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Synthesis and Reactions of *o*-Naphthothioquinone Methides

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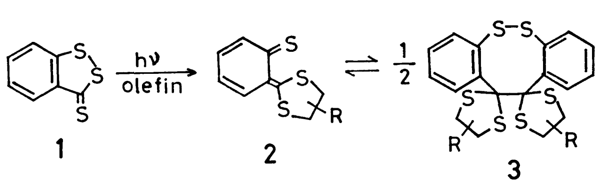
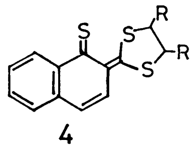
Photochemical reactions of naphtho[1,2-*c*][1,2]dithiole-3-thione (**7**), naphtho[2,1-*c*][1,2]dithiole-1-thione (**10**), and naphtho[2,3-*c*][1,2]dithiole-3-thione (**16**) with cyclohexene and 2,3-dimethyl-2-butene afford the corresponding naphthothioquinone methides. The thioquinone methide from **7** exists only as a monomeric form and is the first isolable *o*-thioquinone methide, while that from **16** exists as a dimer of [4+4] type in the solid state although the chemical behavior suggests the presence of a monomeric form in solution to a very minor extent. In the case of the thioquinone methide from **10**, there exists an equilibrium between a monomer and a dimer of [4+2] type. Some cycloadditions of these thioquinone methides are also described.

In a previous report,[1] we described the photochemical formation of *o*-benzothioquinone methides (**2**) from benzo-1,2-dithiole-3-thione (**1**) and olefins and their some reactions. The deep blue thioquinone methide **2** is equilibrated with colorless dimer **3**, thus representing a unique thermochromic system.



The pure monomeric *o*-thioquinone methide **2**, however, could not be obtained although its existence in solution was established by spectroscopic data and chemical reactions.

The study described in this paper was initiated in the hope that (i) three isomers (*i.e.* **4**, **5**, and **6**), are possible for the naphtho analog of **2** and comparison of them would shed light on the detailed properties of the *o*-thioquinone methide, (ii) **4** and **5** are reasonably expected to be more stable than **2** and hence they might be isolated as monomer.[2]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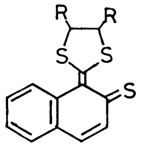
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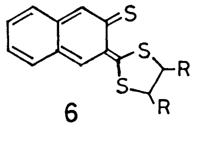
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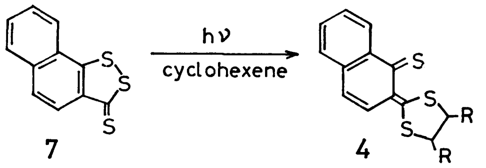
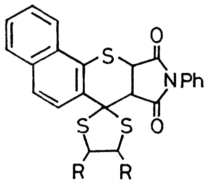
Results and Discussion

*Photoreaction of Naphtho[1,2-*c*][1,2]dithiole-3-thione (**7**) with Cyclohexene.* Irradiation of **7** in the presence of cyclohexene afforded thioquinone methide **4** (RR=$(CH_2)_4$ hereafter in this paper unless otherwise noted) as deep purple cyrstals in a quantitative yield. The monomeric nature of **4** was established by molecular weight determination (Found 319; Calcd 316.5) and by electronic spectrum (λ_{max} 323 (ε 24300), 353 (10800), 392 (sh, 2540), and 540 nm (11800)), which showed no concentration dependence. This is the first example of isolation of stable *o*-thioquinone methide. Reaction of **4** with *N*-phenylmaleimide gave 1:1-adduct **8** in 83% yield.

Photoreaction of **7** with 2,3-dimethyl-2-butene also

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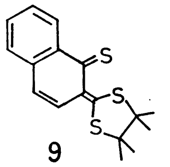
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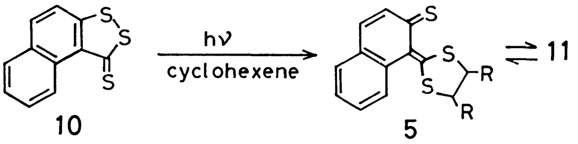
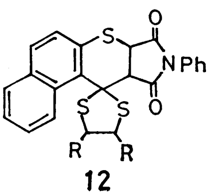
gave deep violet thioquinone methide **9** in a quantitative yield. Here also, there was no evidence which indicated the presence of a dimeric form; the NMR spectrum showed only two resonances due to the methyl group with the intensity ratio of 1:1.[3]

*Photoreaction of Naphtho[2,1-*c*][1,2]dithiole-1-thione (**10**) with Cyclohexene.* Irradiation of **10** with cyclohexene led to a deep red solution, the thin layer chromatography (TLC) of which showed the presence of a single product together with a small amount of the starting **10**. The addition of *N*-phenylmaleimide to the reaction mixture affords 1:1-adduct **12** (54%), the structure of the red compound thus being established as **5**. Purification of the reaction mixture by

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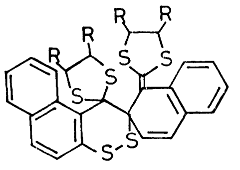
dry column chromatography (DCC) to remove **10**, however, resulted in the formation of a yellow crystalline compound **11** besides the red compound **5** (total yield 95%).

A sample rich in the yellow compound **11** could also be obtained by heating the solution of the red compound **5** at about 60 °C and subsequent cooling. Therefore, attempts to obtain pure **5** by TLC or recrystallization always formed the yellow compound, thus precluding us to get a completely pure specimen of **5**. However, almost pure **5** was obtained by TLC purification and a strong absorption at longer wavelength (496 nm (ε *ca.* 5000)) in the electronic spectrum is consistent with the monomeric structure. The yellow compound **11** free from **5** was obtained by purification with TLC, and was identified as a dimer of **5** on the basis of molecular weight determination (Found 666; Calcd 633) and its reversion to **5** by heating. When the benzene solution of **11** and *N*-phenylmaleimide was heated at about 60 °C, **12** was formed in 64% yield. The structure of the dimer **11** was established as [4+2] adduct **13** or **14** in the following way. The visible absorption at 450 nm (ε 9540) eliminates the possibility of [4+4] dimer, [2+2] dimer other than **15**, and [4+2] dimer other than **13** and **14**, since the [4+4] dimer has only naphthalene chromophore and the dimers of the latter two types have a conjugated thione system which would show an n-π^* absorption around 570 nm.[4] The NMR spectrum with intensity ratio of the aromatic to the olefinic protons of 10:2 rules out the structure **15**. Although we can not determine which of **13** or **14** is correct, the head-to-head structure in **3** suggests that the [4+2] dimer probably has the disulfide structure **13**.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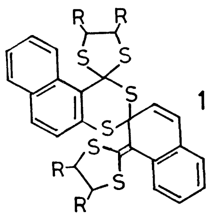
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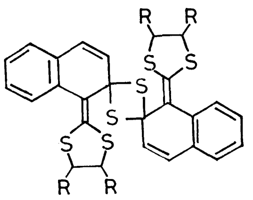
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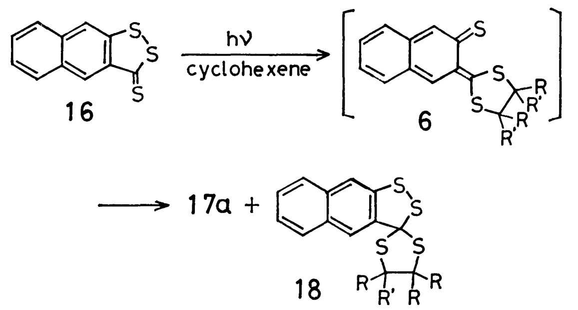
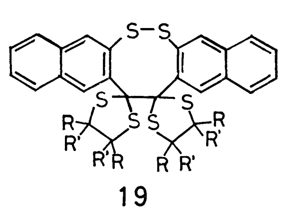
Photoreaction of Naphtho[*2,3-*c][*1,2*]*dithiole-3-thione (**16**) with Cyclohexene.* Irradiation of **16** in the presence of cyclohexene afforded **17a** (61%) and **18** (RR=$(\mathrm{CH}_2)_4$, R'=H) (3.8%) as white and yellow crystals, respectively.

The compound **17a** was found to be [4+4] dimer of naphthothioquinone methide **6a** (RR=$(\mathrm{CH}_2)_4$, R'=H), on the basis of molecular weight determination (Found 629; Calcd 632) and the spectral and analytical data. The UV ($\lambda_{\max}$ 243 (sh, ε 18300), 339 (2340), and 374 nm (sh, 488)) and NMR spectra indicated only the presence of naphthalene and cyclohexane rings, thus [4+4] adducts **19a** (RR=$(\mathrm{CH}_2)_4$, R'=H) and **20a** (RR=$(\mathrm{CH}_2)_4$, R'=H) remaining as possible structures for the photoproduct **17a** to the exclusion of [4+2] and [2+2] adducts.

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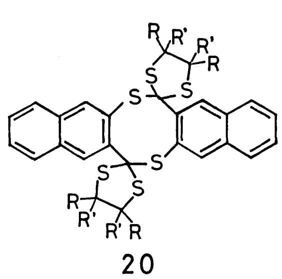
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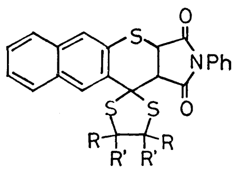
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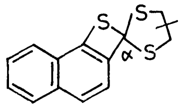
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Desulfurization with Raney nickel resulted in the formation of 1,2-di(2-naphthyl)ethane (4.6%) along with 2-methylnaphthalene (29.8%), suggesting that the dimer is of head-to-head type **19** as in the case of the benzo counterpart.[1] The dimer **17a** reacts with *N*-phenylmaleimide in benzene at room temperature for a month or at 80 °C for 1 h to afford white crystals **21** which is derived from the monomer **6a**.

This fact shows that **19a** is dissociated to the monomer **6a** in solution to a very minor extent in spite of the absence of any color due to the monomer **6a** even upon heating at 80 °C.

In order to observe the monomeric naphthothioquinone methide,[5] a similar photoreaction of **16** with 2,3-dimethyl-2-butene in dichloromethane was carried out at −78 °C, but the color due to monomer **6b** (R=R'=CH_3) was not observed, suggesting that *o*-thioquinone methide of this type is too unstable to be observed even at such a low temperature. This photoreaction in benzene at about 0 °C afforded a dimer **19b** (R=R'=CH_3) in 81%.

Since irradiation of **19a** afforded **18** (75%), the formation of **18** in the photoreaction of **16** with cyclohexene described above is due to a secondary photodecomposition of **19a**. The compound **18** reacted with triphenylphosphine to give **19a** and triphenylphosphine sulfide, indicating that such a 1,2-dithiole as **18** is a good precursor of the *o*-thioquinone methide, which has been demonstrated in our recent report.[6]

*Comparison of the Stability of the Three Isomeric Naphthothioquinone methides **4**, **5**, and **6**.* The above results indicate that the stability of monomeric naphthothioquinone methides **4**, **5**, and **6** is in the order of **4**>**5**>**6**. The instability of **6** compared with **4** and **5** is reasonable in view of the loss of aromaticity in the former structure.[7] The lower stability of **5** than **4** is probably attributed to the steric interaction of the dithiolane ring with the peri hydrogen; dimerization would reduce such an interaction to some extent. The difference in structure of the dimer between benzo **2** and naphtho system **5** (*i.e.* [4+4] *vs.* [4+2]) may also be due to strong steric interaction between the dithiolane ring and the aromatic ring in [4+4] adduct of the latter. The isolation of **4** and **5** suggests that an isomeric naphthothiete structure like **22** is rendered less stable than the corresponding *o*-thioquinone methide structure by the presence of two sulfur atoms on the α carbon. Some benzothietes have recently been reported to be stable isolable compounds.[8]

Experimental

All the melting points were not corrected. NMR spectra were recorded with a Hitachi R-20B or R-24 spectrometer using tetramethylsilane as an internal standard. Electronic spectra were recorded on a Hitachi EPS-3 spectrophotometer. IR spectra were taken with a Hitachi EPI-G2 spectrometer. Mass spectra were measured with a Hitachi RMU-6L spectrometer (beam energy 70 eV). High pressure liquid chromatography was done with a Hitachi 634 liquid chromatograph (column: Hitachi 3010). Molecular weight were measured with a Hitachi 117 Molecular Weight Apparatus (vapor pressure osmometry in benzene at 40 °C). All the photoreactions were carried out using Pyrex-filtered light (100 W medium pressure mercury lamp) while nitrogen was being bubbled through the reaction solution during the reaction. Thin layer (TLC), preparative layer (PLC), and dry column chromatography (DCC) were performed with silica gel.

*Photoreaction of Naphtho[1,2-*c*][1,2]dithiole-3-thione (**7**) with Cyclohexene.* The dithiolethione **7**[9] (534 mg, 2.3 mmol) and cyclohexene (7 cm^3) were dissolved in 70 cm^3 of benzene and the solution was irradiated for 90 min. The evaporation of the solvent gave the thioquinone methide **4** (713.6 mg, *ca.* 100%): mp 153.8—155.3 °C (from ethanol); NMR (CDCl$_3$): δ=1.1—2.3 (8H, m), 3.7—4.2 (2H, m), 7.05 (1H, B part of AB quartet, *J*=10 Hz), 7.42—7.53 (4H in total, m), 7.68 (1H, A part of AB quartet, *J*=10 Hz), and 8.8—9.0 (1H, m); UV (CH$_2$Cl$_2$): 323 (ε 24300), 353 (10800), 392 (sh, 2540), and 540 nm (11800); molecular weight, Found: 319; Calcd for C$_{17}$H$_{16}$S$_3$: 316. Found: C, 64.21; H, 4.97; S, 29.92%. Calcd for C$_{17}$H$_{16}$S$_3$: C, 64.51; H, 5.10; S, 30.39%.

*Reaction of **4** with* N*-Phenylmaleimide.* The thioquinone methide **4** (55 mg, 0.17 mmol) and *N*-phenylmaleimide (36 mg, 0.24 mmol) were dissolved in 16 cm^3 of benzene and the solution was allowed to stand for 1 d at room temperature. The evaporation of the solvent and PLC (CH$_2$Cl$_2$) of the residue gave **8** (71.1 mg, 83%): mp 235.0—237.0 °C (dec) (from ethanol); NMR (CDCl$_3$): δ=1.1—2.2 (8H, m), 3.6—4.0 (2H, m), 4.53 (2H, s), 6.7—8.0 (9H, m), and 8.2—8.6 (2H, m); IR (KBr): 1710 cm^{-1} (C=O); MS: *m/e* (rel intensity) 489 (M$^+$, 14) and 234 (100). Found: C, 66.29; H, 4.76; N, 2.98; S, 19.39%. Calcd for C$_{27}$H$_{23}$NO$_2$S$_3$: C, 66.23; H, 4.74; N, 2.86; S, 19.64%.

*Photoreaction of Naphtho[2,1-*c*][1,2]dithiole-1-thione (**10**) with Cyclohexene.* The dithiolethione **10**[9] (350 mg, 1.5 mmol) and cyclohexene (7 cm^3) were dissolved in 70 cm^3 of benzene and the solution was irradiated for 45 min. After the irradiation, the color of the solution turned deep red. The TLC of the reaction mixture showed a single product, **5**. The solution was evaporated and DCC (CCl$_4$) of the residue gave a mixture of **5** and **11** (450.5 mg, 95%), as indicated by TLC.

Pure **11** free from **5** was obtained by TLC (CH$_2$Cl$_2$) and subsequent recrystallization from ethanol and dichloromethane at −78 °C, and **5** which contained a small amount of **11** was obtained by TLC (CH$_2$Cl$_2$): **5**; NMR (CDCl$_3$): δ=1.0—2.5 (8H, m), 3.2—4.2 (2H, m), 7.3—8.2 (5H, m), and 8.3—8.6 (1H, m); UV (CH$_2$Cl$_2$): 235 (ε 23900), 263 (17800), 295 (12100), 327 (7160), 392 (sh, 3170), 412 (4440), and 496 nm (4630); **11**; mp 119.0—121.0 °C (from CH$_2$Cl$_2$ and ethanol); NMR (CDCl$_3$): δ=1.0—2.5 (16H, m), 3.5—4.2 (4H, m), 6.82 (1H, B part of AB quartet, *J*=9 Hz), 7.2—8.1 (11H in total, m), and 7.55 (1H, A part of AB quartet, *J*=9 Hz); UV (CH$_2$Cl$_2$): 263 (ε 19400), 354 (sh, 4650), and 450 nm (9540); molecular weight, Found: 666; Calcd: 632. Found: C, 63.91; H, 5.15; S, 30.28%. Calcd for C$_{34}$H$_{32}$S$_6$: C, 64.51; H, 5.10; S. 30.39%.

*Reaction of **5** and **11** with* N*-Phenylmaleimide.* The thioquinone methide **5** (26.6 mg, 0.08 mmol) and *N*-phenylmaleimide (19.5 mg, 0.11 mmol) were dissolved in 20 cm^3 of benzene and the solution was kept at 63 °C for 8.5 h under nitrogen atmosphere. The solvent was evaporated and the residue was subjected to PLC (benzene) to give **12** (22.1 mg, 54%). A benzene solution of **11** (91.5 mg, 0.14 mmol) and *N*-phenylmaleimide (63.9 mg, 0.37 mmol) was kept at 63 °C under nitrogen atmosphere for 8.5 h. The solvent was evaporated and the residue was subjected to PLC (benzene) to give **12** (90.5 mg, 64%): mp 238.0—239.5 °C (dec) (from ethanol); NMR (CDCl$_3$): δ=1.0—2.5 (8H, m), 3.8—4.2 (2H, m), 4.62 (AB q, 2H, *J*=9 Hz), and 6.8—8.0 (11H, m); IR (KBr): 1720 cm^{-1} (C=O). Found: C, 65.87; H, 4.69; N, 3.08%. Calcd for C$_{27}$H$_{23}$NO$_2$S$_3$: C, 66.23; H, 4.74; N, 2.86%.

*Photoreaction of Naphtho[2,3-*c*][1,2]dithiole-3-thione (**16**) with Cyclohexene.* The dithiolethione **16**[10] (1.02 g, 4.4 mmol) and 14 cm^3 of cyclohexene were dissolved in 200 cm^3 of benzene and the solution was irradiated for 100 min. The solution was concentrated to afford white crystals of **19a** (531 mg), which contained one molecule of benzene as solvent of crystallization. The filtrate was subjected to DCC (CH$_2$Cl$_2$–CCl$_4$ 1:9) to give **18** (27.9 mg, 3.8%) and **19a** (463 mg), which contained one molecule of CCl$_4$ as solvent of crystallization. The total yield of **19a** was 994 mg (61%). It was recrystallized from CH$_2$Cl$_2$ and the crystals contained one molecule of CH$_2$Cl$_2$ as solvent of crystallization: **19a**; mp 200.0—201.0 °C (dec) (from CH$_2$Cl$_2$); NMR (in C$_6$D$_6$ at 80 °C): δ=1.65 (16H, s), 4.47 (4H, s), 6.7—7.4 (8H, m), 8.15 (1H, bs), 8.26 (1H, bs), 8.38 (1H, bs), and 8.47 (1H, bs); (in CS$_2$ at 50 °C): δ=1.3—2.3 (16H, m), 3.0—4.5 (4H, m), 7.0—7.7 (8H, m), 7.7—7.9 (2H, m), 7.98 (1H, bs), and 8.07 (1H, bs): UV (CH$_2$Cl$_2$): 243 (sh, ε 18300), 339 (2340), and 374 nm (sh, 488); molecular weight, Found: 629; Calcd: 632. Found: C, 58.74; H, 4.99; S, 26.92; Cl, 10.08%. Calcd for C$_{35}$H$_{34}$S$_6$Cl$_2$: C, 58.55; H, 4.77; S, 26.80; Cl, 9.88%. **18**; mp 139—145 °C (from ethanol); NMR (CDCl$_3$): δ=1.2—2.5 (8H, m); 3.8—4.3 (2H, m), 7.2—8.0 (4H, m), 7.70 (1H, s), and 7.99 (1H, s); UV (CH$_2$Cl$_2$): 258 (ε 22000), 285 (sh, 13000), and 342 nm (2750); molecular weight, Found: 355; Calcd: 348; MS: *m/e* (rel intensity) 348 (M^+, 36) and 266 (100). Found: C, 58.58; H, 4.63; S, 36.79%. Calcd for $C_{17}H_{16}S_4$: C, 58.37; H, 4.48; S, 36.63%.

*Photoreaction of **16** with 2,3-Dimethyl-2-butene.* The dithiolethione **16** (1 g, 4.3 mmol) and 5 cm^3 of 2,3-dimethyl-2-butene were dissolved in 80 cm^3 of benzene and the solution was irradiated for 20 min. The solvent was removed and DCC (CCl_4–CH_2Cl_2 5:1) of the residue gave yellow crystals **19b**. The product contained one molecule of CCl_4 as solvent of crystallization. The yield was 1.52 g (81%). The pure product free from CCl_4 was obtained by recrystallization from CS_2 and ethanol: **19b**; mp 172.0—173.5 °C (dec) (from CS_2 and ethanol); NMR ($CDCl_3$): $\delta=1.22$ (6H, bs), 1.35 (6H, bs), 1.66 (6H, bs), 1.78 (6H, bs), 7.1—7.7 (8H, m), 7.87 (2H, s), and 8.28 (2H, s). Found: C, 63.75; H, 5.61; S, 30.28%. Calcd for $C_{34}H_{36}S_6$: C, 64.10; H, 5.70; S. 30.20%.

*Reaction of **19a** with N-Phenylmaleimide.* The dimer **19a** (22.4 mg, 0.06 mmol) and *N*-phenylmaleimide (12.5 mg, 0.07 mmol) were dissolved in 16 cm^3 of benzene and the solution was allowed to stand for 17 d at room temperature. After removal of the solvent, PLC (hexane–ether 1:1) of the residue gave **21** (33 mg, 94%). *N*-Phenylmaleimide (44.4 mg, 0.26 mmol) and **19a** (33 mg, 0.09 mmol) were dissolved in 20 cm^3 of benzene and the solution was refluxed for 1 h. The solvent was evaporated and the residue was recrystallized from benzene to give white crystals **21** (42.2 mg, 83%): mp 258.0—259.5 °C (dec) (from CH_2Cl_2); NMR ($CDCl_3$): $\delta=1.0$—2.3 (8H, m), 3.5—4.4 (2H, m), 4.70 (2H, s), 6.7—7.0 (3H, m), 7.0—8.2 (7H, m), 8.70 (1H, s); NMR (DMSO-d_6): $\delta=1.2$—2.1 (8H, m), 3.8—4.3 (2H, m), 4.70 (2H, s), 6.5—6.9 (3H, m), 7.2—8.1 (7H, m), and 8.68 (1H, s); IR (KBr): 1716 cm^{-1} (C=O); MS: *m/e* (rel intensity) 489 (M^+, 6) and 234 (100). Found: C, 66.30; H, 4.68; N, 2.93%. Calcd for $C_{27}H_{23}NO_2S_3$: C, 66.23; H, 4.74; N, 2.86%.

*Desulfurization of **19a** by Raney Nickel.* Under nitrogen atmosphere at 30 °C, **19a** (206 mg, 0.29 mmol) was added to Raney Ni (W-4), prepared from 20 g of Raney Ni alloy, in 100 cm^3 of benzene and the mixture was kept stirring for 45 min. After **19a** was consumed, the mixture was refluxed for 30 min. Raney Ni was removed by filtration and 1,2-di(2-naphthyl)ethane and 2-methylnaphthalene were analyzed for the filtrate with high pressure liquid chromatography by comparison with authentic samples (solvent: NH_3–MeOH 1:10 for 1,2-di(2-naphthyl)ethane; NH_3–MeOH 1:19 for 2-methylnaphthalene). The yields of 1,2-di(2-naphthyl)ethane and 2-methylnaphthalene were 4.6 and 29.8%, respectively. 1,2-Di(2-naphthyl)ethane was prepared by bromination (*N*-bromosuccinimide) of 2-methylnaphthalene followed by coupling with magnesium; mp 194—194.3 °C ($CHCl_3$).

*Photolysis of **19a**.* A benzene solution (50 cm^3) of **19a** (50 mg, 0.14 mmol) was irradiated for 100 min. The solvent was evaporated and the residue was subjected to PLC (benzene) to give **18** (17.8 mg, 75%). The spectral data of **18** were in agreement with those obtained in the photoreaction of **16** with cyclohexene.

*Desulfurization of **18** with Triphenylphosphine.* Triphenylphosphine (116 mg, 0.44 mmol) and **18** (128 mg, 0.37 mmol) were dissolved in 30 cm^3 of benzene and the solution was allowed to stand for 1 d at room temperature. The solvent was removed and PLC (benzene–hexane 1:1) of the residue gave **19a** and triphenylphosphine sulfide quantitatively.

*Photoreaction of **16** with Olefins at −78 °C.* The dithiolethione **16** (29 mg, 0.12 mmol) and 0.5 cm^3 of cyclohexene were dissolved in 5 cm^3 of dichloromethane and the solution was irradiated at −78 °C for 90 min, but the color derived from **6** was not observed. Dichloromethane solution (5 cm^3) of **16** (5 mg, 0.02 mmol) and 2,3-dimethyl-2-butene (0.5 cm^3) was irradiated for 30 min under the same conditions. However, the color of **6** was not observed.

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