# Synthesis and Properties of *o*-Thioquinone Methides Having Ketene Aminal, Ketene Acetal, Ketene Monothioacetal, or Ketene Dithioacetal Group

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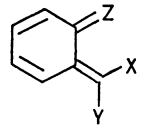
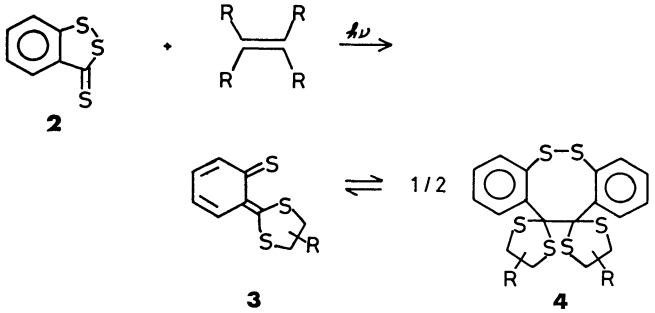
Reaction of 1,2-benzodithiole-3-thione with *N,N'*-dialkyl-1,2-ethanediamine afforded *o*-thioquinone methides with a ketene aminal group (**6**) in high yields. Two similar thionaphthoquinone methides were also prepared. *o*-Thioquinone methide derived from *N,N'*-dimethyl-*o*-phenylenediamine was prepared from 3-chloro-1,2-benzodithiol-3-ylium chloride (**10**). These compounds were found to exist as a monomer of a considerable betaine nature. Reactions of **6a** (*N,N'*-dimethyl derivative) with dimethyl acetylenedicarboxylate and dibenzoylacetylene led to [4+2] adducts. *o*-Thioquinone methides with a ketene acetal group were obtained from desulfurization of spiro[1,3-benzodioxole-2,3'-[1,2]benzodithiole] with trimethyl phosphite, which are equilibrated with two kinds of aggregates; one is a dimer and the other is a trimer or a higher oligomer. Reactions of **10** with *o*-mercaptophenol and 1,2-benzenedithiols gave spiro[1,2-benzodithiole-3,2'-[1,3]benzoxathiole] (**29**) and spiro[1,2-benzodithiole-3,2'-[1,3]benzodithiole] (**39** and **40**), respectively. *o*-Thioquinone methide with a ketene monothioacetal group (**30**) was prepared by desulfurization of **29**. The violet compound **30** is equilibrated with a colorless dimer. This *o*-thioquinone methide reacted with olefins and an acetylene having electron-withdrawing groups to give 1,4-cycloaddition products. Similar desulfurization of **39** and **40** gave *o*-thioquinone methides with dithioacetal group. Their properties were very similar to those of *o*-thioquinone methides with dithioacetal group prepared by the photoreaction of **2** with olefins.

Chemistry of *o*-quinonoid compounds (**1**) has been a subject of increasing interest in recent years because of their interesting, chemical and physical properties and synthetic applications.[1,2] For thioquinone methide (**1**, Z=S), however, there has been only a few reports which demonstrated its existence as a transient species.[3]



**1**

Recently, de Mayo[4] and we[5] described the synthesis of stable *o*-thioquinone methides with a ketene dithioacetal group (**3**) from the photoreaction of 1,2-benzodithiole-3-thione (**2**) with olefins, **3** being equilibrated with a colorless head-to-head [4+4] dimer (**4**).

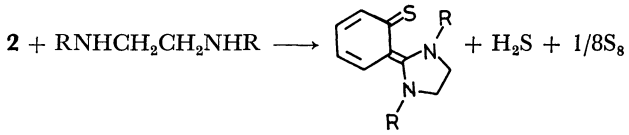


**2** **3** **4**

In this paper we report the synthesis and properties of other types of *o*-thioquinone methides (**1**, Z=S) which have a ketene aminal (**1**, X, Y=$NR_2$), a ketene acetal (**1**, X, Y=OR) or a ketene monothioacetal group (**1**, X=OR, Y=SR). *o*-Thioquinone methides of type **3** (**1**, X=Y=SR) derived from 1,2-benzenedithiols are also described. These *o*-thioquinone methides were found to show significantly different properties from one another.[6]

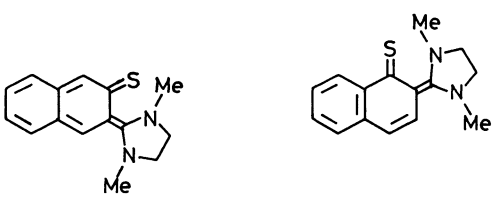
## Results and Discussion

*o-Thioquinone Methides with a Ketene Aminal Group.* Reaction of 1,2-benzodithiole-3-thione (**2**) with *N,N'*-dialkyl-1,2-ethanediamine (**5**) in ethanol afforded **6** in high yields.[7] In the reaction of **2** with **5a**, the formation of hydrogen sulfide (91% as PbS) and sulfur (94%) was also confirmed.



| | **5** | **6** | | |
|---|---|---|---|---|
| **a**: | R=Me | 99% | 91% | 94% |
| **b**: | R=Et | 64% | | |
| **c**: | R=*n*-Pr | 61% | | |
| **d**: | R=*i*-Pr | 78% | | |
| **e**: | R=*n*-Bu | 72% | | |
| **f**: | R=*n*-$C_6H_{13}$ | 56% | | |

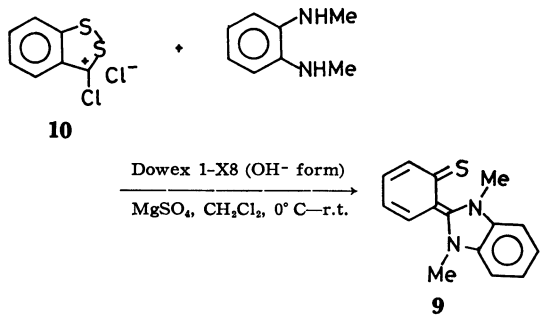
*o*-Thioquinone methides (**7** (78%) and **8** (85%)) were also prepared in a similar way from 3*H*-naphtho[1,2-*c*]-[1,2]dithiole-3-thione and 3*H*-naphtho[2,3-*c*][1,2]-dithiole-3-thione, respectively.[8]



**7** **8**

Compound **9** (69%) was synthesized by the reaction of the more reactive 3-chloro-1,2-benzodithiol-3-ylium chloride (**10**)[9] with *N,N'*-dimethyl-*o*-phenylenediamine[10] using ion exchange resin as a base. The use

of the resin made the isolation of the water soluble **9** easier.




These thioquinone methides (**6**—**9**) were not developed on silica gel even if ether was used as an eluent, suggesting their polar nature. The color of the solution of **6** is pale yellow or colorless, depending on the solvent. The electronic spectra of **6b** in benzene and ethanol showed no concentration dependence, indicating that it exists as a monomer in solution. This is in marked contrast with **3** which is in equilibrium with the dimer. The NMR spectra of **6**—**9** are very similar to one another, implying that other thioquinone methides synthesized here are also monomeric in solution.

Table 1. NMR spectra ($\delta$) of **6**—**9**, **11**, and **13** in methanol-$d_4$

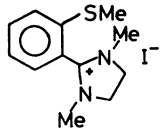
| Compound | *N*-Alkyl | Ethylene | Aromatic |
|---|---|---|---|
| **6a** | 2.91(s) | 4.00(s) | 6.9—7.4 |
| **6b** | 1.18(t)<br>3.27(q) | 4.04(s) | 6.9—7.6 |
| **6c** | 0.81(t)<br>1.61(sext)<br>3.20(t) | 4.05(br s) | 6.9—7.9 |
| **6d** | 1.12(d)<br>1.34(d)<br>3.70(sept) | 3.96(br s) | 6.85—7.74 |
| **6e** | 0.6—1.9(m)<br>3.25(t) | 4.04(br s) | 6.9—7.7 |
| **6f** | 0.6—1.9(m)<br>3.15(t) | 4.06(br s) | 6.9—7.7 |
| **7** | 2.93(s) | 4.06(s) | 7.20—8.97 |
| **8** | 2.90(s) | 4.01(s) | 6.87—7.84(5H)<br>8.85—9.15(1H) |
| **9** | 3.78(s) | — | 7.65—8.15 |
| **11** | 2.92(s) | 4.14(s) | 7.4—7.8<br>2.61[a](3H, s) |
| **13** | 2.86(s)<br>3.55(s) | 3.62(m)<br>3.91(m) | 7.39(5H, s)<br>5.77[b](1H, s) |

a) SMe protons. b) Methine proton.

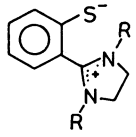
Table 2. Electronic spectra of **6b** in various solvents

| Solvent | $\lambda_{max}$/nm | log $\varepsilon$ |
|---|---|---|
| Water | 252 | 4.00 |
| Acetic acid | 263 | 3.57 |
| Ethanol | 278 | 4.18 |
| Acetonitrile | 299 | 4.26 |
| *N*,*N*-Dimethylformamide | 303 | 4.18 |
| Dichloromethane | 299 | 4.06 |
| Benzene | 307 | 4.27 |

In the NMR spectra ($CD_3OD$) of **6a**, **7**, **8**, and **9**, the *N*-methyl protons exhibit very far downfield shift (Table 1). These chemical shifts are almost the same as that of **11** prepared from **6a** and methyl iodide, indicating the large contribution of an ionic canonical structure (*e.g.*, **12** for **6**). This is reflected in the



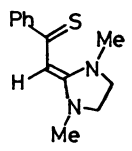
**11**



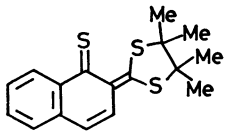
**12**

solubility of these compounds; for example, **6a** is very soluble in water and alcohols, but only slightly soluble in chloroform and benzene. The importance of the ionic contribution (**12**) to the ground state of **6** was also shown by the solvent effect of the UV spectra of **6b** (Table 2). The more polar the solvent, the shorter the absorption maximum, which indicates the stabilization of the ionic ground state by polar solvents. Here again, these *o*-thioquinone methides are quite different from those with a ketene dithioacetal group (**3**) whose electronic spectra show no essential solvent dependence.[5d]

In the NMR spectra of **6a**, the ethylene protons of the imidazolidine ring appear as a sharp singlet at $\delta$ 4.00. At −80 °C it becomes broad but no coalescence occurs, which shows that the imidazolidine ring is rotating freely at this temperature. On the other hand, the ethylene protons of **13** prepared from the reaction of 5-phenyl-1,2-dithiole-3-thione[11] with **5a** appear as AA'BB' multiplet centered at $\delta$ 3.62 and 3.91, suggesting the higher double bond nature of the *exo* methylene bond of the imidazolidine.



**13**



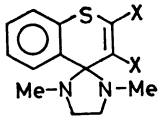
**14**

In the case of **6**, when R is bulkier than the *n*-propyl group (*i.e.*, **6c**—**6f**), the ethylene protons appear as a broad singlet. In the isopropyl derivative (**6d**), the methyl and ethylene protons appear as a broad singlet at $\delta$ 3.96 and a doublet of doublet at $\delta$ 1.12 and 1.34 in methanol-$d_4$, respectively. In 1-chloronaphthalene, however, the ethylene protons appear as AA'BB' multiplet centered at $\delta$ 2.72 and 2.98, indicating that the imidazolidine ring is not rotated on NMR time scale. The most reasonable explanation of these observations is that the ring is perpendicular to the benzene ring. In this conformation, the two methyl groups of the isopropyl group are magnetically nonequivalent if the rotation is restricted. The methyl protons of **14**, prepared from the photoreaction of 3*H*-naphtho[1,2-*c*]-[1,2]dithiole-3-thione with 2,3-dimethyl-2-butene in benzene,[12] appear as two singlets at $\delta$ 1.56 and 1.62.

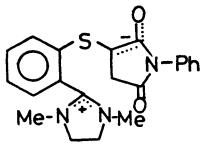
Since this type of *o*-thioquinone methide is known to exist as a monomer,[13] the observation of the two singlets indicates the restricted rotation of the dithiole ring. This is in sharp contrast to the fact that the imidazolidine ring in **8** is freely rotating and we regard this as another demonstration of the higher betaine nature of the *o*-thioquinone methides with a ketene aminal group.

Of particular interest is the isolation and stability of **7**, since compounds with 2,3-naphthoquinone structure are usually very unstable[2g,14] and can be isolated only in special cases.[15]

The *o*-thioquinone methides (**6**) are strong enophiles and react with acetylenes having electron-withdrawing groups at room temperature to afford 1,4-cycloaddition products. The reaction of **6a** with dimethyl acetylenedicarboxylate and dibenzoylacetylene gave **15** (76%) and **16** (53%), respectively, and that with *N*-phenylmaleimide afforded rapidly **17** (80%) at 7—8 °C in benzene. The structure of **17** was tentatively assigned by the spectral data; the NMR spectrum showed the *N*-methyl protons as a singlet at $\delta$ 3.02 and a broad peak due to six methylene protons at $\delta$ 4.0, two protons of which disappeared upon addition of $D_2O$.

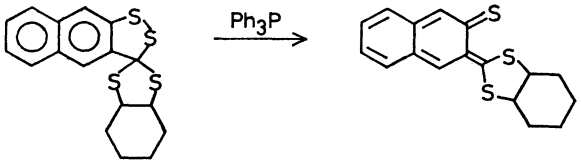


**15**: X=$CO_2$Me
**16**: X=COPh

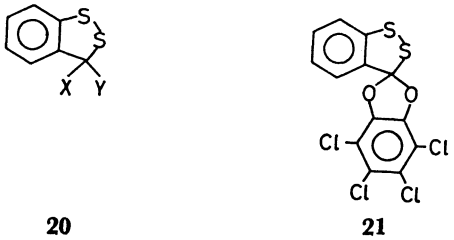


**17**

o-*Thioquinone Methides with a Ketene Acetal Group.* We considered that 3,3-disubstituted 3*H*-1,2-benzodithiole would be a suitable precursor of *o*-thioquinone methides (**1**, Z=S) with hetero atoms X and Y, because we previously found[12] that desulfurization of spiro compound (**18**) with trivalent phosphorus compound gave in a high yield *o*-thioquinone methide (**19**) which actually exists as a dimer. The only reported example of a compound with a general formula (**20**; X, Y= hetero atom) is **21** which was prepared by the reaction of **2** with *o*-chloranil.[16]



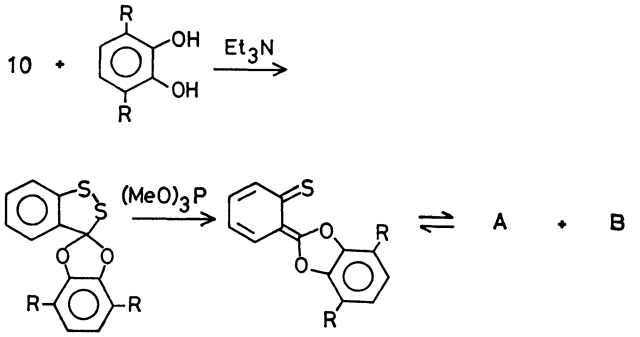
**18** **19**



**20** **21**

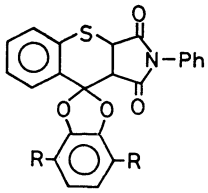
Reaction of the dithiolium salt (**10**) with pyrocatechols gave spiro compounds (**22** and **23**). This reaction has also been applied successfully to the synthesis of spiro compounds, **29**, **39**, and **40** (*vide infra*).

The spiro compounds (**22** and **23**) reacted rapidly with trimethyl phosphite in benzene at room temperature to give white crystals, **24A** and **25A**, respectively. When the filtrate was evaporated and the residue was left for some time, other white crystals (**24B** and **25B**, respectively) were formed.



**22**: R=H 83% **24**: R=H **24A** 88% **24B** 3%
**23**: R=Me 53% **25**: R=Me **25A** 50% **25B** 28%

The NMR spectra, melting points, and reactivity of **A** and **B** were different from each other both for **24** and **25**; however, the same 1,4-cycloadducts (*i.e.*, **26** and **27**) were obtained by the reaction with *N*-phenylmaleimide irrespective of whether the starting material was **A** or **B**. Their UV spectra depend upon the concentration, indicating that these aggregates, **A** and **B**, are equilibrated with the monomer **24** and **25** in both cases.



| | From **A** | From **B** |
|---|---|---|
| **26**: R=H | 85% | 91% |
| **27**: R=Me | 85% | 79% |

On the basis of molecular weight determination by vapor pressure osmometry in benzene (Found 440, Calcd 456), it was found that the aggregate **24B** was a dimer. High resolution mass spectrum of **24B** also showed the parent peak as a dimer at *m/e* 456.0509 (Calcd for $C_{26}H_{16}O_4S_2$: 456.0491).

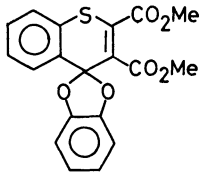
Since the aggregates **24A** and **25A** decomposed in benzene at room temperature, the correct molecular weight could not be determined. For example, the molecular weight of **24A** was observed to be 662 at the beginning of the measurement but it decreased gradually by decomposition. Since it takes some time to make a sample for the measurement and **24A** might decompose during this time, we infer that **24A** is a trimer or a higher oligomer.

The NMR spectrum ($CDCl_3$) of **25B** showed its methyl signal at $\delta$ 2.30 as a singlet. However, **25A** showed a sharp and weak singlet at $\delta$ 2.30 and a broad and strong singlet at $\delta$ 2.07 in the methyl region at the

beginning of measurement, but the spectral pattern changed very rapidly; the intensity of the peak at $\delta$ 2.30 increased and that of the peak at $\delta$ 2.07 decreased. After several hours the NMR pattern of **25A** became very similar to that to **25B**, suggesting the occurrence of the change **25A**→**25B** probably *via* the monomer.

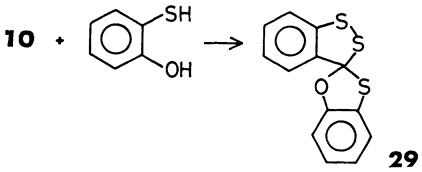
The existence of two types of aggregates is an interesting phenomenon, although their structures could not be determined exactly. However, it is clear that the equilibrium between the aggregate **A** and the monomer is more favorable toward the monomer than the equilibrium for the aggregate **B**, because the afore-mentioned reaction with *N*-phenylmaleimide proceeds much more rapidly for **A** (1 h for **A** *vs.* 20 h for **B** in refluxing benzene) and it is reasonably assumed that the monomer, not the aggregates, reacts with *N*-phenylmaleimide.

The reaction of **24A** with dimethyl acetylenedicarboxylate in refluxing benzene for 5 h gave **28** in 80% yield. The formation of these [4+2] adduct clearly indicates the presence of the monomer in solution, but we could not find any spectroscopic evidence for it.

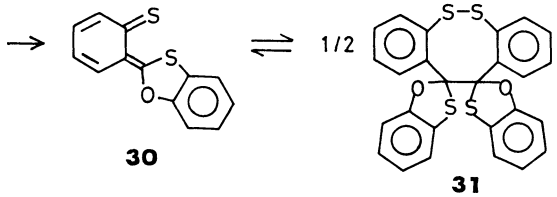


**28**

*o-Thioquinone Methides with a Monothioacetal Group.* Spiro compound **29**, prepared from **10** and *o*-mercaptophenol, reacted with trimethyl phosphite at room temperature to afford **31** in 92% yield. The structure of **31** was established by its cycloaddition leading to [4+2] adduct (*vide infra*), as in the case with all other *o*-thioquinone methides.



**29**

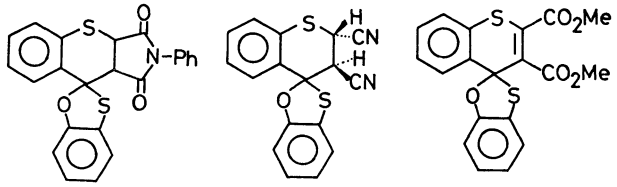


**30** **31**

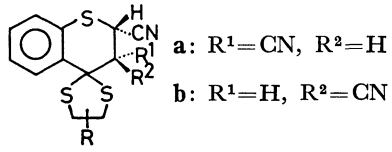
The color of the solution of **31** depends on solvent and temperature. For example, **31** shows violet in dichloromethane or benzene at room temperature, but the cyclohexane solution is almost colorless. Recrystallization of **31** from benzene–ethanol afforded white crystals but the dissolution of the crystals in an appropriate solvent (*e.g.*, dichloromethane) led to a violet solution. The colorless cyclohexane solution turned violet when heated, but the violet color was discharged when the solution was left at room temperature. These facts and the dependence of UV spectrum of **31** on the concentration suggest that the colorless aggregate **31** is also equilibrated with a monomer **30**. The molecular weight determination (vapor pressure osmometry) indicates that the aggregate is a dimer (Found 480, Calcd 488). Although we do not have any experimental evidence for the structure of the dimer, we infer that **31** is a head-to-head dimer by analogy with the equilibrium between **3** and **4**.[5]

The *o*-thioquinone methide **30** also reacted with *N*-phenylmaleimide, fumaronitrile and dimethyl acetylenedicarboxylate to afford **32**, **33**, and **34** in 99, 81, and 85% yields, respectively.

Two methine protons $\alpha$ to the cyano group in **33** appeared as two sets of doublet of doublet of AX type in the NMR spectra of the crude product. The intensity ratio of the two was about 5 : 1 ($J_{AX}$=6.6 Hz for the major one and $J_{AX}$=7.8 Hz for the minor one). In the light of the reported value[5c,d] for **35a** ($J_{AX}$=3.4 Hz) and **35b** ($J_{AX}$=9.1 Hz), the coupling constants observed for **33** imply that it is a *trans* adduct, suggesting the stereoselectivity of the cycloaddition, although the results for reaction of **30** with maleonitrile is necessary for definite conclusion. The two sets of the doublets of



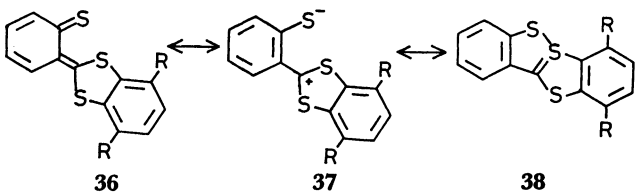
**32** **33** **34**



**35**

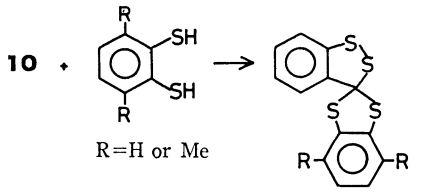
doublet observed for **35** are considered to correspond to two isomers with respect to the direction of the oxygen and sulfur atoms of the thioxolane ring.

*o-Thioquinone Methides Derived from 1,2-Benzenedithiols.* *o*-Thioquinone methides (**36**) derived from 1,2-benzenedithiols were prepared with an expectation that they might exist as **38** because of the large contribution of the canonical structure of 18$\pi$ system as in the case of trithiapentalene systems.[18] There was also another anticipation that there might be a large contribution from the ionic canonical structure (**37**) which would favor the equilibrium between the monomer and the dimer, like **3**⇌**4**, for the monomer.

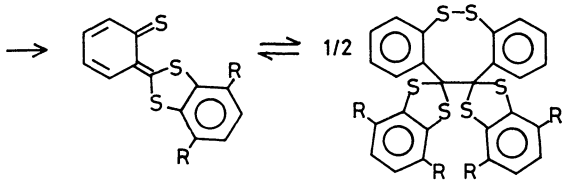


**36** **37** **38**

Reaction of the dithiolium salt (**10**) with 1,2-benzenedithiols gave new spiro compounds **39** and **40**. Desulfurization of **39** and **40** with trimethyl phosphite gave **41** and **42**, respectively, in high yields.




**39** R=H 55%
**40** R=Me 62%

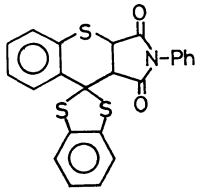



**41** R=H 91%
**42** R=Me 96%

**43** R=H
**44** R=Me

Contrary to the above expectations, the properties of **41** and **42** were found to be very similar to those of **3**, and both **41** and **42** exist as an equilibrium mixture between the monomer and the dimer. The structure of the dimers **43** and **44** was assigned a head-to-head dimer by analogy with the case of **3**.[5]

*o*-Thioquinone methide (**41**) reacted with *N*-phenylmaleimide to give a [4+2] cycloadduct (**45**).




**45**

## Experimental

NMR spectra were recorded with a Hitachi R-20B or R-24B spectrometer, using tetramethylsilane as an internal standard unless otherwise stated. UV and IR spectra were recorded on Hitachi ESP-3 and EPI G-2 spectrometers, respectively. Mass spectra were determined on a Hitachi RMU-6L mass spectrometer (70 eV). High resolution and chemical ionization mass spectra were taken with a JEOL JMS-D300. Molecular weights were measured with a Hitachi 117 Molecular Weight Apparatus (vapor pressure osmometry in benzene at 40 °C). All the melting points were not corrected.

*Preparation of* o-*Thioquinone Methides (6—8).* An ethanol solution (4 ml) of **2**[19] (567 mg, 3.08 mmol) and *N,N'*-dimethyl-1,2-ethanediamine (320 mg, 3.64 mmol) was refluxed for 4 h. Concentration of the reaction mixture followed by addition of benzene and cooling yielded **6a** (621 mg, 99%) as yellow solid, which was recrystallized from benzene–ethanol; mp 153—155 °C; MS: *m/e* 206 ($M^+$, 100%), 173 (39), and 135 (16). Found: C, 63.94; H, 7.14; N, 13.39; S, 15.88%. Calcd for $C_{11}H_{14}N_2S$: C, 64.04; H, 6.84; N, 13.58; S, 15.54%.

Thioquinone methides **6b**, **6c**, **6e**, **6f**, **7**, and **8** were also prepared in a similar way from the corresponding dithiolethiones, the yield being 64, 61, 72, 56, 78, and 85%, respectively. In the case of **6d**, it was necessary to heat at 160 °C for 30 h in a sealed tube (78% yield). These *o*-thioquinone methides were purified by recrystallization from benzene–ethanol. Since **6c**, **6e**, and **6f** could not be obtained as crystals, the resultant oils were purified by washing with benzene–hexane.

**6b**: mp 148—149 °C; MS: *m/e* 234 ($M^+$, 100%), 201 (87), and 135 (55). Found: C, 66.45; H, 8.00; N, 11.84; S, 13.86%. Calcd for $C_{13}H_{18}N_2S$: C, 66.63; H, 7.74; N, 11.95; S, 13.68%. **6d**: NMR (1-chloronaphthalene): $\delta$ (hexamethyldisiloxane) 0.25 (6H, d, $J$=6.6 Hz), 0.90 (6H, d, $J$=6.6 Hz), 2.6—2.85 (2H, m), 2.85—3.10 (2H, m), and 3.60 (2H, sept, $J$=6.6 Hz); MS: *m/e* 262 ($M^+$, 100%), 230 (98), 220 (43), and 188 (43). **7**: mp 230—232 °C; $UV_{max}$ (EtOH) (log $\varepsilon$): 218 (4.82), 262 (4.58), and 314 nm (4.31); MS: *m/e* 256 ($M^+$, 100%), 233 (70), and 200 (12). Found: C, 65.63; H, 6.68; N, 10.17; S, 11.71%. Calcd for $C_{15}H_{16}N_2S \cdot H_2O$: C, 65.66; H, 6.61; N, 10.21; S, 11.68%. **8**: mp 204—206.5 °C; $UV_{max}$ (EtOH) (log $\varepsilon$): 223 (4.78), 245 (sh) (4.44), and 348 nm (4.11); MS: *m/e* 256 ($M^+$, 92%), 233 (100), 200 (12), and 185 (21). Found: C, 70.02; H, 6.32; N, 10.71; S, 12.77%. Calcd for $C_{15}H_{16}N_2S$: C, 70.28; H, 6.29; N, 10.93; S, 12.51%.

*Preparation of* **9**. To a cold (0 °C), stirred mixture of *N,N'*-dimethyl-*o*-phenylenediamine (594 mg, 4.37 mmol), ion exchange resin (Dowex 1-X8 $OH^-$ form, 10 g), anhydrous magnesium sulfate (638 mg) in dichloromethane (30 ml), was added the dithiolium salt (**10**) (792 mg, 3.55 mmol) in small portions for 1 h and the mixture was stirred at room temperature for 11 h. The resins were collected by filtration and washed with ethanol thoroughly. After removal of the ethanol, the residue was triturated with ethyl acetate to afford **9** (620 mg, 69%); mp 221.5—223 °C; MS: *m/e* 254 ($M^+$, 41%) and 239 (100).

*Preparation of* **11**. An acetone solution (7 ml) of **6a** (207 mg, 1.01 mmol) and methyl iodide (1.58 g, 11 mmol) was refluxed for 1.5 h. Evaporation of the solvent gave a crystalline material (329 mg, 94%) whose purity was confirmed by the NMR spectrum. Mp 178.5—180 °C ($C_6H_6$–EtOH); NMR ($CDCl_3$): $\delta$ 2.57 (3H, s), 2.93 (6H, s), 4.13 (2H, m), 4.52 (2H, m), 7.3—7.7 (3H, m), and 8.05—8.22 (1H, m); $UV_{max}$ (EtOH) (log $\varepsilon$): 217 (4.52), 247 (4.21), and 297 (sh) nm (3.29). Found: C, 41.34; H, 5.02; N, 7.95; S, 9.69; I, 36.25%. Calcd for $C_{12}H_{17}N_2SI$: C, 41.39; H, 4.92; N, 8.04; S, 9.21; I, 36.44%.

*Preparation of* **13**. An ethanol solution (10 ml) of 5-phenyl-1,2-dithiole-3-thione (597 mg, 3.01 mmol) and **5a** (293 mg, 3.33 mmol) was refluxed for 4 h. After removal of the solvent, the residue was recrystallized from benzene–ethanol (430 mg, 62%). A specimen for elemental analysis was obtained by recrystallization from methanol; mp 186—187.5 °C; $UV_{max}$ (EtOH) (log $\varepsilon$): 235 (3.98) and 351 nm (4.36); MS: *m/e* 232 ($M^+$, 100%) and 200 (28). Found: C, 67.52; H, 7.10; N, 11.93; S, 14.28%. Calcd for $C_{12}H_{16}N_2S$: C, 67.20; H, 6.94; N, 12.06; S, 13.80%.

*Reaction of* **6a** *with Dimethyl Acetylenedicarboxylate.* An acetonitrile solution (10 ml) of **6a** (207 mg, 1.00 mmol) and dimethyl acetylenedicarboxylate (148 mg, 1.04 mmol) was stood for 10 h at room temperature. After removal of the solvent, the crystalline residue was recrystallized from benzene–hexane to give **15** (264 mg, 76%); mp 148.5—150 °C; NMR ($CDCl_3$); $\delta$ 2.31 (6H, s), 3.1—3.4 (4H, m), 3.89 (3H, s), 3.95 (3H, s), and 7.23 (4H, s); MS: *m/e* 348 ($M^+$, 6%), 290 (100), and 206 (70). Found: C, 58.79; H, 5.91;

N, 8.11; S, 9.57%. Calcd for $C_{17}H_{20}N_2O_4S$: C, 58.60; H, 5.79; N, 8.04; S, 9.20%.

*Reaction of **6a** with Dibenzoylacetylene.* An acetonitrile solution (10 ml) of **6a** (281 mg, 1.37 mmol) and dibenzoylacetylene (358 mg, 1.53 mmol) was stood for 4 days at room temperature. After removal of the solvent, the oily residue was triturated with methanol to give **16** (316 mg, 53%) as yellow crystals. A pure specimen could not be obtained since this was partially decomposed by heating in ethanol. Mp 124—125.5 °C (EtOH); NMR ($CDCl_3$): $\delta$ 2.27 (6H, s), 2.93 (4H, s), and 7.0—8.0 (14H, m); MS: *m/e* 440 ($M^+$, trace), 335 (6%), 234 (37), and 206 (100); IR (KBr): 1730 and 1740 $cm^{-1}$ (C=O).

*Reaction of **6a** with N-Phenylmaleimide.* To a cold (7—8 °C), stirred benzene solution (10 ml) of *N*-phenylmaleimide (154 mg, 0.89 mmol) was added **6a** (175 mg, 0.85 mmol) in portions over a period of 1 h to form red crystals. Stirring was continued at room temperature for 10 h to give **17** (265 mg, 80%). The purification was impossible since it decomposed to an unidentifiable material even when simply washed with ethanol, but the structure was tentatively established by the spectral data. Mp 131—135 °C (dec); NMR (DMSO-$d_6$): $\delta$ 3.02 (6H, s), 3.99 (6H, br s), and 6.6—7.7 (14H, m); MS: *m/e* 348 (2%), 289 (2), 206 (100), 205 (50), and 173 (54); IR (KBr); 1710 $cm^{-1}$ (C=O).

*Preparation of **22** and **23**.* To a cold (0 °C) and stirred dichloromethane solution (20 ml) of pyrocatechol (1.02 g, 9.30 mmol) and triethylamine (5 ml) was added the salt **10** (1.68 g, 7.56 mmol) in small portions during 1 h, and the solution was stirred at room temperature for 4 h. The reaction mixture was washed with water and the dichloromethane layer was evaporated. The oily residue was subjected to dry column chromatography (DCC) (silica gel, $CH_2Cl_2$–$CCl_4$ (1:3)) to give 1.63 g (83%) of **22**; mp 140.5—141.5 °C (ethyl acetate); MS: *m/e* 260 ($M^+$, 66%) and 196 (100). Found: C, 60.11; H, 2.81; S, 24.53%. Calcd for $C_{13}H_8O_2S_2$: C, 59.98; H, 3.10; S, 24.63%.

Compound **23** was prepared similarly in 53% yield using 3,6-dimethyl-1,2-benzenediol.[20] DCC (silica gel, $CH_2Cl_2$–$CCl_4$ (1:9)), PLC (silica gel, ether–hexane (1:3)) and recrystallization from ethanol gave pure **23**; mp 119—120 °C; NMR ($CDCl_3$): $\delta$ 2.24 (6H, s), 6.73 (2H, s), and 7.2—7.6 (4H, m); MS: *m/e* 288 ($M^+$, 93%) and 224 (100). Found: C, 62.35; H, 4.06; S, 22.13%. Calcd for $C_{15}H_{12}O_2S_2$: C, 62.47; H, 4.20; S, 22.23%.

*Preparation of **24** and **25**.* A benzene solution (2 ml) of **22** (342 mg, 1.32 mmol) and trimethyl phosphite (168 mg, 1.35 mmol) was stirred at room temperature for 20 min. The color of the solution turned from yellow to colorless, and white precipitates were formed. Dry ether was added into this solution with stirring and the crystalline material (**24A**) was collected and washed with ether (264 mg, 88%). The filtrate was evaporated, and stood for some time to obtain another crystalline material, **24B** (8.0 mg, 3%). **24A**: mp 111.5—113 °C (benzene–ether); MS (CI): *m/e* 457 (dimer $+H^+$) and 485 (dimer$+C_2H_5^+$) were observed, but fragments higher than the dimer were not observed. Found: C, 68.30; H, 3.26; S, 13.89%. Calcd for $C_{13}H_8O_2S$: C, 68.40; H, 3.53; S, 14.05%. **24B**: mp 212—213 °C (ethyl acetate); MS (CI): *m/e* 456 ($M^+$, 5%), 365 (3), 231 (49), 229 (13), 197 (2), 153 (3), 137 (47), 123 (7), and 111 (100). Found: C, 67.84; H, 3.18; S, 14.20%. Calcd for $C_{13}H_8O_2S$: C, 68.40; H, 3.53; S, 14.05%.

Compounds **25A** and **25B** were prepared similarly in 50% and 28% yields, respectively. **25A**: mp 130—131 °C ($C_6H_6$–$Et_2O$); NMR ($CDCl_3$); $\delta$ 2.30 (s) and 2.07 (bs containing a sharp singlet at $\delta$ 2.14) (6H in total), and 6.3—8.0 (6H, m); MS: *m/e* 512 (trace) and 256 (100%). **25B**: mp 187.5—188 °C (AcOEt); NMR ($CDCl_3$): $\delta$ 2.30 (6H, s), 6.69 (2H, s), 7.14—7.33 (2H, m), and 7.5—7.8 (2H, m); MS: *m/e* 512 (trace) and 256 (100%).

*Reactions of **24** and **25** with N-Phenylmaleimide.* A benzene solution (1.5 ml) of **24A** (116 mg, 0.51 mmol as a monomer) and *N*-phenylmaleimide (97 mg, 0.56 mmol) was refluxed for 1 h under argon. Addition of ethanol to the cooled, stirring solution gave 173 mg (85%) of **26**, which was also prepared (91%) in a similar manner from **24B**, but in this case refluxing for 20 h was necessary. The identity of the adduct **26** from **24A** and **24B** was confirmed by the IR and NMR spectra. Mp 205 °C (dec); MS: *m/e* 401 ($M^+$, 47%), 292 (72), and 228 (100); IR (KBr): 1715 $cm^{-1}$ (C=O); NMR ($C_6D_6$): $\delta$ 3.16 (1H, d, $J$=9.6 Hz), 3.83 (1H, d, $J$=9.6 Hz), 6.4—7.2 (12H, m), and 7.5—7.7 (1H, m).

**27** was prepared from both **25A** (reflux for 1 h, 85%) and **25B** (reflux for 50 h, 79%). The adduct **27** from **25A** and **25B** was also confirmed to be the same by the spectral data (IR and NMR) and the fact that there was no depression of mixed melting point. Mp 208—209.5 °C (AcOEt–EtOH); NMR ($CDCl_3$): $\delta$ 2.18 (3H, s), 2.29 (3H, s), 3.95 (1H, d, $J$=9.6 Hz), 4.59 (1H, d, $J$=9.6 Hz), 6.63 (2H, s), and 6.9—7.9 (9H, m); IR (KBr): 1720 $cm^{-1}$ (C=O); MS: *m/e* 429 ($M^+$, 31%), 292 (23), and 256 (100). Found: C, 70.12; H, 4.32; N, 3.08; S, 7.52%. Calcd for $C_{25}H_{19}NO_4S$: C, 69.91; H, 4.46; N, 3.26; S. 7.46%.

*Reaction of **24A** with Dimethyl Acetylenedicarboxylate.* A benzene solution (3 ml) of **24A** (204 mg, 0.89 mmol as a monomer) and dimethyl acetylenedicarboxylate (141 mg, 1.00 mmol) was refluxed for 5 h under argon. After removal of the solvent, the oily residue was triturated with methanol to give 264 mg (80%) of **28** as white crystals; mp 118—119 °C (EtOH); NMR ($CDCl_3$): $\delta$ 3.53 (3H, s), 3.79 (3H, s), and 6.7—7.8 (8H, m); MS: *m/e* 370 ($M^+$, 45%), 311 (100), and 228 (15); IR (KBr): 1745 $cm^{-1}$ (C=O). Found: C, 61.72; H, 3.70; S, 8.81%. Calcd for $C_{19}H_{14}O_6S$: C, 61.62; H, 3.81; S, 8.66%.

*Preparation of **29**.* The dithiolium salt **10** (213 mg, 0.95 mmol) was added in portions at 0 °C to a stirred dichloromethane solution (5 ml) of *o*-mercaptophenol (140 mg, 1.11 mmol) and triethylamine (0.8 ml). Stirring was continued at room temperature for 3 h, after which the reaction mixture was washed with water. After removal of the solvent, the residue was subjected to PLC (silica gel, $CH_2Cl_2$–$CCl_4$ (1:3)) to give yellow crystals of **29** (159 mg, 61%); mp 134—135 °C (EtOAc); MS: *m/e* 276 ($M^+$, 100%), 244 (17), 212 (56), and 184 (53). Found: C, 56.77; H, 2.62; S, 34.39%. Calcd for $C_{13}H_8OS_3$: C, 56.49; H, 2.92; S, 34.80%.

*Preparation of **31**.* A benzene solution (2 ml) of **29** (563 mg, 2.04 mmol) and trimethyl phosphite (275 mg, 2.21 mmol) was stirred at room temperature for 20 min. The color of the solution turned from yellow to violet, and pale violet precipitates were formed. Ethanol was added to this solution with stirring and the crystalline material was collected (486 mg, 92%). Mp 117 °C (dec) ($C_6H_6$); MS: *m/e* 456 ($M^+$—S, 2%), 276 ($M^+/2$+S, 53), 244 ($M^+/2$, 100), 213 (32), and 184 (45).

*Reaction of **31** with N-Phenylmaleimide.* A mixture of **31** (116 mg, 0.24 mmol) and *N*-phenylmaleimide (88 mg, 0.51 mmol) in benzene (2 ml) was stirred at room temperature for 12 h. After removal of the solvent, the oily residue was triturated with ethanol to give **32** (193 mg, 99%), mp 193 °C (dec) ($C_6H_6$); NMR ($C_6D_6$): $\delta$ 3.58 (2H, s), 6.5—7.3 (12H, m), and 7.7—7.9 (1H, m); IR (KBr): 1720 $cm^{-1}$ (C=O); MS: *m/e* 417 ($M^+$, 12%) and 244 (100). Found: C, 66.52; H, 3.49; N, 3.54; S, 15.02%. Calcd for

$C_{23}H_{15}NO_3S_2$: C, 66.17; H, 3.62; N, 3.55; S, 15.36%.

*Reaction of **31** with Fumaronitrile.* A mixture of **31** (248 mg, 0.51 mmol) and fumaronitrile (89 mg, 1.14 mmol) was refluxed in benzene (2 ml) for 40 min. After removal of the solvent, the NMR (in $CDCl_3$) of the residue was measured for the methine protons of the dihydrobenzothiopyran ring. The two methine protons appeared as two sets of AX type doublet of doublet whose intensity was 5: 1; the major one: $\delta$ 4.13, 4.24, 4.53, and 4.64 and the minor one: $\delta$ 3.88, 4.01, 4.53, and 4.64. In order to remove excess fumaronitrile the crude product was twice washed with ethanol giving **33** (280 mg, 85%). The major isomer was obtained by repeated recrystallization from ethanol; mp 138.5—140 °C (dec); NMR ($CDCl_3$): $\delta$ 4.18 (1H, d, $J$=6.6 Hz), 4.58 (1H, d, $J$=6.6 Hz), and 6.8—8.1 (8H, m); IR (KBr): 2250 $cm^{-1}$ (C≡N); MS: *m/e* 322 ($M^+$, 37%) and 244 (100).

*Reaction of **31** with Dimethyl Acetylenedicarboxylate.* A benzene solution (2 ml) of **31** (123 mg, 0.25 mmol) and dimethyl acetylenedicarboxylate (87 mg, 0.62 mmol) was stirred at room temperature for 13 h and refluxed for 5 min. After removal of the solvent, the residue was subjected to PLC (silica gel, $CH_2Cl_2$–$CCl_4$ (1: 1)) to give **34** (158 mg, 81%), mp 140—141 °C (EtOH); NMR ($CDCl_3$): $\delta$ 3.76 (3H, s), 3.88 (3H, s), and 6.9—7.9 (8H, m); MS: *m/e* 386 ($M^+$, 21%) and 327 ($M^+-CO_2Me$, 100).

*Preparation of **39** and **40**.* To a cold (0 °C) and stirred dichloromethane solution (10 ml) of 1,2-benzenedithiol (332 mg, 2.33 mmol) and triethylamine (1.5 ml) was added the salt **10** (463 mg, 2.07 mmol) in portions over a period of 1 h and stirring was continued at room temperature for 4 h. The reaction mixture was washed with water and the organic layer was evaporated. The oily residue was subjected to PLC (silica gel, $CH_2Cl_2$–$CCl_4$ (1: 3)) to afford 335 mg (55%) of **39**; mp 144.5—146 °C (AcOEt); MS: *m/e* 292 ($M^+$, 98%) and 228 (100). Found: C, 53.80; H, 2.50; S, 43.30%. Calcd for $C_{13}H_8S_4$: C, 53.39; H, 2.76; S, 43.85%.

**40** was prepared similarly in 62% yield using 3,6-dimethyl-1,2-benzenedithiol, which was synthesized by the same method as that of the unsubstituted derivative. Mp 117—117.5 °C (AcOEt); NMR ($CDCl_3$): $\delta$ 2.24 (6H, s), 6.91 (2H, s), 7.2—7.5 (3H, m), and 7.8—8.0 (1H, m); MS: *m/e* 320 ($M^+$, 91%), 288 (46), and 255 (100). Found: C, 56.33; H, 3.64; S, 39.60 %. Calcd for $C_{15}H_{12}S_4$: C, 56.21; H, 3.78; S, 40.01%.

*Preparation of **43** and **44**.* A benzene solution (1.5ml) of **39** (203 mg, 0.69 mmol) and trimethyl phosphite (112 mg, 0.90 mmol) was stirred at room temperature for 1 h. The color of the solution turned rapidly from yellow to blue, and pale blue precipitates were formed. To this solution was added ethanol and the crystalline material **41** (probably mainly **43**) was collected by filtration (165 mg, 92%). Mp 184.5 °C (dec); MS: *m/e* 488 ($M^+-S$, 4%), 456 ($M^+-2S$, 2), 292 ($M^+/2+S$, 99), 260 ($M^+/2$, 20), and 238 ($M^+/2-S$, 100). Because the solubility of **43** was very low in any solvent, it could not be recrystallized, but the structure of **43** was confirmed by its cycloaddition with *N*-phenylmaleimide leading to [4+2] adduct, **45**.

**44** was synthesized similarly in 96% yield; mp 196.5— 197 °C ($C_6H_6$–EtOH); NMR ($CDCl_3$): $\delta$ 2.66 (6H, s) and 6.7—7.4 (4H, m); MS: *m/e* 544 ($M^+-S$, 2%), 320 ($M^+/2+S$, 28), 288 ($M^+/2$, 100), and 273 ($M^+/2-CH_3$, 65). Found: C, 62.51; H, 4.05; S, 32.94%. Calcd for $C_{30}H_{24}S_6$: C, 62.46; H, 4.19; S, 33.34%.

*Reaction of **43** with N-Phenylmaleimide.* A toluene solution (10 ml) of **43** (131 mg, 0.25 mmol) and *N*-phenylmaleimide (88 mg, 0.51 mmol) was refluxed for 1.5 h. After removal of the solvent, the residue was recrystallized from ethanol–benzene to give **45** (177 mg, 82%), mp 178—179 °C; NMR ($CDCl_3$): $\delta$ 4.37 (1H, d, $J$=15 Hz), 4.84 (1H, d, $J$=15 Hz), and 6.8—8.2 (13H, m); IR (KBr): 1720 $cm^{-1}$ (C=O); MS: *m/e* 433 ($M^+$, 15%) and 260 (100). Found: C, 63.79; H, 3.19; N, 3.25; S, 22.20%. Calcd for $C_{23}H_{15}NO_2S_3$: C, 63.72; H, 3.49; N, 3.23; S, 22.18%.

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