Synthesis and Reactions of *o*-Benzothioquinonemethides

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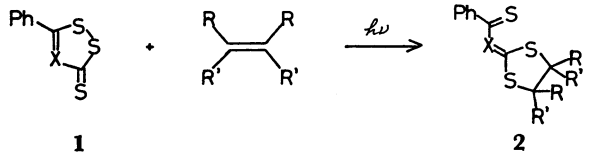
Photoreactions of 1,2-benzodithiole-3-thione with olefins (cyclopentene, cyclohexene, cyclooctene, and 2,3-dimethyl-2-butene) afforded deep blue *o*-thioquinonemethides (**4**) in high yields. The thione **4** is equilibrated with a colorless head-to-head dimer having an eight-membered ring. The mode of the dimerization has been discussed in comparison with other *o*-quinonoid compounds. Cycloaddition reactions of **4** with electron-deficient acetylenes and olefins gave rise to [4+2] adducts. It was confirmed that these cycloadditions proceeded stereoselectively as well as regioselectively. Reactions of **4** with diphenylketene, phenyl isocyanate, and phenyl isothiocyanate led to six-membered 1:1 adducts. Reduction by hydride reagents has been also described.

Chemistry of *o*-quinonoid compounds has extensively been investigated in recent years because of the interesting chemical and physical properties and the synthetic application.[1,2] However, there had been no report concerning *o*-thioquinonemethides, when we started this study, except those which described their existence as a transient species.[3]

Our previous study on the photochemical reactions of 1,2,4-dithiazole-3-thiones or 1,2-dithiole-3-thiones (**1**) with olefins leading to the corresponding 1:1 adducts (**2**)[4] suggested that a similar ring-opening-cycload-



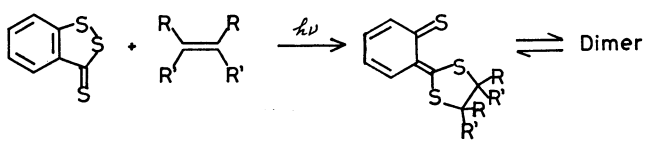
1 **2**

X=N, CH, CPh

dition reaction with 1,2-benzodithiole-3-thione (**3**) would give 6-methylene-2,4-cyclohexadiene-1-thione (referred to *o*-thioquinonemethide hereafter) (**4**) (see below), and indeed this expectation was fulfilled.[5,6] The purpose of this paper is to describe a detailed account of the preparation and some reactions of *o*-thioquinonemethides (**4**) thus formed.

Results and Discussion

Synthesis of o-*Benzothioquinonemethides and Equilibrium with Dimers.* Irradiation of benzo-1,2-dithiole-3-thione (**3**) in the presence of an olefin (cyclopentene, cyclohexene, cyclooctene or 2,3-dimethyl-2-butene) afforded deep blue *o*-thioquinonemethide (**4**). The structure of **4** was established by its cycloaddition leading to [4+2] adduct (see below) and analogy with the photoproducts from **1** and olefins.[4] The color of the



3 **4** **5**

a: RR=$(CH_2)_3$ R′=H 68%
b: RR=$(CH_2)_4$ R′=H 89%
c: RR=$(CH_2)_6$ R′=H 84%
d: R=R′=CH_3 87%

Table 1. Electronic spectra of **4b** in various solvents [a]

Solvent	λ_{max}(nm) (ε)[b]		
cyclohexane	262(5010)	355(700)	580(≈0)
benzene		354(1460)	585(915)
ethanol	264(6100)	350(1940)	580(1180)
dichloromethane	269(10900)	351(4050)	584(2610)

a) Concentration: 1.23×10^{-4} mol/l (as a monomer).
b) Apparent molar extinction coefficient.

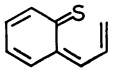
Table 2. Electronic spectra of **4** in dichloromethane[a]

4	λ_{max} (nm)(ε)		
4a	267(7480)	350(2200)	585(1390)
4b	269(10900)	351(4050)	584(2610)
4c	269(10000)	350(3720)	584(2380)
4d	—[b]	351(10500)	585(6660)

a) Concentration: $1.23—1.27\times10^{-4}$ mol/l (as a monomer).
b) Could not be determined at this concentration. In 0.492×10^{-4} mol/l, λ_{max} 269 nm (ε 23500).

solution of **4** depends on solvent, temperature, and irradiation with light (Tables 1 and 2). For example, the color of **4b** is deep blue in dichloromethane or tetrahydrofuran (THF) at room temperature, but in cyclohexane it is almost colorless. Recrystallization of **4b** from carbon tetrachloride at −23 °C affords white crystals, the dissolution of which in an appropriate solvent, however, leads to a deep blue solution. The colorless cyclohexane solution of **4b** turns blue on heating or irradiation, but the blue color is discharged when the solution is left at room temperature. These facts and the dependence of the UV spectrum of **4b** on the concentration suggest that **4** is equilibrated with a colorless aggregate. It was found that the aggregate was a dimer on the basis of cryoscopic measurement of the molecular weight for the adduct with cyclohexene (**5b**) in cyclohexane (Found 542, Calcd 532). Other *o*-thioquinonemethides **4a**, **4c**, and **4d** behave similarly, although the blue color of the solution of **4d** is the strongest in any solvent as expected by the highest apparent molar extinction coefficient among **4a**—**4d** (Table 2). It is obvious that the 580 nm band responsible for the blue color is due to the monomer. Although the value of 580 nm is in the range of n-π^* band of conjugate thiones,[4,7] the absorption of **4** is considered to be of π-π^* nature, because the extinction coefficient is too high

for n-π^* bands. In this connection, it is interesting that the visible absorption of **4** bears a close resemblance to that of 6-allylidene-2,4-cyclohexadiene-1-thione (**6**) generated from a photoreaction of 2*H*-thiochromene at 77 K in a rigid matrix (a broad band with its center around 570 nm), though no molar extinction coefficient was given for the latter.[3b]



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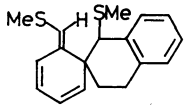
Since the intensity change of the 270 and 350 nm bands parallels that of the 580 nm band, the former two are also due to the monomer.

When **4b** was heated in refluxing xylene for 45 min under argon, **3** was formed in a quantitative yield.

Structure of the Dimer. Since the NMR spectrum of the cyclohexene adduct (**5b**) in carbon tetrachloride at −20 °C, where it is almost colorless and hence essentially dimeric, shows eight proton signals between δ 7.3—9.0 ascribed to aromatic or olefinic protons, the dimerization should occur using the thiocarbonyl and/or ketene thioacetal units. The absence of the 580 nm band in the spectrum of **5b** in cyclohexane suggests that it represents that of the dimer, which shows no strong absorption above 300 nm. These facts imply that [4+2] and [2+2] type adducts can be eliminated among many possible structures of the dimer, because they must have a conjugated ketene thioacetal(s) which should have a strong band above 350 nm [*e.g.*, for **7**, λ_{max} 345 nm (ε 6760)][8] or a conjugated thione(s) which should have an absorption in the visible region.[4,7] The dimer, therefore, must be **8** or **9** of [4+4] type.



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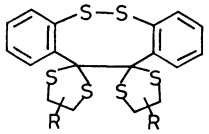

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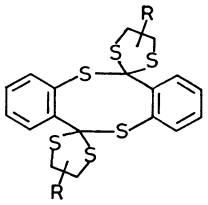

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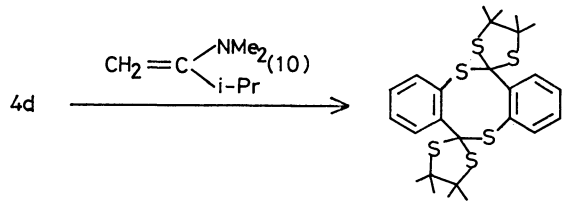
Since it is reasonably assumed that **4a—4d** have almost identical molar extinction coefficients each other, irrespective of the substituents of the 1,3-dithiolane ring, the data in Table 2 show that the proportion of the monomer increases with increasing bulkiness of the added olefins, that is, the dissociation into the monomer increases with bulkiness of the thioacetal moiety of the dimer **5**. This fact is more compatible with a head-to-head dimer (**8**) than a head-to-tail dimer (**9**) in view of the higher steric repulsion between the two dithiolane rings in the former.

Desulfurization of **4b** with Raney nickel leading to bibenzyl (5%) along with toluene (41%) is another piece of evidence for the head-to-head structure, although the possibility can not be excluded that the former may be formed from the monomer.[9]

More confirmative evidence comes from isolation of another [4+4]dimer of **4d**.[5b] When **4d** was allowed to react with enamine (**10**) at 60 °C in THF–acetonitrile, a colorless crystalline compound (**11**) with a molecular formula of $(C_{13}H_{16}S_3)_2$ (from elemental analysis and molecular weight determination) was obtained in 38% yield.

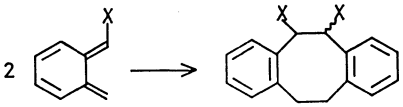


11

The NMR spectrum of the dimer (**5d**) obtained from the photochemical reaction showed four singlets due to the methyl groups (δ 1.22, 1.33, 1.57, and 1.76), while the new dimer (**11**) from above reaction had a singlet (δ 1.52) in the methyl region along with aromatic multiplet (δ 7.0—8.3). The difference can be readily accounted for if we consider that the 11*H*,12*H*-dibenzodithiocin ring of **5d** is less symmetric than that of **11** because of the steric interaction between the two dithiolane rings. Thus, we conclude that the photodimer (**5d**) and the new dimer (**11**) are a head-to-head and a head-to-tail [4+4] type dimers, respectively, although X-ray analysis will be necessary for the final answer.

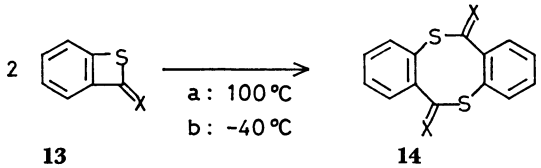
Dimer (**11**) is thermally stable and does not show thermal equilibrium with the monomer, although it dissociates into an equilibrium mixture of **4d** and **5d** as evidenced by UV and NMR spectra.

It should be noted here that the mode of dimerization of **4** under normal conditions (*i.e*, the formation of a head-to-head dimer) parallels that of *o*-quinodimethanes (**12a-c**)[8,10,11] rather than that of benzothietes (**13a, b**) leading to **14a,b**,[12,13] which might proceed *via* *o*-thioquinonemethide.



12

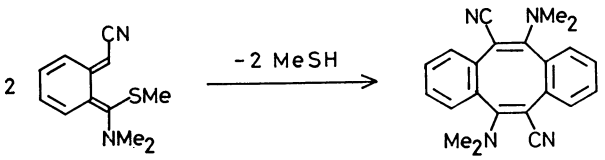
a: X=CONHR[10]
b: X=SMe[8]
c: X=P(O)(OMe)$_2$[11]



13 **14**

a: X=H_2
b: X=O

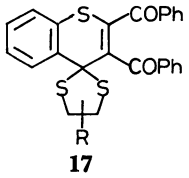
It has been reported that quinodimethane (**15**) is stable at −40 °C in *N*,*N*-dimethylformamide but undergoes dimerization, followed by elimination of methanethiol, to give **16**.[14]



15 16

The reason for these different chemical behaviors is not clear, but one possible explanation is involvement of homolytic processes in the dimerization of **4** and **12**.

Reactions of o-*Thioquinonemethides.* *a) Reactions with Acetylenes or Olefins*: The *o*-thioquinonemethide (**4**) is a strong enophile and rapidly reacts with acetylenes and olefins having electron-withdrawing groups at room temperature to afford 1,4-cycloaddition adducts. The reaction of **4b** with dibenzoylacetylene and *N*-phenylmaleimide gave **17** (83%) and **18** (93%) respectively. The regioselectivity and stereoselectivity of the cycloaddition were examined with mono- and di-substituted olefins, respectively. Reaction of **4b** with methyl vinyl ketone in refluxing benzene for 5 min afforded only one kind of 1: 1 adduct (**19**) in a quantitative yield. Raney nickel desulfurization of the product gave 3-methyl-4-phenyl-2-butanone (**20**, 64%) and 3-methyl-4-phenyl-2-butanol (**21**, 12%), thus establishing the regioselectivity of the reaction. Acrylamide reacted with **4b** to give 1: 1 adduct (**22**, 64%), the similarity of whose NMR spectrum to that of **19** suggested the same regioselectivity also in this case.



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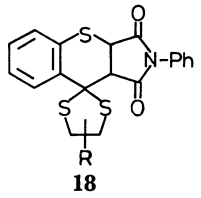

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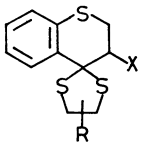
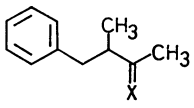
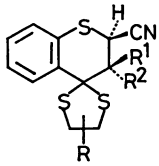


19: X=$COCH_3$
22: X=$CONH_2$



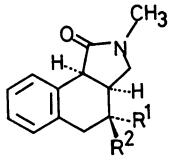
20: X=O
21: X=H, OH

When maleonitrile and fumaronitrile were allowed to react with **4b** in dichloromethane at room temperature for 1 or 2 days, *cis*- (**23a**) and *trans*-adducts (**23b**) were obtained in 66 and 88% yields, respectively. The NMR spectra of the crude reaction products from both dicyanoolefins showed the presence of two methine protons α to a cyano group which appeared as two sets of double doublets of AX type. The intensity ratio of the two double doublets was about 4: 1 (J_{AX}=3.4 Hz for the both doublets) for **23a** and about 5: 1 (J_{AX}= 9.1 Hz for the both doublets) for **23b**. In light of the reported values[10] of 4.5 (J_{HR^1}) and 10 Hz (J_{H,R^1}) for similar compounds **24** and **25** respectively, the coupling constants observed for **23a** and **23b** indicate they are *cis*- and *trans*-adducts respectively, the stereoselectivity of the cycloaddition thus being established.



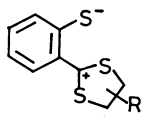
23

a: R^1=CN, R^2=H
b: R^1=H, R^2=CN



24: R^1=H, R^2=Cl
25: R^1=Cl, R^2=H

The stereoselectivity for cycloaddition of **4** with olefins is noteworthy, because it means the cycloaddition of **4** proceeds probably in a concerted manner, although possible contribution of ionic canonical structure (**26**) might lead to a stepwise ionic reaction resulting in non-stereoselective addition.



26

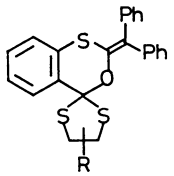
The two sets of the spectra for **23a** and **23b** are considered to correspond to two isomers with respect to the direction of the cyclohexane ring. We previously isolated such a sort of isomers in cycloadditions of similar conjugated systems.[15] Recrystallization of **23a** and **23b** gave pure specimens of the corresponding major isomers.

We previously reported that **4** also reacted with electron-rich olefins (*i.e.*, enamines) to give [4+2]adducts.[16]

b) Reactions with Heterocumulenes: Reaction with diphenylketene proceeds very rapidly at room temperature to afford a mixture of **27** and **28** in 73% yield. The primary product (**27**) is unstable and easily isomerizes to **28** or decomposes to **4b** when heated or left on silica gel for a long time. The thioester (**28**) is stable and purified by usual work-up.

4b reacts with phenyl isocyanate at room temperature for 6 days to afford **29** in 88% yield.

Major reaction product with phenyl isothiocyanate in benzene at 80 °C for 21 h was **31** (73%). Although **31** is stable in the presence of the excess isothiocyanate,



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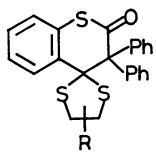

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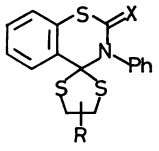
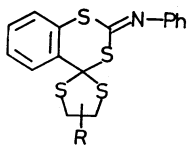


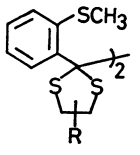
29: X=O
30: X=S



31

it decomposes mainly to **4b** and phenyl isothiocyanate when the isothiocyanate is removed. A compound tentatively assigned as **30** was also isolated in the decomposition product.

c) Reduction and Other Reactions: Reduction with hydride reducing reagents (lithium aluminum hydride and sodium bis(2-methoxyethoxy)dihydridaluminate) followed by methylation were carried out in order to get **32** which would be formed from the dimer (**5b**). The product, however, was not an expected one but **33** (64%) when quenched with aqueous alkali and methyl iodide or **34** (24%) when quenched with dilute sulfuric acid. The formation of these products can be explained in terms of the preferential attack of the hydride on **4b** because of much higher reactivity of **4b** than that of **5b** and/or of facile decomposition of intermediate **35**, even if it is formed from the dimer **5b**.



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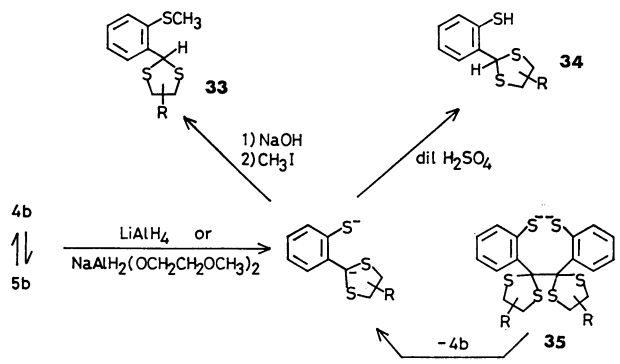
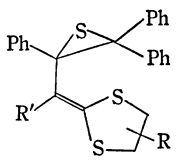


Thiophenol (**34**) was unstable and was gradually oxidized by atmospheric oxygen to afford **4b**.

4b did not react with diphenyldiazomethane or phenyldiazomethane, which readily reacts with thiones to afford episulfides.[17] This is in marked contrast with the reactivity of similar conjugate thiones **2** (X=CH, CPh) which react with diphenyldiazomethane to give **36**.[15]



36: R'=H, Ph

Inertness of **4b** toward these diazomethanes is indicative of a greater contribution of the ionic resonance structure of type **26** for **4** as expected from its aromatic stabilization.

Experimental

NMR spectra were recorded with a Hitachi R-20B or R-24 spectrometer using tetramethylsilane as an internal standard. UV and visible absorption spectra were recorded on a Hitachi ESP-3 spectrophotometer. IR spectra were taken with a Hitachi EPI-G2 spectrometer (beam energy 70 eV). 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.

Synthesis of o-Thioquinonemethides (4). A solution of 1,2-benzodithiole-3-thione (**3**)[18] (460 mg, 2.5 mmol) and cyclohexene (7 ml) in ether (70 ml) was irradiated under nitrogen for 45 min with 100 W medium pressure mercury lamp through Pyrex filter. After 35 or 40 min the color of the solution turned deep blue. The reaction mixture was subjected to dry column chromatography (DCC) (SiO_2, 2: 1 benzene–hexane) to give **4b** (614 mg, 89%). Essentially the same result was obtained when benzene was used as solvent. Recrystallization from carbon tetrachloride at −23 °C afforded white crystals, whose color gradually changed pale blue upon standing under diffused light. Mp 166—167 °C (dec); NMR (CCl_4): δ 1.0—2.5 (br s, 8H), 3.3—4.4 (m, 2H), and 6.8—7.8 (m, 4H); UV (cyclohexane at 7 °C): λ_{max} 260 nm (ε 1.04×10^4). For the spectra in other solvents, see Table 2. Found: C, 58.99; H, 5.20; S, 35.59%. Calcd for $C_{13}H_{14}S_3$: C, 58.60; H, 5.30; S, 36.10%. There formed slightly green crystals when the reaction solution in ether was stood overnight at −5—0 °C. The crystals thus formed, after filtration and washing with ether, were pure enough for further use without purification. The yield of the crystals was about 60%.

Photoreactions of **3** with cyclopentene, cyclooctene, and tetramethylethylene were carried out in a similar way, the yield, after DCC, being 68, 84, and 87%, respectively. In the case of the last olefin, the color of the reaction solution turned deep blue after 10 minutes' irradiation. These o-thioquinonemethides were purified by recrystallization from dichloromethane and methanol. **4a**: mp 159—161 °C (dec); NMR ($CDCl_3$): δ 1.7—2.3 (br s, 6H), 3.8—4.4 (m, 2H), and 6.8—7.9 (m, 4H). Found: C, 57.65; H, 4.90; S, 37.35%. Calcd for $C_{12}H_{12}S_3$: C, 57.10; H, 4.79; S, 38.10%. **4c**: mp 153—154 °C (dec); NMR ($CDCl_3$): δ 1.1—2.4 (m, 12H), 3.3—3.9 (m, 1H) 4.0—4.4 (m, 1H), 6.9—7.1 (m, 2H), and 7.25—7.90 (m, 2H). Found: C, 61.46; H, 6.30; S, 32.22%. Calcd for $C_{15}H_{18}S_3$: C, 61.18; H, 6.16; S, 32.66%. **4d**: mp 137—140 °C (dec); NMR ($CDCl_3$): δ 1.22, 1.33, 1.57, and 1.76 (s, 3H each), 6.8—7.4 (m, 3H), and 7.8—8.0 (m, 1H). Found: C, 58.38; H, 6.33; S, 35.06%. Calcd for $C_{13}H_{16}S_3$: C, 58.16; H, 6.01; S, 35.83%.

Desufurization of 4b. Tetrahydrofuran (THF) solution (8 ml) of **4b** (576 mg, 2.16 mmol) and 5 g of Raney nickel (W-4) were stirred for 6 h at room temperature and then refluxed for 4 h. The reaction solution was analyzed by high speed liquid chromatography (Hitachi 634; column: Hitachi 3010; solvent: 10: 1 methanol–28%NH_4OH (v/v)) for toluene (41%) and bibenzyl (4.6%).

Reaction of 4d with 2-Dimethylamino-3-methyl-1-butene. To **4d** (523 mg, 1.95 mmol) in a mixture (13 ml) of THF and acetonitrile (1: 3) was added 2-dimethylamino-3-methyl-1-butene (**10**; 410 mg, 3.6 mmol) and the solution was heated at reflux temperature for 6.5 h. DCC (SiO_2, 1: 1 hexane–

dichloromethane) afforded **11** (200 mg, 0.745 mmol, 38%) as white crystals. Mp 190—191 °C (from hexane); NMR ($CDCl_3$): δ 1.52 (s, 24H), 7.1—7.6 (m, 6H), and 7.9—8.1 (m, 2H). UV (EtOH): λ_{max} (log ε) 250 (sh) nm (4.22); mol wt: Found 568. Calcd for $(C_{13}H_{16}S_3)_2$ 537. Found: C, 58.02; H, 6.26; S, 35.75%. Calcd for $C_{26}H_{32}S_6$: C, 58.16; H, 6.01; S, 35.83%.

*Reaction of **4b** with N-Phenylmaleimide.* A benzene solution (4 ml) of **4b** (55 mg, 0.21 mmol) and *N*-phenylmaleimide (38 mg, 0.22 mmol) was stood overnight at room temperature. After evaporation of the solvent, the residue was purified by preparative layer chromatography (PLC) (SiO_2, benzene) to give white crystals **18** (82 mg, 93%). Mp 217—218 °C (ethanol); NMR ($CDCl_3$) δ 1.0—2.2 (m, 8H), 3.6—4.0 (m, 1H), 4.0—4.3 (m, 1H), 4.45 (s, 2H), 6.8—7.4 (m, 8H), and 8.1—8.4 (m, 1H). IR (KBr): 1710 cm^{-1} (C=O); MS: *m/e* 439 (M^+, 5%), 326 (45), and 184 (100). Found: C, 62.98; H, 4.80; N, 3.08; S, 21.67%. Calcd for $C_{23}H_{21}NO_2S_3$: C, 62.84; H, 4.82; N, 3.19; S, 21.88%.

*Reaction of **4b** with Dibenzoylacetylene.* A solution of dibenzoylacetylene (51 mg, 0.22 mmol) and **4b** (53 mg, 0.20 mmol) in benzene (4 ml) was stood overnight at room temperature. Purification by PLC (SiO_2, benzene) and recrystallization from benzene-ethanol gave **17** (83 mg, 83%) as pale yellow crystals: mp 181—183 °C; NMR ($CDCl_3$): δ 0.9—2.3 (m, 8H), 3.7—4.1 (m, 2H), and 7.0—8.2 (m, 14H); IR (KBr): 1650 and 1665 cm^{-1} (C=O); MS: *m/e* 500 (M^+, 4%), 370 (100), and 105 (80). Found: C, 69.59; H, 4.95; S, 19.13%. Calcd for $C_{29}H_{24}O_2S_3$: C, 69.57; H, 4.83; S, 19.21%.

*Reaction of **4b** with Methyl Vinyl Ketone.* A benzene solution (100 ml) of the ketone (0.82 ml, 10 mmol) and **4b** (1.01 g, 3.8 mmol) was refluxed for 5 min. The solvent was evaporated and the residue was recrystallized from benzene to afford **19** (835 mg). The filtrate was subjected to PLC (SiO_2, 1:1 dichloromethane-hexane) to afford **19** (438 mg). The total yield was 1.273 g (100%). Mp 155—156 °C (from benzene); NMR ($CDCl_3$): δ 1.0—2.5 (m, 8H), 2.25 (s, 3H), 2.8—4.4 (m, 5H), 6.8—7.4 (m, 3H), 8.1—8.4 (m, 1H); IR (KBr): 1715 cm^{-1} (C=O); MS: *m/e* 336 (M^+, 2%), 184 (81), and 43 (100). Found: C, 60.79; H, 6.07; S, 28.49%. Calcd for $C_{17}H_{20}OS_3$: C, 60.67; H, 6.00; S, 28.58%.

*Raney Nickel Desulfurization of **19**.* To a solution of **19** (803 mg, 2.4 mmol) in benzene (50 ml) was added Raney nickel (W-4) prepared from Raney alloy (7 g) and the mixture was refluxed for 2.5 h with stirring. Raney nickel was removed by filtration and the filtrate was evaporated under reduced pressure. The residue was subjected to DCC (SiO_2, 1:1 dichloromethane-hexane) to afford oily compounds **20** (246 mg, 63.5%) and **21** (45 mg, 11.5%). **20**: NMR (CCl_4): δ 1.04 (d, J=6 Hz, 3H), 1.95 (s, 3H), 2.1—3.0 (m, 3H), and 7.0—7.3 (m, 5H); MS: *m/e* 162 (M^+, 5.9%) and 43 (100); IR (neat): 1710 cm^{-1} (C=O). **21**: NMR (CCl_4): δ 0.79, 0.83 (a pair of doublet due to diastereomers, J=7 Hz, 3H), 1.15 (d, J=5 Hz, 3H), 1.64 (br s, 1H, disappeared by D_2O), 2.0—3.1 (m, 3H), 3.4—3.9 (m, 1H), and 7.1 (br s, 5H); MS: *m/e* 164 (M^+, 2.3%) and 91 (100); IR (neat): 3100—3600 cm^{-1} (OH).

*Reaction of **4b** with Acrylamide.* A dichloromethane solution (50 ml) of acrylamide (1.163 g, 16.4 mmol), **4b** (248 mg, 0.94 mmol), and a small amount of hydroquinone was allowed to stand at room temperature for a week. The solution was washed with water, dried (Na_2SO_4), and the solvent was evaporated. The residue was washed with a small amount of dichloromethane to give white crystals **22** (198 mg, 63.8%). Mp 242.5—243.0 °C (dec) (from ethanol); NMR (DMSO-d_6): δ 1.0—2.3 (m, 8H), 2.9—4.2 (m, 7H), 6.7—7.6 (m, 3H), and 8.0—8.4 (m, 1H); MS: *m/e* 337 (M^+, 11%), 184 (84), and 179 (100); IR (KBr): 3480, 3370 (NH), 1695 cm^{-1} (C=O). Found: C, 56.95; H, 6.09; N, 4.10; S, 28.11%. Calcd for $C_{16}H_{19}NOS_3$: C, 56.94; H, 5.67; N, 4.15; S, 28.50%.

*Reactions of **4b** with Fumaronitrile and Maleonitrile.* Fumaronitrile (238 mg, 3.05 mmol) and **4b** (396 mg, 1.48 mmol) dissolved in dichloromethane (30 ml) were stood for 2 days at room temperature. After removal of the solvent, the NMR (in $CDCl_3$) of the residue was taken for methine protons of the dihydrobenzothiopyran ring. The two methine protons appeared as two sets of AX type double doublet whose intensity ratio was 5:1; the major one: δ 3.69, 3.84, 4.67, and 4.82; the minor one: δ 3.80, 3.54, 4.52, and 4.67. No signal due to *cis*-isomer **23a** was observed. In order to remove excess fumaronitrile the crude reaction mixture was twice washed with ethanol giving **23b** (453 mg, 88%). Since some isomerization was observed during purification by TLC (SiO_2), **23b** thus obtained was purified by repeated recrystallization from ethyl acetate to give a pure specimen of the major isomer; mp 154—157 °C; NMR ($CDCl_3$): δ 1.78 (m, 8H), 4.27 (m, 2H), 3.76 (d, J=9.1 Hz, 1H), 4.74 (d, J=9.1 Hz, 1H), 7.25 (m, 3H), and 8.25 (m, 1H); IR (KBr): 2240 cm^{-1} (CN); MS: *m/e* 344 (M^+, 17%) and 184 (100). Found: C, 59.43; H, 4.57; N, 8.26; S, 27.87%. Calcd for $C_{17}H_{16}N_2S_3$: C, 59.27; H, 4.68; N, 8.13; S, 27.92%.

Dichloromethane solution (20 ml) of maleonitrile (154 mg, 1.97 mmol) and **4b** (263 mg, 0.99 mmol) was stood for 1 day at room temperature. The crude reaction mixture was checked for the methine protons by NMR as above. There were found two sets of double doublets, the chemical shifts being δ 4.06, 4.12, 5.07, and 5.13 for the major one, and 4.12, 4.19, 4.92, and 4.99 for the minor one with no signal of **23b**. The reaction mixture was washed with ethanol to afford **23a** (276 mg, 66%), which was recrystallized from ethyl acetate to give the major isomer contaminated with a small amount of the minor isomer (by NMR); mp 168—170 °C; NMR ($CDCl_3$): δ 1.84 (m, 8H), 3.98 (m, 2H), 4.04 (d, J=3.4 Hz, 1H), 5.08 (d, J=3.4 Hz, 1H), 7.15 (m, 3H), and 8.17 (m, 1H); IR (KBr): 2240 cm^{-1} (CN); MS: *m/e* 344 (M^+, 17%) and 184 (100). Found: C, 59.54; H, 4.76; N, 8.20; S, 27.68%. Calcd for $C_{17}H_{16}N_2S_3$: C, 59.27; H, 4.68; N, 8.13; S, 27.92%.

*Reaction of **4b** with Diphenylketene.* Diphenylketene (260 mg, 1.34 mmol) in benzene (10 ml) was added slowly to a solution of **4b** (261 mg, 0.98 mmol) in benzene (20 ml).

The color of the solution turned very rapidly from deep blue to yellow, but slowly reverted to blue. After all the solution was added the color did not revert to blue. The solution was kept at 40 °C for 30 min. After removal of the solvent, the residue was subjected to DCC (SiO_2, 1:3 chloroform-carbon tetrachloride) at about 0 °C to give two fractions, one (201.8 mg) containing **27** and **28** and the other (126.8 mg) containing **28**. PLC (SiO_2, 1:1 hexane-ether) was twice carried out at about 0 °C to obtain **27**, but it was unstable because of isomerization to **28** or decomposition to **4b** when heated in solution or left on silica gel for a long time. The total yield of **27** and **28** was 73%. **28** was stable and purified by recrystallization from ethanol. **28**: mp 222.0—223.5 °C (from ethanol); NMR ($CDCl_3$): δ 1.0—2.5 (m, 8H), 2.5—3.0 (m, 1H), 3.2—4.6 (m, 1H), 6.7—7.6 (m, 13H), and 8.3—8.7 (m, 1H); MS: *m/e* 460 (M^+, 3%) and 184 (100); IR (KBr): 1670 cm^{-1} (C=O). Found: C, 69.92; H, 5.20; S, 20.56%. Calcd for $C_{27}H_{24}OS_3$: C, 70.40; H, 5.25; S, 20.88%. **27**: NMR ($CDCl_3$): δ 1.0—2.3 (m, 8H), 3.3—3.7 (m, 2H), 6.7—7.5 (m, 13H), and 7.6—8.1 (m, 1H); IR (KBr): 1587 1580 cm^{-1} (C=C).

*Reaction of **4b** with Phenyl Isocyanate.* A benzene solution (50 ml) of **4b** (536 mg, 2.0 mmol) and phenyl isocyanate

(242 mg, 2.0 mmol) was allowed to stand for 6 days at room temperature. The solvent was evaporated under reduced pressure and the residue was subjected to DCC (SiO_2, chloroform) to give **29** (677 mg, 88%). Mp 164.5—166.0 °C (from benzene); NMR ($CDCl_3$): δ 1.0—2.3 (m, 8H), 3.5—3.9 (m, 2H), 7.1—7.6 (m, 8H), and 8.1—8.4 (m, 1H); IR (KBr): 1650 cm^{-1} (C=O); MS: *m/e* 385 (M^+, 0.4%) and 119 (100). Found: C, 62.20; H, 4.86; N, 3.53; S, 24.70%. Calcd for $C_{20}H_{19}NOS_3$: C, 62.30; H, 4.97; N, 3.63; S, 24.95%.

*Reaction of **4b** with Phenyl Isothiocyanate.* A solution of **4b** (246 mg, 0.92 mmol) and phenyl isothiocyanate (249 mg, 1.84 mmol) in benzene (25 ml) was refluxed for 21 h under argon atmosphere. The solvent was evaporated and the residue was subjected to PLC (SiO_2, benzene) to give crude **31** (269 mg, 73%). Although **31** was stable in solution in the presence of excess phenyl isothiocyanate, it was unstable, if the isothiocyanate was removed, and slowly decomposed to **4b** and phenyl isothiocyanate, thus precluding the isolation of an analytically pure specimen. Among the decomposition product there was formed a small amount of product (15 mg, 4%) tentatively assigned as **30**. **31**: mp 46—52 °C (white crystals from hexane); NMR (CCl_4): δ 1.0—2.4 (m, 8H), 3.6—4.1 (m, 2H), 6.7—7.5 (m, 8H), and 7.9—8.3 (m, 1H); UV (cyclohexane): λ_{max} (ε) 318 (7330), 275 (11400), and 244 (sh) nm (17200); IR (KBr): 1565 cm^{-1} (CN). **30**: NMR (CCl_4): δ 1.0—2.0 (m, 8H), 3.6—3.9 (m, 2H), 7.1—7.5 (m, 8H), and 7.9—8.3 (m, 1H); IR (KBr): no band due to C=N.

*Reduction of **4b** with Lithium Aluminum Hydride.* Lithium aluminum hydride (120 mg, 3.2 mmol) was added to a THF solution (50 ml) of **4b** (269 mg, 1.0 mmol) with stirring under nitrogen atmosphere, and the mixture was refluxed for 5 h. Though a small amount of **4b** still remained, 10% aq sodium hydroxide and methyl iodide (0.5 ml) were added successively with stirring. The solvent was evaporated under reduced pressure, and ether was added. The ethereal solution was washed with water, dried and the ether was evaporated. The residue was subjected to DCC (SiO_2, 1: 1 hexane–ether) to give **33** (184 mg, 64.4%) and a trace amount of 2-methylthiobenzyl alcohol (by NMR). When the reaction mixture was treated with dil sulfuric acid instead of aq sodium hydroxide and methyl iodide, the product was **34** (24%), which was unstable and was rapidly oxidized by air to afford **4b**. **33**: mp 107.0—109.0 °C (from ethanol); NMR ($CDCl_3$): δ 1.0—2.5 (m, 8H), 2.49 (s, 3H), 3.7—4.1 (m, 2H), 6.38 (s, 1H), 7.1—7.4 (m, 3H), and 7.8—8.2 (m, 1H); MS: *m/e* 282 (M^+, 19%) and 153 (100). Found: C, 59.60; H, 6.17; S, 33.89%. Calcd for $C_{14}H_{18}S_3$: C, 59.53; H, 6.42; S, 34.05%. **34**: NMR ($CDCl_3$): δ 1.0—2.5 (m, 8H), 3.55 (s, 1H), 3.6—4.0 (m, 2H), 6.14 (s, 1H), 7.0—7.5 (m, 3H), and 7.7—8.2 (m, 1H).

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