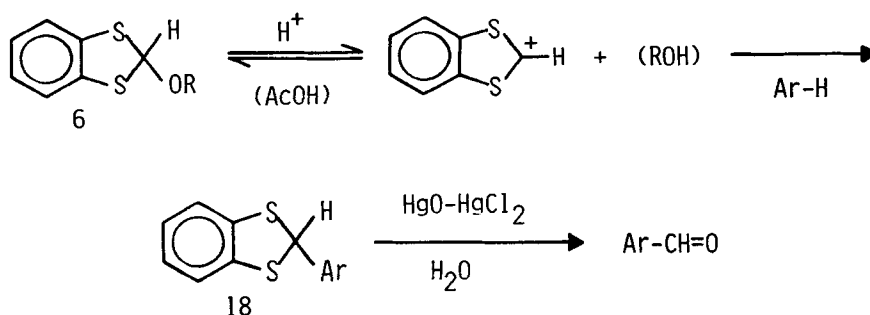
more delocalized in the former ions, and hence aromatic character is present in the 1,3-dithiolium ring.<sup>23</sup> However, a similar study by others reaches the opposite conclusion.<sup>24</sup>

2-Alkoxy-1,3-benzodithioles **6** can be stored for a long period of time in a refrigerator. They are sensitive to acid hydrolysis. For example, storing a solution of **6** in acetic acid containing water for a few days gives the partial hydrolysis product **16**.<sup>25</sup> The hydrolysis proceeds via the 1,3-benzodithiolium ion produced by protonation of the ether oxygen atom of **6**.

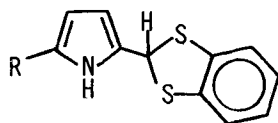
## REACTIONS OF 2-ALKOXY-1,3-BENZODITHIOLES AND 1,3-BENZODITHOLIUM SALTS. SYNTHETIC APPLICATIONS

### 1. Formation of Carbon-Carbon Bonds

2-Alkoxy-1,3-benzodithioles **6** dissociate into the 1,3-benzodithiolium ion and the corresponding alcohols in acetic acid. The resulting dithiolium ion is capable of undergoing electrophilic aromatic substitution with arenes activated by a strongly electron-donating substituent such as *N,N*-dialkylamino and methoxyl groups to provide a variety of 2-aryl-1,3-benzodithioles (**18**) in excellent yields.<sup>25</sup> For example, a mixture of **6** and a slight excess of *N,N*-dimethylaniline in acetic acid at room temperature gives 2-[4-(*N,N*-dimethylamino)phenyl]-1,3-benzodithiole in 98 % yield. Hydrolysis of the above product by the conventional method affords 4-(*N,N*-dimethylamino)benzaldehyde in 57 % yield. This is the first example where **6** was used for an aldehyde synthesis.

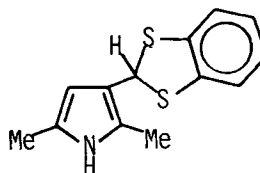


The dithiole **6** also reacts with pyrroles and indoles.<sup>26</sup> The reaction of pyrrole with excess pyrrole (4 mol. equiv.) in acetic acid gives 2-(1,3-benzodithiol-2-yl)pyrrole (**19a**), whereas the corresponding reaction with a molar ratio of 2:1 affords the 2,5-disubstituted product (**19b**) exclusively. In the case where the 2- and 5-positions of pyrrole are blocked by methyl groups, substitution occurs at the 3-position to give compound (**19c**). Indole reacts with **6** in the 3-position to yield compound (**20a**). In a similar way, compounds (**20b-d**) were obtained in excellent yields.

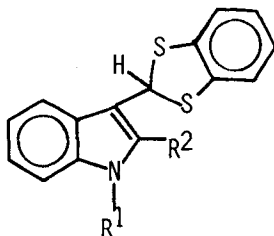


19a : R = H (97%)

19b : R = 1,3-benzodithiol-2-yl  
(90%)



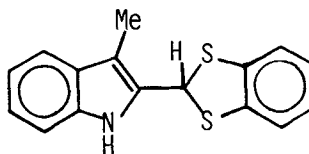
19c (96%)



20a : R<sup>1</sup> = R<sup>2</sup> = H (93%)

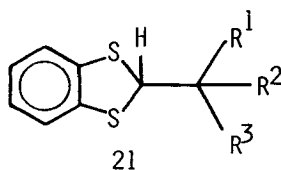
20b : R<sup>1</sup> = Me, R<sup>2</sup> = H (95%)

20c : R<sup>1</sup> = H, R<sup>2</sup> = Me (98%)

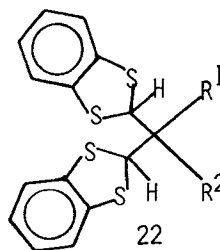


20d (96%)

Introduction of a 1,3-benzodithiol-2-yl group at an active methylene carbon is readily accomplished.<sup>27</sup> The reaction of **6** with a series of active methylene compounds in acetic acid afforded compounds **21** in moderate to excellent yields. The compounds **22** possessing a masked formyl group on a functionalized carbon might function as useful intermediates in synthesis. In some cases the disubstituted products



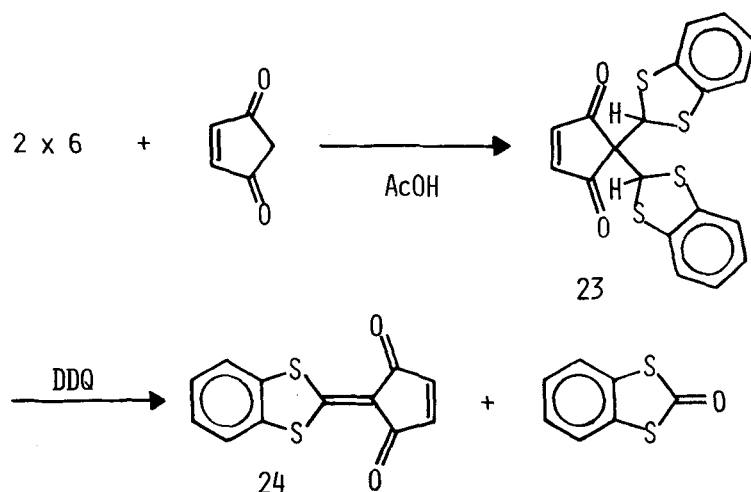
R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	yield (%)
H	MeCO	COMe	92
Me	MeCO	COMe	73
H	-CO(CH <sub>2</sub> ) <sub>3</sub> CO-		79
H	-COCH <sub>2</sub> Me <sub>2</sub> CH <sub>2</sub> CO-		74
CHO	-CO(CH <sub>2</sub> ) <sub>3</sub> -		55
CHO	-CO(CH <sub>2</sub> ) <sub>4</sub> -		50
H	MeCO	CO <sub>2</sub> Et	74
H	PhCO	CN	86
H	PhCH <sub>2</sub> CO	SPh	54
H	-CO(CH <sub>2</sub> ) <sub>4</sub> -		33
H	-CO(CH <sub>2</sub> ) <sub>3</sub> -		29



R <sup>1</sup>	R <sup>2</sup>	yield (%)
CN	CN	96
CN	CO <sub>2</sub> Me	82
CN	CONH <sub>2</sub>	66
-S-C(S)-NH-CO-		93

**22** predominantly formed even when the reaction was carried out with an equimolar mixture of **6** and an active methylene compound. Hydrolysis of **21** yields the corresponding aldehydes.<sup>28</sup> Compounds **21** are also obtained by reaction of **4a** with active methylene compounds.<sup>12</sup>

The structurally interesting compound **24** was prepared by using the above reaction. The reaction of 4-cyclopentene-1,3-dione with 2 mol. equiv. of **6** gives a good yield of **23**, which in turn can be converted to **24** and 1,3-benzodithiol-2-one by oxidation with excess DDQ.<sup>29</sup> Several compounds related to **24** have been synthesized and subjected to X-ray analysis.<sup>30-32</sup>



The dithiole **6** reacts with Grignard and organolithium reagents to provide 2-substituted 1,3-benzodithioles (**25**) in 64–89 % yield.<sup>33</sup> Upon treatment with butyllithium at  $-30^\circ\text{C}$  in tetrahydrofuran, compounds **25** generate stable carbanions **26**, which subsequently react with various electrophiles such as aldehydes, ketones, enones, epoxides, and alkyl iodides to afford compounds **27** in good yields.<sup>34</sup> Results are summarized in Table 4. Hydrolysis of 2-butyl-2-propyl-1,3-benzodithiole affords 4-octanone in 89 % yield. Incidentally the above transformation cannot be achieved with 1,3-dithiolanes since this ring system is susceptible to base-induced fragmentation.

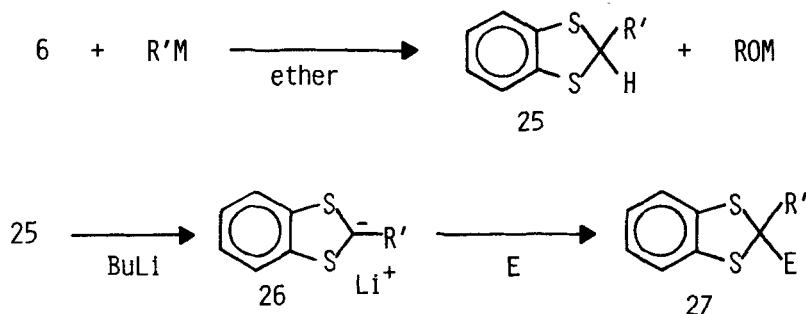





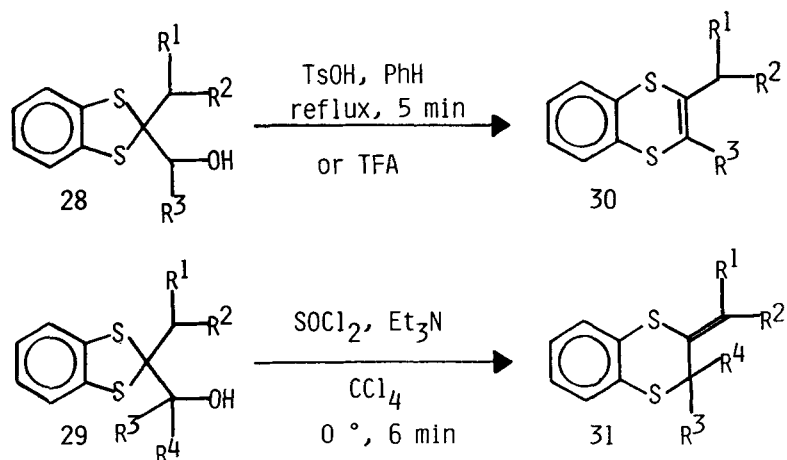


TABLE 4

Preparation of 2,2-Disubstituted 1,3-benzodithioles (27)			
R' of 25	Electrophile	Nature of E in Products 27	Yield (%)
H	PrI	Pr-	91
Me	EtCHO	EtCH(OH)-	94
Me			81
Me <sub>2</sub> CH	PhCHO	PhCH(OH)-	79
Pr	PhCHO	PhCH(OH)-	67
Pr	MeCHO	MeCH(OH)-	94
Pr	Me <sub>2</sub> CHCH <sub>2</sub> CHO	Me <sub>2</sub> CHCH <sub>2</sub> CH(OH)-	89
Pr			79
Pr	MeCOPh	Ph-C(OH)- Me	77
Pr	BuI	Bu-	93
Pr	MeI	Me-	98
Pr	Me 	MeCH(OH)CH <sub>2</sub> -	92

The ring expansion of compounds **28** and **29** (obtained by reaction of **26** with aldehydes and ketones) opens new routes to benzodithiins (**30**) and benzodithians (**31**), respectively.<sup>35</sup>



Reaction of **26** with trialkylboranes followed by oxidation provides a convenient method for the preparation of ketones.<sup>36</sup> Initial complex formation is followed by a spontaneous migration of an alkyl group from boron to carbon with simultaneous expulsion of thiophenolate anion. Oxidation of the resulting **32** with hydrogen peroxide affords ketones in 69–90 % yields (Table 5). This method is far less subject to steric hindrance than analogous reactions using anions derived from bis(phenylthio)alkanes.

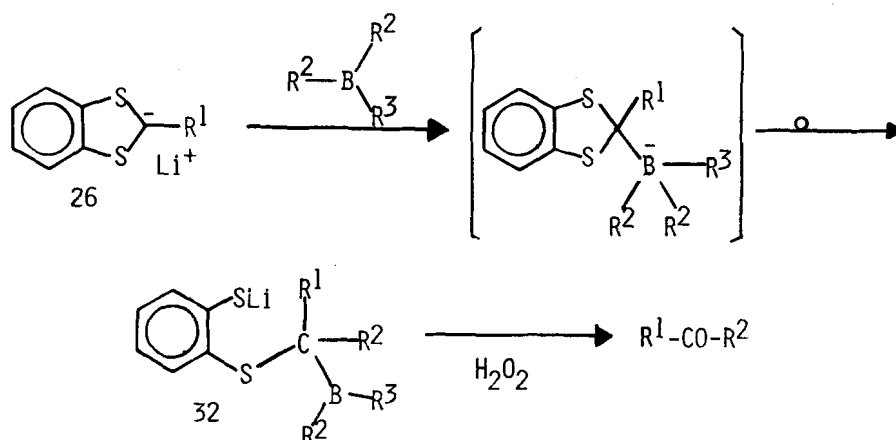
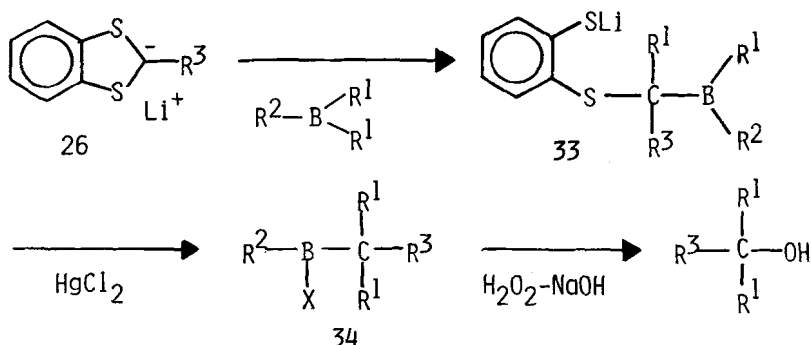


TABLE 5

## Preparation of Ketones via Organoboranes and Anions 26

R <sup>1</sup>	Trialkylboranes		Product	Yield (%)
	R <sup>2</sup>	R <sup>3</sup>		
c-hexyl	n-hexyl	n-hexyl	R <sup>1</sup> -CO-R <sup>2</sup>	76
c-hexyl	c-pentyl	c-pentyl	R <sup>1</sup> -CO-R <sup>2</sup>	78
n-propyl	c-pentyl	c-pentyl	R <sup>1</sup> -CO-R <sup>2</sup>	73
c-hexyl	<i>exo</i> -norbornyl	<i>exo</i> -norbornyl	R <sup>1</sup> -CO-R <sup>2</sup>	90
n-propyl	c-hexyl	n-octyl	R <sup>1</sup> -CO-R <sup>2</sup>	46
			R <sup>1</sup> -CO-R <sup>3</sup>	23
n-propyl	n-octyl	thexyl	R <sup>1</sup> -CO-R <sup>2</sup>	71
c-hexyl	9-BBN	n-hexyl	R <sup>1</sup> -CO-R <sup>2</sup>	76

Treatment of **26** with trialkylboranes and then with mercuric chloride followed by oxidation with hydrogen peroxide opens an efficient route to tertiary alcohols.<sup>37</sup> The procedure involves two migration steps; one of which is the same as that described above and gives **33**, and the other is induced by mercuric chloride (and in one case with methyl fluorosulfonate) to produce **34** from **33**. Oxidation of **34** with hydrogen peroxide gives tertiary alcohols (Table 6). The method is applicable to reactions of hindered organoboranes that fail to react with 1-lithio-1,1-bis(phenylthio)-alkanes.



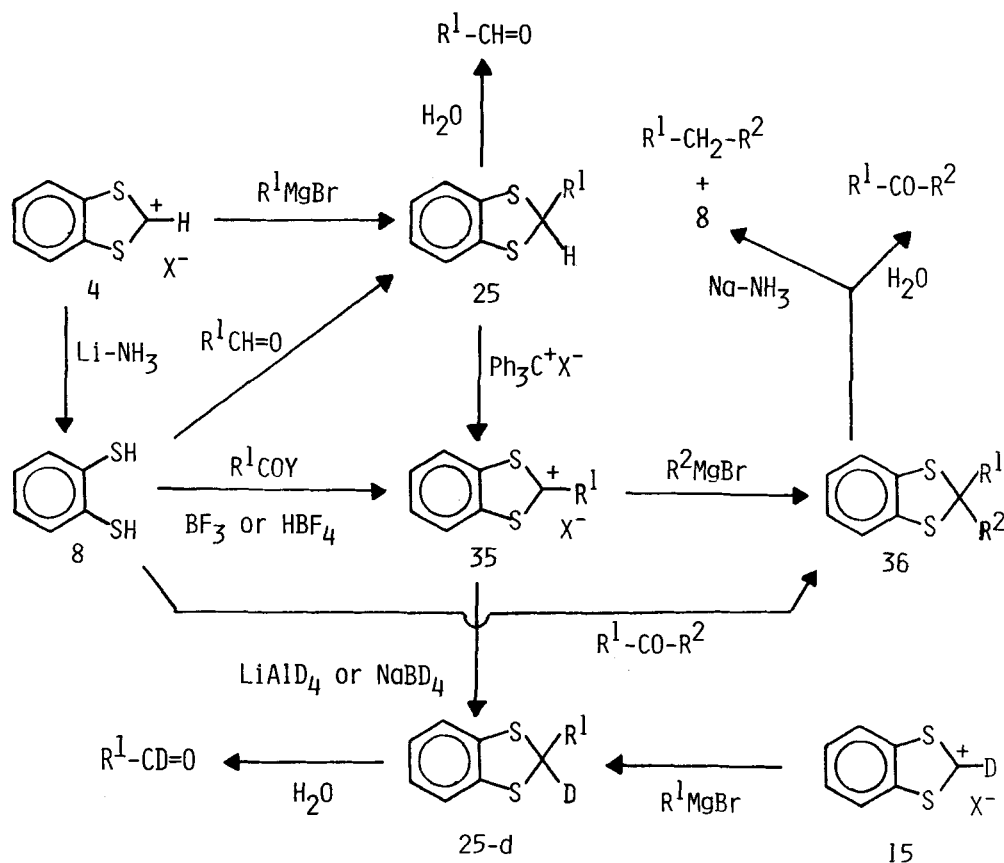
**TABLE 6**  
**Preparation of Tertiary Alcohols via Organoboranes and Carbainons 26**

R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	Product	Yield (%)
n-hexyl	n-hexyl	n-propyl	R <sup>1</sup> <sub>2</sub> R <sup>3</sup> COH	79
norbornyl	norbornyl	n-propyl	R <sup>1</sup> <sub>2</sub> R <sup>3</sup> COH	74
n-hexyl	n-hexyl	c-hexyl	R <sup>1</sup> <sub>2</sub> R <sup>3</sup> COH	85
c-pentyl	c-pentyl	c-hexyl	R <sup>1</sup> <sub>2</sub> R <sup>3</sup> COH	67
n-octyl	n-octyl	H	R <sup>1</sup> <sub>2</sub> R <sup>3</sup> COH	73
c-pentyl	thexyl	n-propyl	R <sup>1</sup> <sub>2</sub> R <sup>3</sup> COH	74
c-pentyl	thexyl	c-hexyl	R <sup>1</sup> <sub>2</sub> R <sup>3</sup> COH	80
n-octyl	thexyl	n-propyl	R <sup>1</sup> <sub>2</sub> R <sup>3</sup> COH	41
			R <sup>1</sup> R <sup>2</sup> R <sup>3</sup> COH	35
n-octyl	thexyl	n-propyl	R <sup>1</sup> R <sup>2</sup> R <sup>3</sup> COH	59

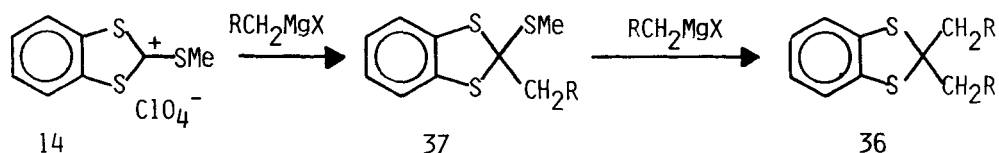
The perchlorate salt **4b** reacts with Grignard reagents to afford compounds **25** in good yields. Upon hydrolysis with chloramine-T and mercuric chloride, **25** are converted to the corresponding aldehydes nearly quantitatively (Table 7).<sup>38</sup> Treatment of **25** with a trityl salt results in the formation of a 2-substituted 1,3-benzodithiolium salt (**35**) in good yield. Reduction of **35** with LiAlD<sub>4</sub> or NaBD<sub>4</sub> affords the corresponding deuterated dithioles (**25-d**), and hence ultimately 1-deuterio aldehydes after hydrolysis. 1-Deuterio aldehydes are also prepared by reaction of 2-deuterio-1,3-benzodithiolium salts (**15**) with Grignard reagents followed by hydrolysis.<sup>16</sup> Reactions of **35** with Grignard reagents furnishes 2,2-disubstituted 1,3-benzodithioles (**36**), which are converted to the corresponding ketones on hydrolysis.<sup>38</sup> Reduction of **36** with sodium in liquid ammonia gives the corresponding methylene compounds and 1,2-benzenedithiol (**8**).<sup>40</sup> Reduction of the fluoroborate salt **4a** with lithium in liquid ammonia provides an excellent method for the preparation of **8**.<sup>13</sup> Condensation of **8** with aldehydes and ketones gives **25** and **36**, respectively, in high yields.<sup>40</sup> Carboxylic acids and a variety of their derivatives are all able to condense with **8** in the presence of boron trifluoride or tetrafluoroboric acid to provide the dithiolium salts **35**.<sup>40, 41</sup>

**TABLE 7**  
**Preparation of Aldehydes from 4b and Grignard Reagents**

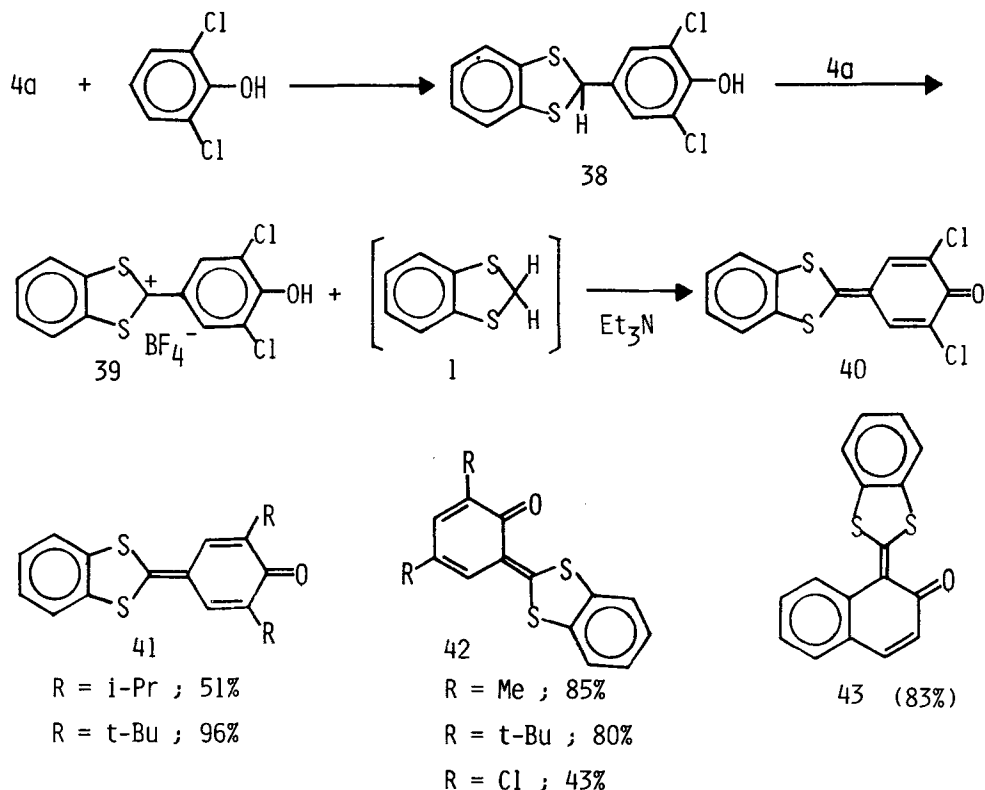
R <sup>1</sup>	yield (%)	
	4b → 25	25 → aldehyde
C <sub>6</sub> H <sub>5</sub>	87	99
MeOC <sub>6</sub> H <sub>4</sub>	87	94
n-pr	88	90
c-hexyl	53	90



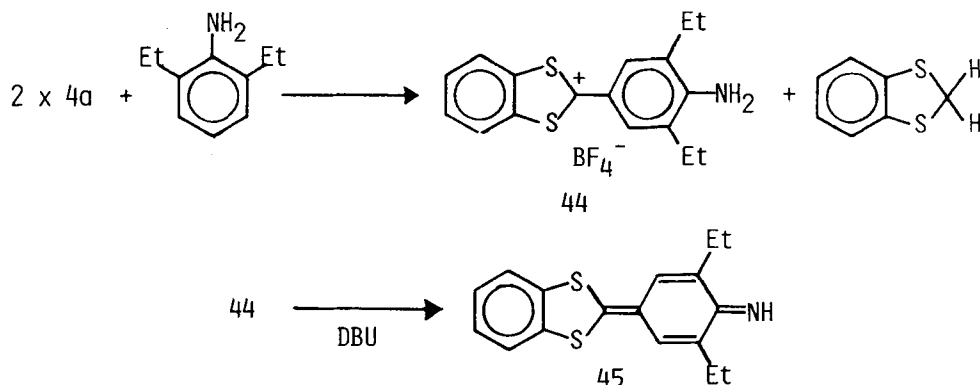
Reaction of the 2-methylthio-1,3-benzodithiolium salt **14** with Grignard reagents provides another route to **36**.<sup>42</sup> The initial adduct **37** could not be isolated, even when **14** was used in excess.



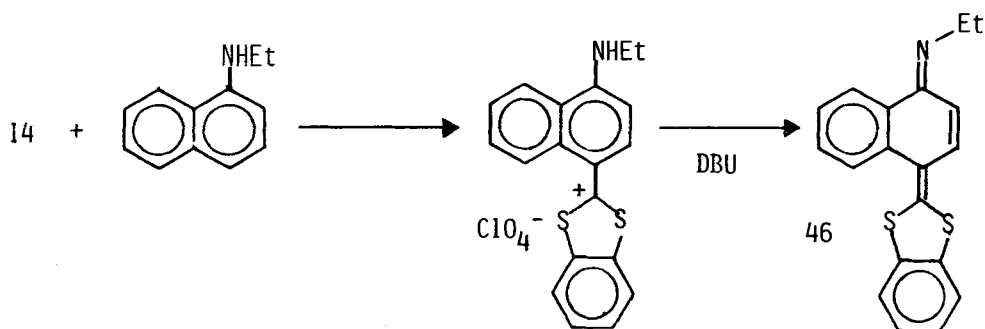
The reaction of 2,6-dichlorophenol with an equivalent of **4a** in the presence of pyridine at room temperature affords compound **38** quantitatively, whereas the reaction with a 1 : 2 molar ratio under the same conditions followed by treatment with triethylamine produces the stable quinone methide **40** in 91 % yield along with 1,3-benzodithiolo (1). The parent 1,3-benzodithiolium ion is less stable than the dithiolium ion **39** which is stabilized by an aryl group. Thus, an equimolar amount of **4a** is consumed to abstract a hydride ion from the initial product **38** yielding **39** and **1**, the former being converted to the quinone methide **40** by treatment with triethylamine. In a similar way a variety of quinone methides including **41–43** have been synthesized.<sup>43</sup> Quinone methides of this type are also obtained by reaction of the salt **14** with phenols.<sup>15</sup>



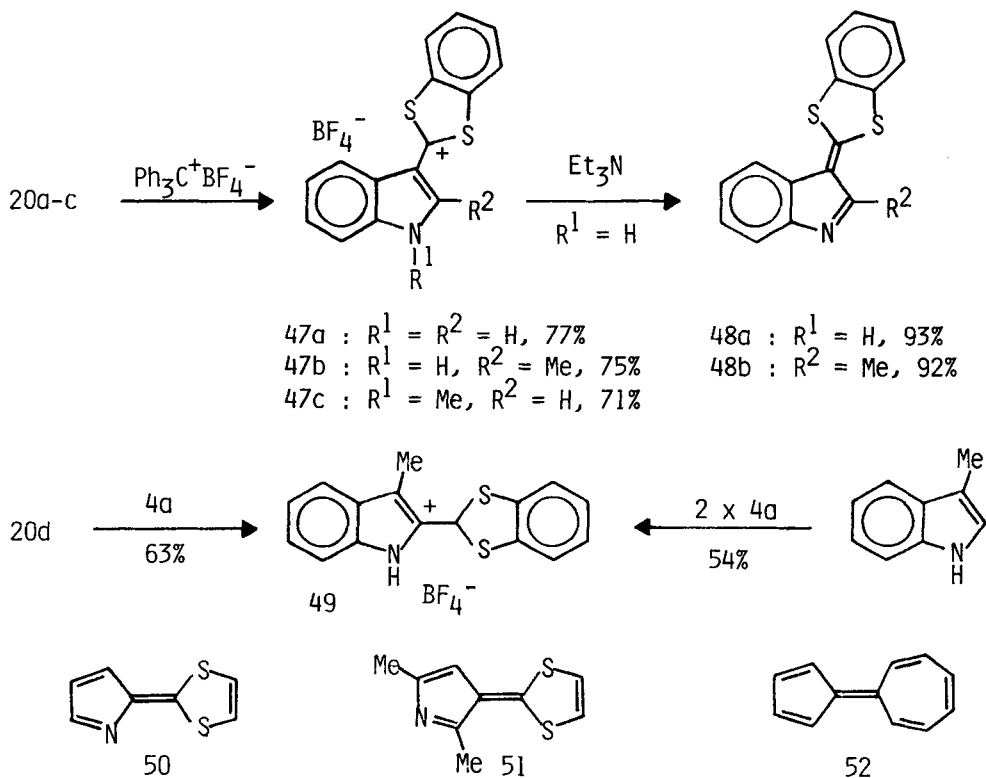
Substitution reactions of primary and secondary aromatic amines with 1,3-dithiolium ions usually occur at the nitrogen atom. In case of this being sterically hindered, however, electrophilic aromatic substitution occurs preferentially. Thus the reaction of 2,6-diethylaniline with 2 mol. equiv. of **4a** leads to the dithiolium salt **44**. The reaction proceeds as described in the case of quinone methides. Treatment of **44** with DBU results in the formation of the quinone methide imine **45**. Triethylamine cannot bring about this conversion. The quinone methide imine **46** has been prepared by reaction of the salt **14** with *N*-ethyl-1-naphthylamine followed by treatment with DBU. Several other stable quinone methide imines have been prepared in similar ways.<sup>44</sup>





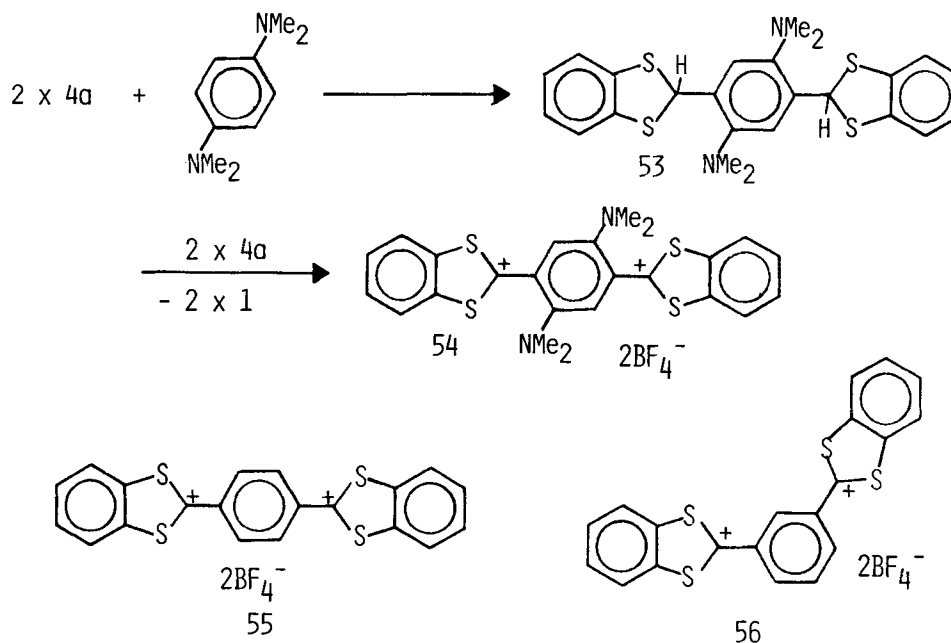


Compounds **20a–c**, products of the reaction of indoles with the dithiole **6**, react with trityl tetrafluoroborate to form the dithiolium salts **47a–c** in good yields. Treatment of **47a,b** with triethylamine affords the dithiafulvalene derivatives **48a,b**.<sup>45</sup> Compound **20d** reacts with **4a** to provide the dithiolium salt **49**. This conversion cannot be brought about by a trityl salt. The salt **49** is directly obtained from 3-methylindole and 2 mol. equiv. of **4a**. In similar ways a variety of azadithiafulvalene derivatives including **50** and **51** have been prepared and their properties examined.<sup>46,47</sup> Compounds **50** and **51** are iso- $\pi$ -electronic with sesquifulvalene (**52**).

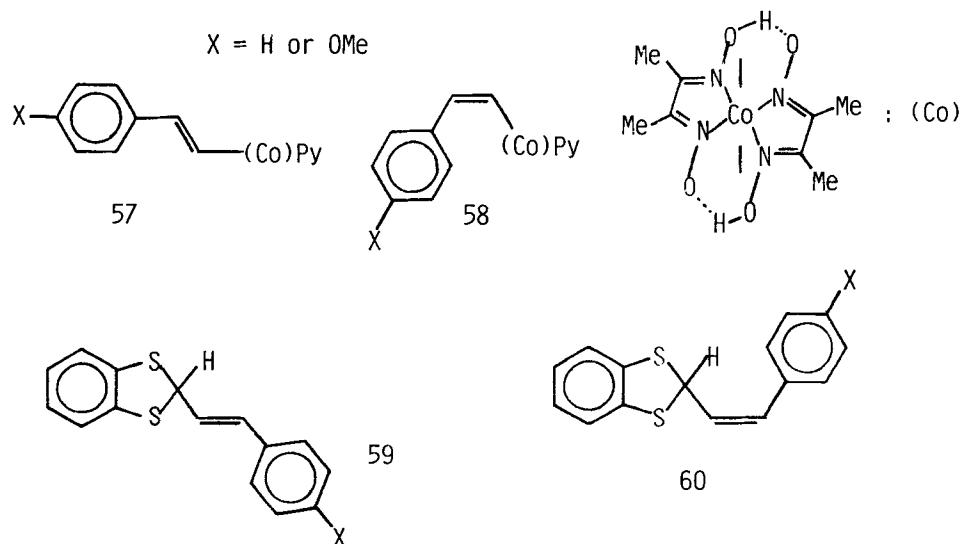


The bis-1,3-benzodithiolium salt (**54**) has been prepared by reaction of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine with the salt **4a**. Reaction of *N,N,N',N'*-tetra-

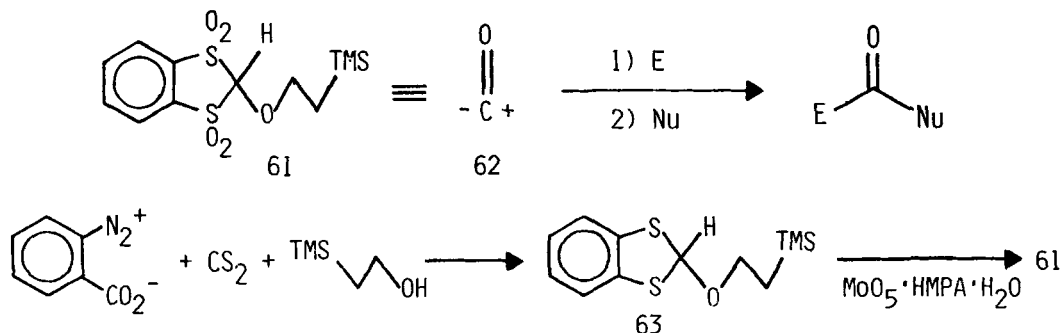
methyl-*p*-phenylenediamine with 2 mol. equiv. of **4a** affords compound **53** (51 %), further reaction of which with **4a** provides the bis-salt **54** as dark green crystals in 74 % yield.<sup>48</sup> The bis-dithiolium salts **55** and **56** were also prepared by condensation of terephthalaldehyde and isophthalaldehyde with 1,2-benzenedithiol followed by treatment with 2 mol. equiv. of trityl tetrafluoroborate.<sup>48,49</sup>



Cobaloximes of the type **57** react with **4a** to give 2-(*trans*-styryl)-1,3-benzodithioles (**59**) with retention of the original stereochemistry in good yields. The reaction of **58** with **4a**, however, gives a mixture of *cis*- and *trans*-isomers (**59** and **60**) in low yields.<sup>50</sup>



Recently the 2-alkoxy-1,3-benzodithiole 1,1,3,3-tetraoxide (**61**) was shown to function as carbonyl 1,1-dipole synthon (**62**).<sup>51</sup> Compound **61** was prepared by oxidation of the dithiole **63**, which was obtained from anthranilic acid by the author's procedure.



Alkylation of the sulfone **61** with alkyl halides was best performed by using  $\text{Cs}_2\text{CO}_3$  in DMF to provide compounds **64** in 30–87 % yields (see Table 8). The unmasking of **64** for the generation of reactive acylating agents is induced by Lewis acids such as boron trichloride and titanium tetrachloride. Thus, treatment of **64a** with boron trichloride at  $-78^\circ\text{C}$  followed by addition of methanol produces the methyl ester **65a** in 75 % yield. Similarly treatment of **64b** with boron trichloride followed by addition of aniline provides the amide **65b**. Intramolecular trapping of a reactive acylating agent by a carbon nucleophile is also satisfactory. Treatment of **64c** with titanium tetrachloride results in regioselective cyclization to provide the cyclic ketones **65c**. Some other applications are included in the same paper.

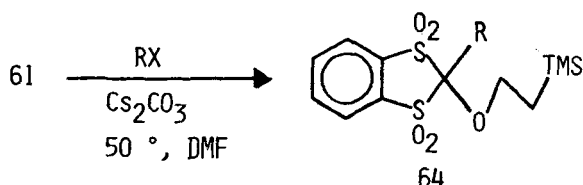
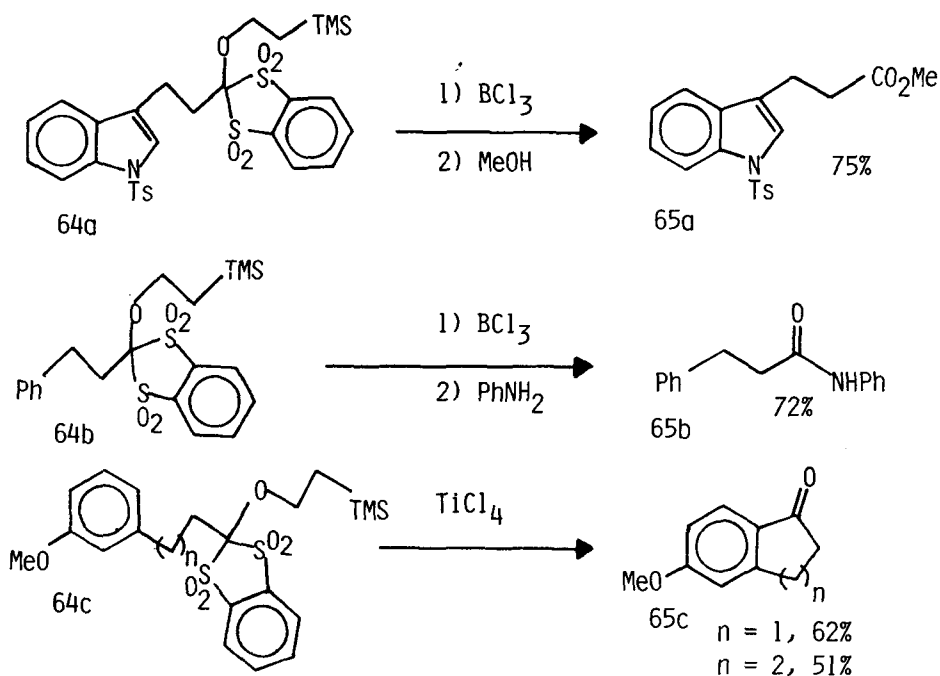


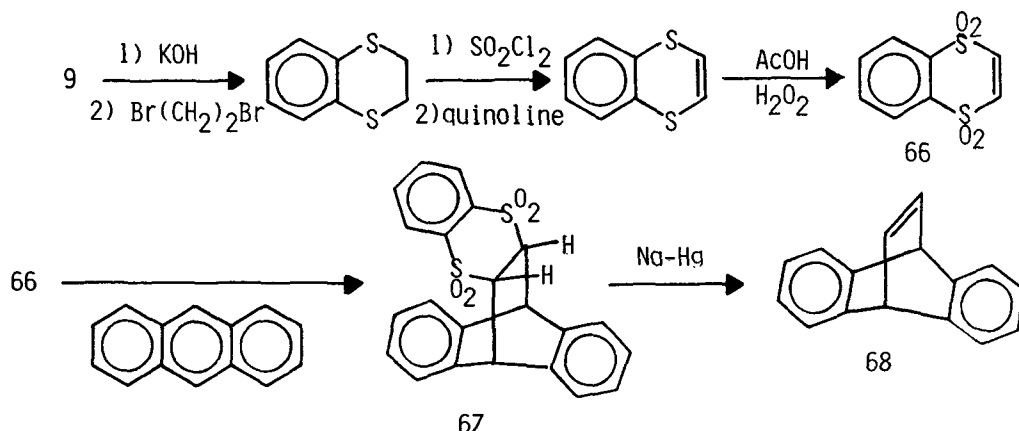
TABLE 8

Preparation of **64** by Alkylation of **61** with Alkyl Halides

alkylating agent	yield of <b>64</b>	alkylating agent	yield of <b>64</b>
	73		30
	73		64
	81		48
	87		65
	55		

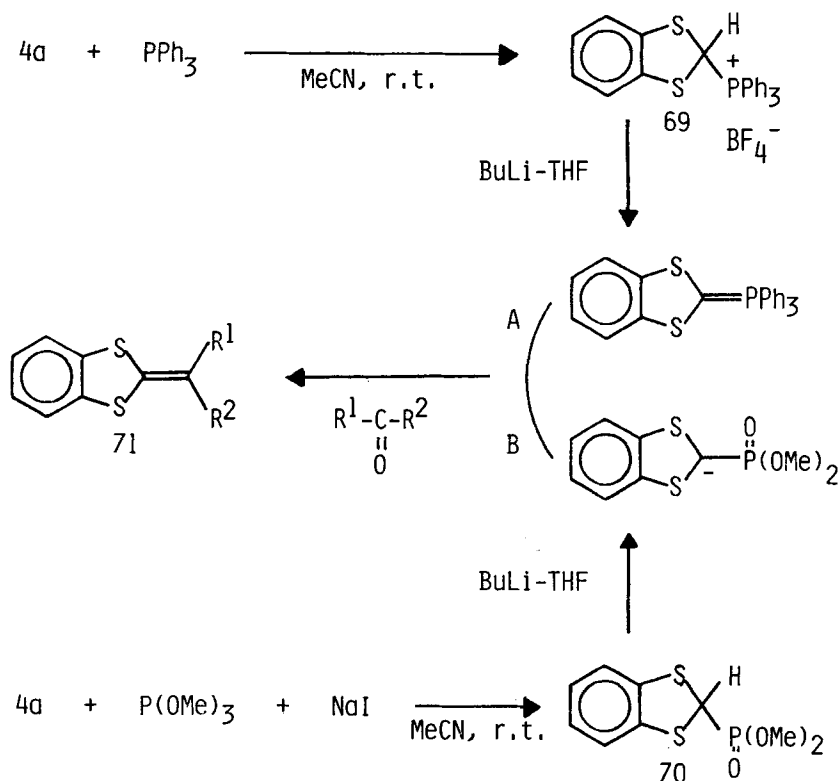


1,4-Benzodithiin 1,1,4,4-tetroxide (**66**) can be prepared in three steps from **9**, which has recently become readily obtainable from the dithiolo **6**. The sulfone **66** acts as a strong dienophile and undergoes Diels-Alder reactions with a variety of dienes.<sup>52</sup> For example, heating **66** and anthracene in refluxing toluene for 1 h affords the adduct **67** in 93 % yield. Desulfurization of **67** with sodium amalgam provides dibenzobarrelene (**68**) in 73 % yield. Therefore **66** functions as a reactive acetylene synthon.



Triphenylphosphine reacts with **4a** to give the phosphonium salt **69** in 87 % yield. The reaction of trimethyl phosphite with **4a** in the presence of sodium iodide gives the phosphonate **70** in 93 % yield.<sup>53</sup> Preparation of **70** from the dithiolo **6** has also been reported.<sup>54</sup> The compounds **69** and **70** rapidly react with a variety of aldehydes and ketones under the conditions of the Wittig (Wittig-Horner) reaction to provide

1,4-benzodithiafulvenes (**71**) in excellent yields (Table 9).<sup>53,55</sup> The fulvenes **71** might function as useful intermediates in synthesis.



The fulvenes **72** were prepared in excellent yields (95–98 %) by application of the above reaction. The fulvenes **72** undergo an acid-catalyzed (*p*-toluenesulfonic acid)

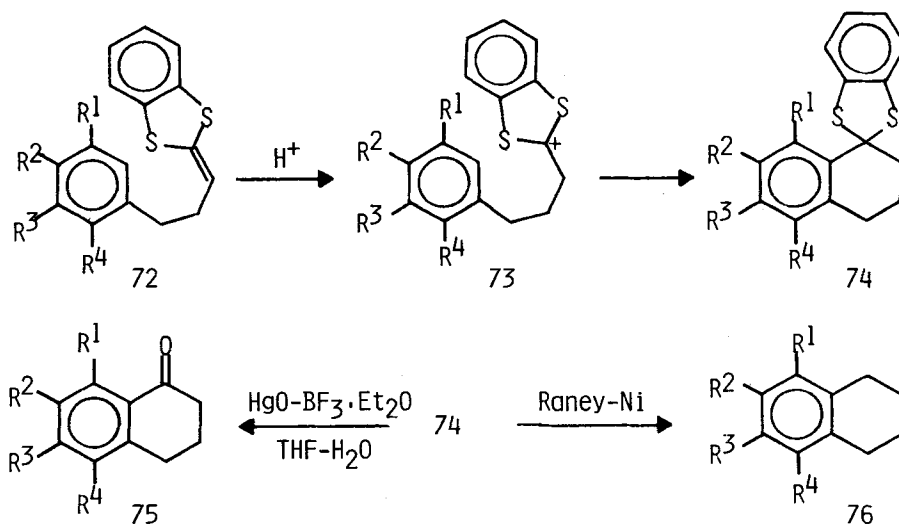


TABLE 9  
Preparation of 1,4-Benzodithiafulvenes **71**

R <sup>1</sup>	R <sup>2</sup>	Method <sup>a)</sup>	Yield of <b>71</b> (%)
p-MeOC <sub>6</sub> H <sub>4</sub>	H	A	77
p-MeC <sub>6</sub> H <sub>4</sub>	H	A	75
		B	94
Ph	H	A	74
p-ClC <sub>6</sub> H <sub>4</sub>	H	A	82
Ph-CH=CH	H	A	78
Me-CH=CH	H	B	95
-(CH <sub>2</sub> ) <sub>4</sub> -		B	96
-(CH <sub>2</sub> ) <sub>5</sub> -		B	98
p-MeC <sub>6</sub> H <sub>4</sub>	Me	B	92
p-ClC <sub>6</sub> H <sub>4</sub>	p-ClC <sub>6</sub> H <sub>4</sub>	B	95

<sup>a)</sup> Method A: The phosphonium salt **69** as the precursor.

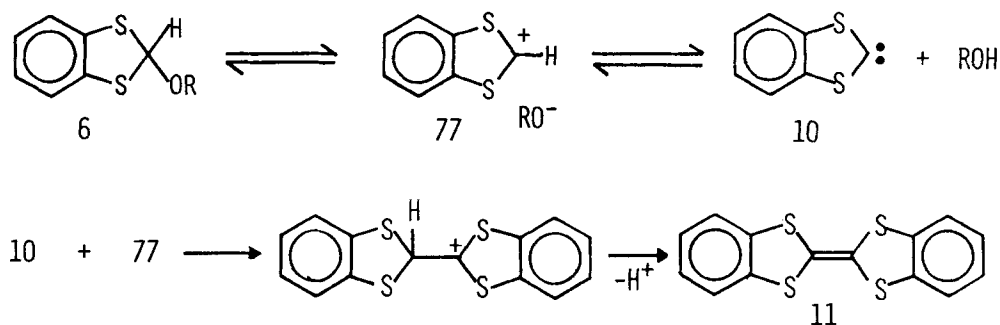
Method B: The phosphonate **70** as the precursor.

intramolecular cyclization to afford the compounds **74** in good yields.<sup>56</sup> This 1,3-benzodithiolium ion (**73**) mediated annulation occurs regioselectively (Table 10). The benzodithioles **74** thus obtained can be hydrolyzed to the corresponding tetralones **74** or desulfurized with Raney-Nickel (W-2) to the related tetralins **76** in good yield.

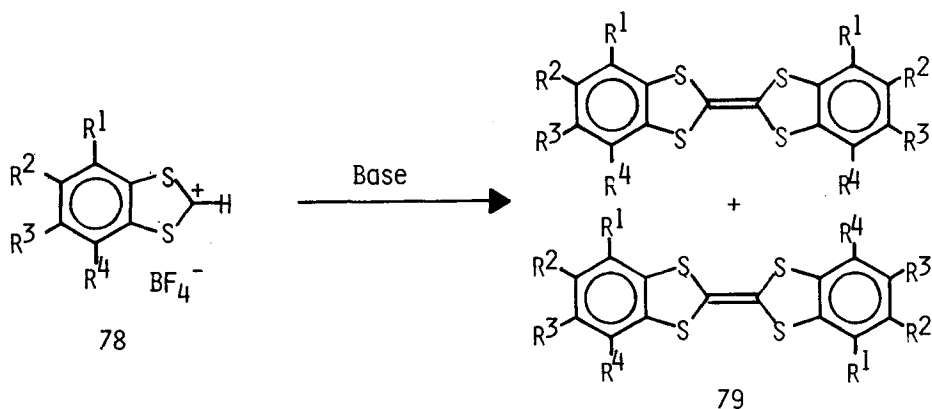
TABLE 10  
Preparation of Tetralones **75** and Tetralins **76** by 1,3-Benzodithiolium Ion Mediated Annulations

R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	yield (%) 72 → 74	yield (%) 74 → 75	yield (%) 74 → 76
H	MeO	MeO	H	76	60	69
H	H	MeO	MeO	56	55	75
H	-OCH <sub>2</sub> O-	H	H	75	55	91
H	H	MeO	H	62	62	95
H	MeO	H	H	74	56	-

Dibenzotetrathiafulvalene (**11**) is produced in moderate yields by thermal decomposition of 2-alkoxy-1,3-benzodithioles (**6**).<sup>57</sup> The dithioles **6** thermally dissociate into the 1,3-benzodithiolium ion and an alkoxide ion, and then the former loses a proton to yield the carbene **10**. Reaction of the dithiolium ion with **10** followed by deprotonation results in the formation of **11**.

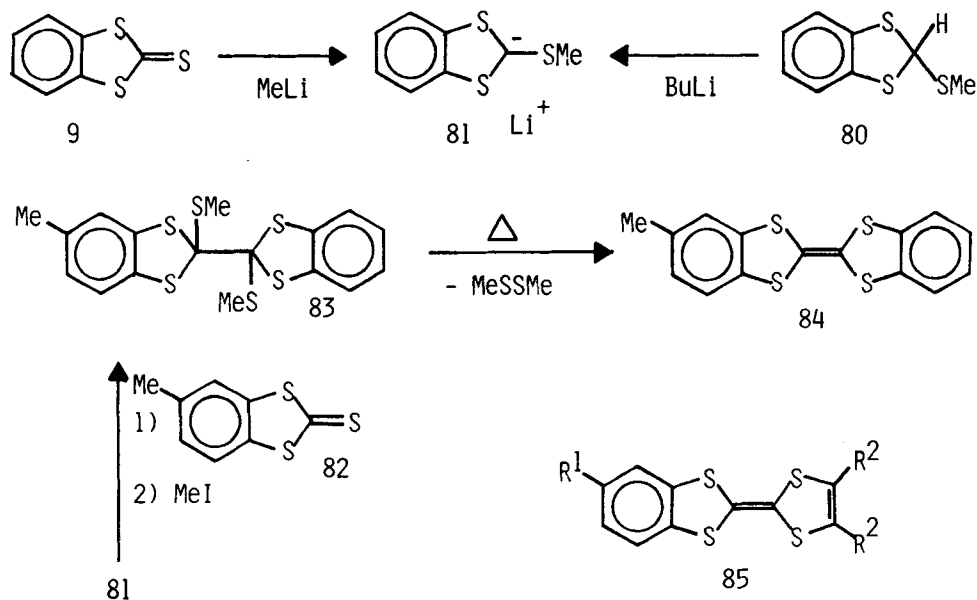


More conveniently a variety of dibenzotetrathiafulvalenes (**79**) have been prepared by treatment of 1,3-benzodithiolium salts (**78**) with bases. Although until recently only trialkylamines, especially triethylamine, were used for this conversion, *N,N*-dimethylformamide and DBU also produce satisfactory results.<sup>10,12</sup>

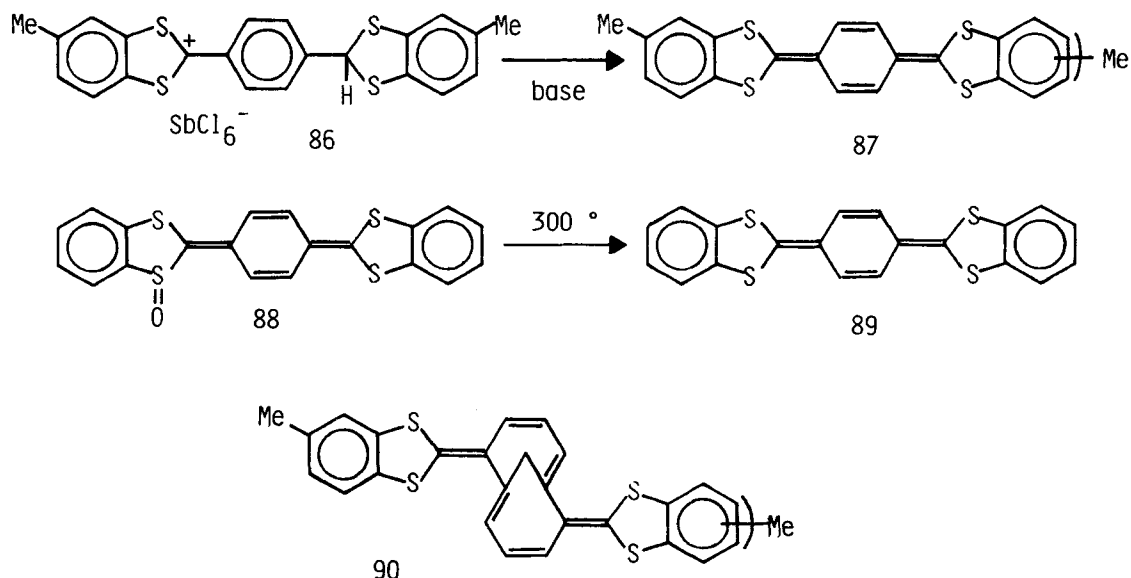


R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	Yield of 79 (%)
H	H	H	H	96
Me	H	H	H	92
H	Me	H	H	89
H	Cl	H	H	91
H	I	H	H	87
H	NO <sub>2</sub>	H	H	79
-CH=CH-CH=CH-				88

2-Lithio-2-(methylthio)-1,3-benzodithiole (**81**) can be generated either by thiophilic addition of methyl lithium to **9** or by deprotonation of **80** with butyllithium. The reaction of **81** with the carbonate **82** followed by methylation with methyl iodide gives the hexathioorthoaxalate **83** in good yield. Thermolysis of **83** provides the unsymmetrical dibenzotetrathiafulvalene **84**. By using similar sequences the tetrathiafulvalenes **85** have been prepared in good overall yields.<sup>58,59</sup>



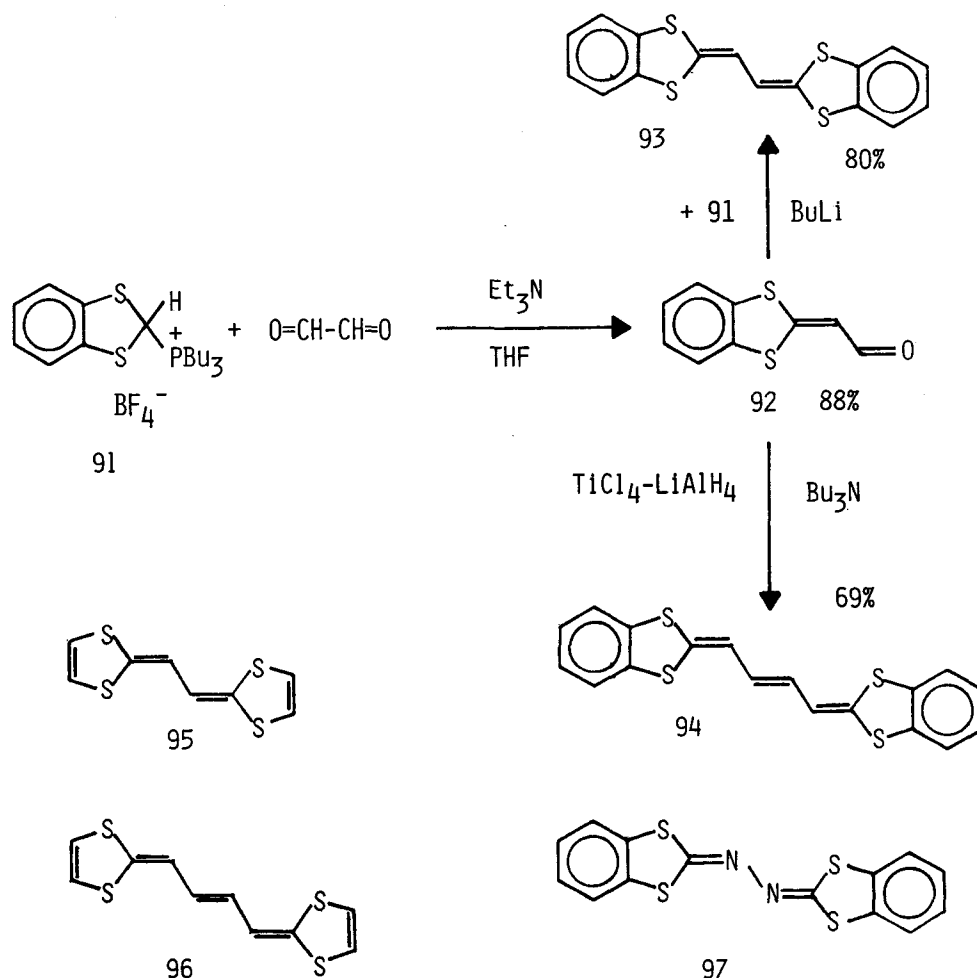
Quinonoid compounds like **87** and **89** are known. The relationship between this system and dibenzotetrathiafulvalene corresponds to that between tetracyanoethylene (TCNE) and tetracyanoquinodimethane (TCNQ). The dimethyl derivative **87** has been prepared by deprotonation of the dithiolium salt **86**.<sup>60</sup> The unsubstituted compound **89** was obtained by thermolysis of compound **88**.<sup>61</sup> The synthesis of a similar compound **90** has also been reported.<sup>62</sup>



Ethanediyldene- and 1,4-butanediylidene-2,2'-(1,3-benzodithiole) (**93** and **94**) have been prepared by application of the above reaction.<sup>63-65</sup> The Wittig reaction of



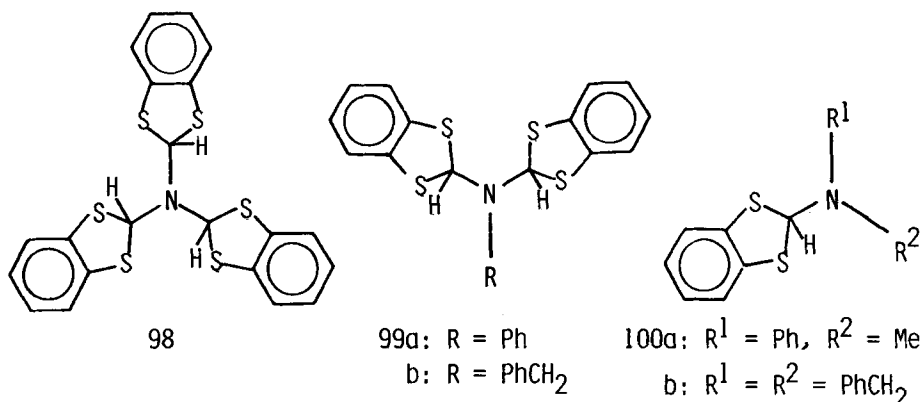
the phosphonium salt **91** with glyoxal (40 % aqueous solution) induced by triethylamine gives the formyl compound **92** in 88 % yield. Compound **92** reacts with **91** in the presence of butyllithium to provide **93** in 80 % yield. The reductive coupling reaction of **92** with low-valent titanium affords compound **94** in 69 % yield. The same authors also describe the preparation of the parent compounds **95** and **96**.<sup>63,64</sup> The preparation of the aza analog **97** of **93** has been reported.<sup>66</sup>



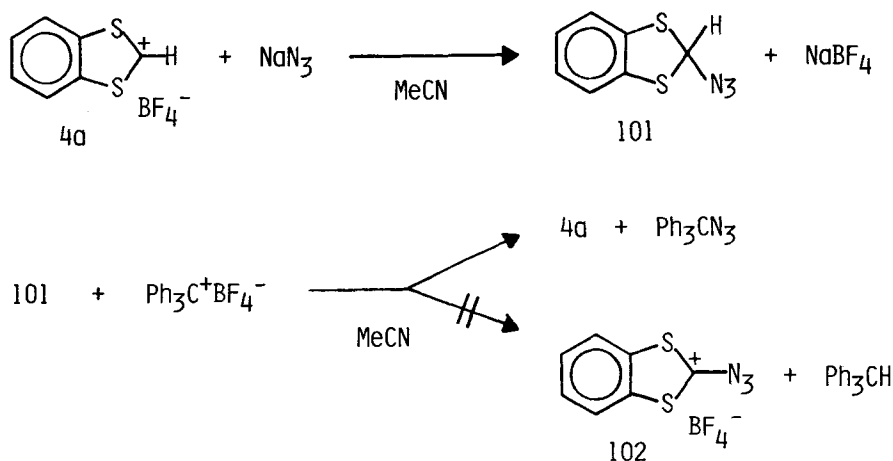
## 2. Formation of Carbon-Hetero Atom Bonds

Amines as nucleophiles react with the dithiolium salt **4a**.<sup>12</sup> Ammonium acetate reacts with 3 mol. equiv. of **4a** in the presence of pyridine to give tris-(1,3-benzodithiol-2-yl)amine (**98**) in 86 % yield. Primary amines such as aniline and benzylamine react with 2 mol. equiv. of **4a** to afford compounds **99** in good yields. Secondary amines, such as *N*-methylaniline and dibenzylamine, give compounds **100** on reaction with **4a**. As already described, nucleophilic aromatic substitution predominates in aromatic primary and secondary amines in which substitution on nitrogen is sterically hindered.

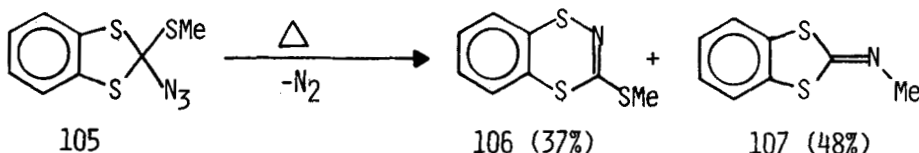
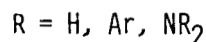
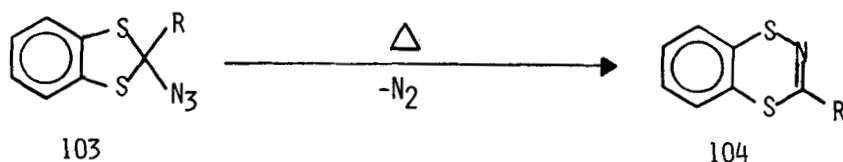
Tertiary trialkylamines such as triethylamine deprotonate **4a** to provide dibenzotetraphiafulvalene as the final product. Aromatic tertiary amines undergo nucleophilic aromatic substitution upon reaction with **4a**; the reaction of *N,N*-dimethylaniline with **4a** produces 2-[4-(*N,N*-dimethylamino)phenyl]-1,3-benzodithiole in 89 % yield.



1,3-Benzodithiol-2-yl azide (**101**) has been prepared in 89 % yield by reaction of **4a** with sodium azide in acetonitrile. Action of trityl tetrafluoroborate on **101** affords the salt **4a** (87 %) and trityl azide (90 %), none of the expected dithiolium salt **102** being obtained.<sup>67</sup> This provides an interesting example of an azide-transfer reaction.

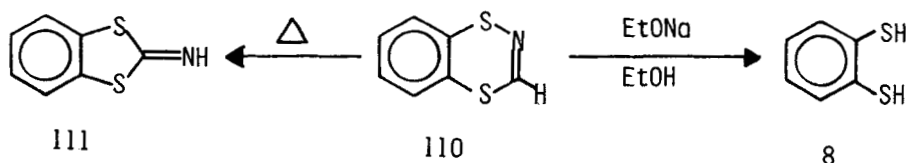
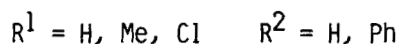
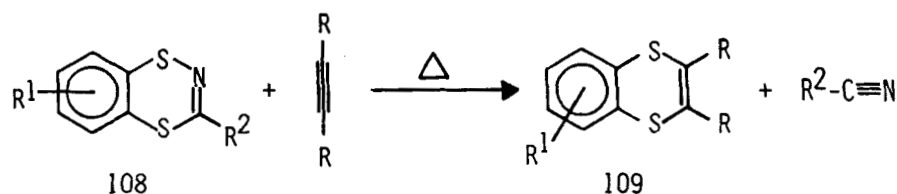


A variety of azides **103** have been prepared and subjected to thermolysis.<sup>68</sup> The thermolysis is facilitated by neighboring group participation of the sulfur atoms, and hence occurs readily in boiling toluene to give the ring-expanded products, the 1,4-benzodithiazines **104**, in good yields. The azide **105**, whose decomposition is facilitated by three sulfur atoms, decomposes at lower temperature to afford the compounds **106** and **107** in comparable amounts.<sup>68-70</sup>

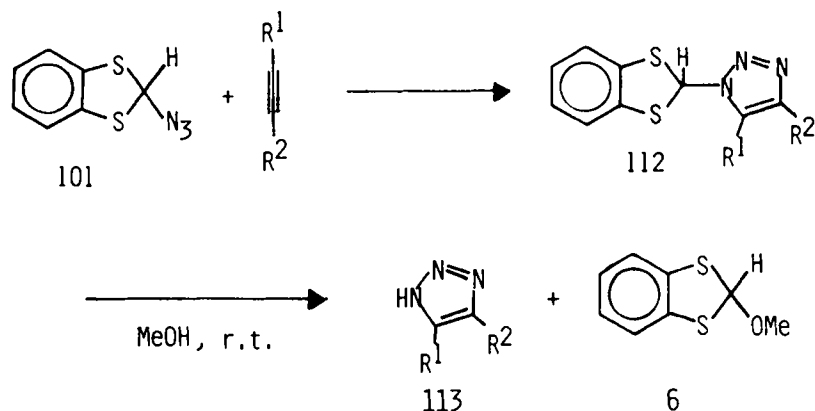


The benzodithiazines **108** undergo a novel type of cycloaddition-elimination with reactive acetylenes such as dimethyl acetylenedicarboxylate, ethyl propiolate, and benzyne to provide the benzodithiins **109**.<sup>71</sup>

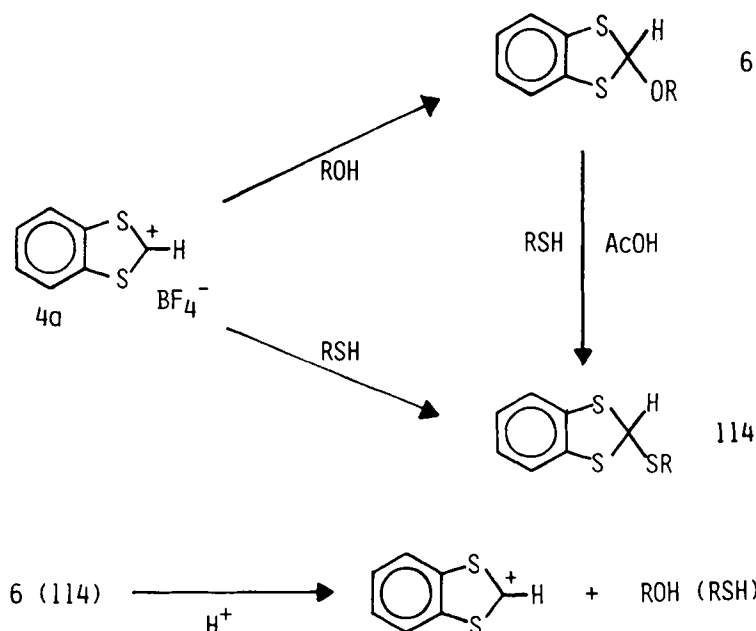
The dithiazine **110** undergoes a thermal rearrangement yielding 2-imino-1,3-benzodithiolo (**111**) when it is heated without solvent.<sup>72</sup> Action of sodium ethoxide on **110** in ethanol opens a new route to 1,2-benzenedithiol (**8**).<sup>73</sup>



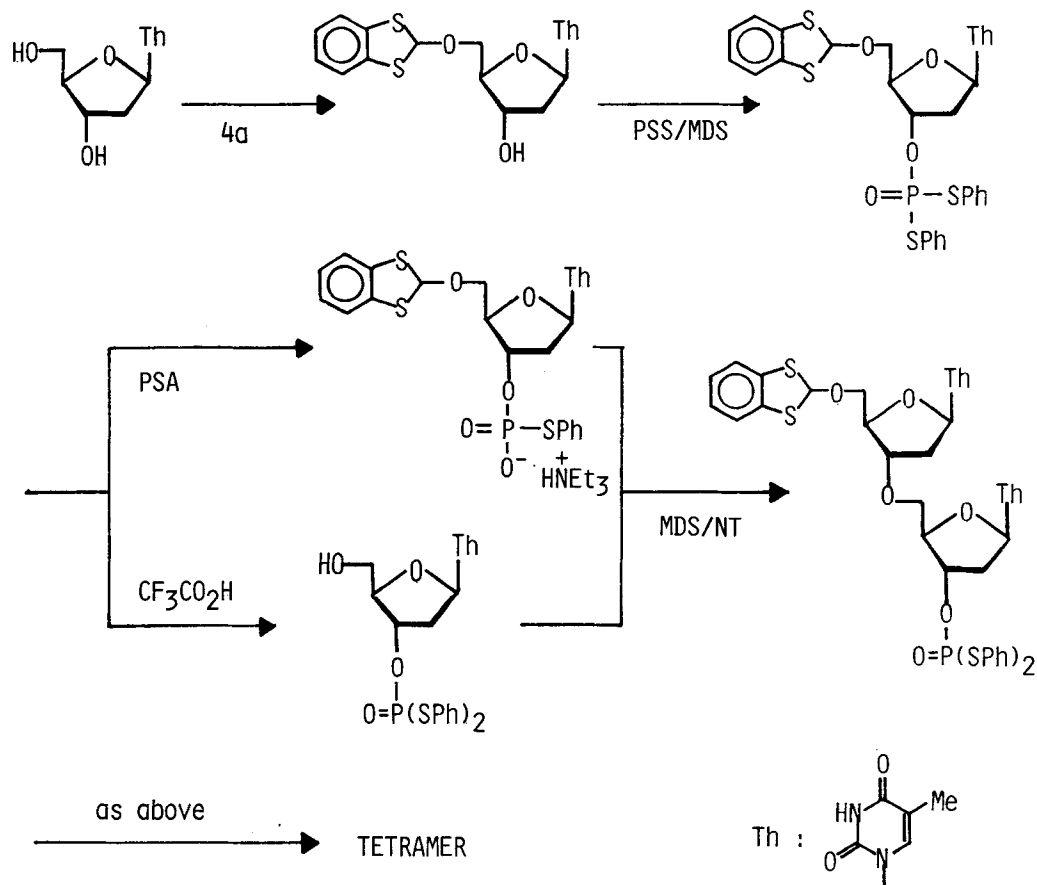
The azide **101** reacts with dimethyl acetylenedicarboxylate and ethyl propiolate, respectively, to give moderate yields of the 1,3-dipolar cyclo-addition products **112**, which are readily converted to the triazoles **113** and 2-methoxy-1,3-benzodithiolo (**6**) by treatment with methanol at room temperature.<sup>74</sup> Although this indicates that **101** functions as a hydrogen azide equivalent, the cycloaddition is unfortunately accompanied by thermal decomposition of **101** producing **110**, and hence is of limited use. Some reactive olefins such as enamines also undergo a similar cycloaddition with **101**.<sup>74</sup>



The salt **4a** reacts with alcohols and thiols to give 2-alkoxy- and 2-alkylthio-1,3-benzodithioles (**6** and **114**), respectively.<sup>12</sup> The dithioles **114** are also obtained by reaction of **6** with thiols in acetic acid.<sup>18</sup> The formation of **6** from **4a** is the reverse process of the preparation of **4a** from **6**, and therefore **6** and **114** regenerate the dithiolium ion and the corresponding alcohols and thiols by treatment with acids. This conversion is also brought about by the action of a trityl salt.<sup>75</sup>



We therefore suggested in a previous review that **4a** might function as a protecting group of protic functional groups.<sup>2c</sup> In fact, **4a** was recently elegantly used as a protecting group of the hydroxyl groups in nucleosides and the synthesis of oligothymidylates was achieved by this technique.<sup>76,77</sup> The following is an example.



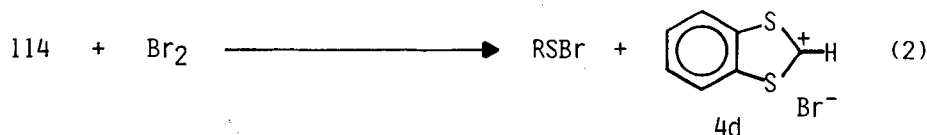
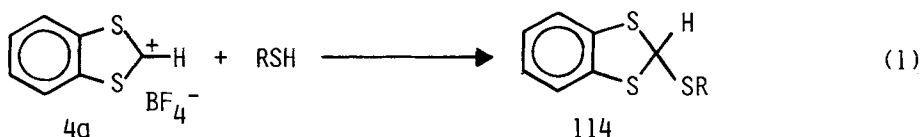
PSS: cyclohexylammonium *S,S*-diphenyl phosphorodithioate

MDS: mesitylene-1,3-disulfonyl chloride

PSA: pyridinium phosphinate

NT : 3-nitro-1,2,4-triazole

In the presence of the salt **4a** thiols are oxidized to the corresponding disulfides in good yields by molecular bromine.<sup>78</sup> The reaction proceeds as depicted below. The salt **4a** consumed in step 1 is regenerated by steps 2 and 3, and therefore a catalytic amount of **4a** is enough for this conversion.



A variety of 1,3-benzodithiol-2-ylidene carbenes **117** react with elemental sulfur and selenium to provide 2--thioxo- and 2-selenoxo-1,3-benzodithioles (**118** and **119**) in good yields.<sup>14</sup> The carbenes **117** were generated either by thermal decomposition of the dithioles **115** or by deprotonation of the dithiolium salts **116**. Thus, **115** were heated with elemental sulfur or selenium in refluxing *o*-dichlorobenzene for several hours or **116** were heated with elemental sulfur or selenium in boiling pyridine for 1 h, thereby providing the results shown in Table 11.

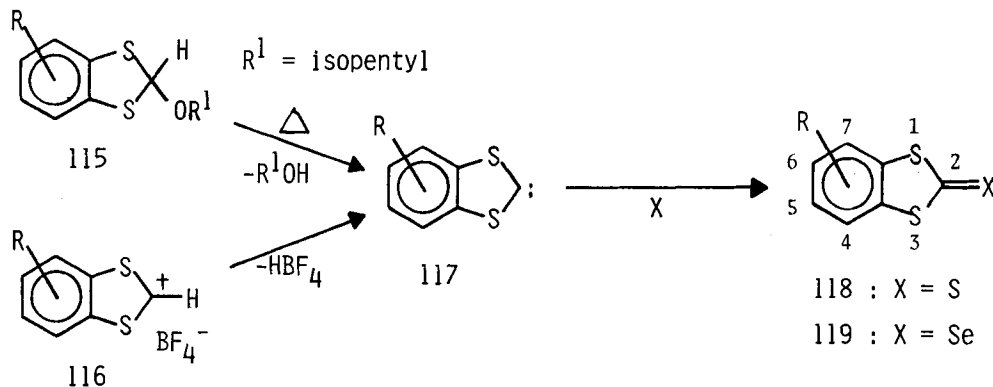


TABLE 11

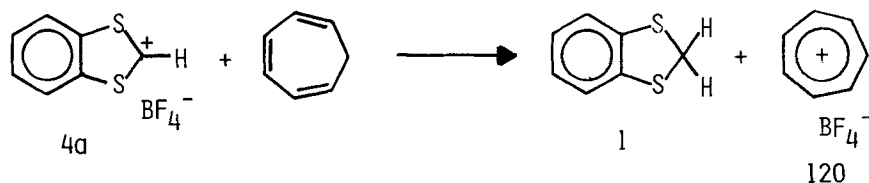
## Preparation of 2-Thioxo- and 2-Selenoxo-1,3-benzodithioles

R	yield of 118 (%)	method for <sup>d</sup> generation of 117	R	yield of 119 (%)	method for <sup>d</sup> generation of 117
H	86	A	H	87	A
H	70	B	H	29	B
4-Me	95	A	4-Me	64	A
5-Me	89	A	5-Me	73	A
5-Cl	70	A	5-Cl	43	
5-NO <sub>2</sub>	55	A			

<sup>a</sup> Method A : Thermal decomposition of 115.

Method B : Deprotonation of 116.

The salt **4a** reacts with cycloheptatriene to give tropylium tetrafluoroborate (**120**) and 1,3-benzodithiole (**1**).<sup>12</sup> The dithiole **1** is also formed by reduction of **4a** with sodium borohydride or lithium aluminum hydride. Sodium hydrogen telluride reduces **4a** to afford **1** as the main product. Some other dithiolium salts are also reduced by this reagent to the corresponding dithioles.<sup>79</sup>



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