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Photo-reaction of β-Ketovinyl Sulfur Compounds[1]

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Photolysis of mono- and di-β-ketovinyl sulfones in benzene solution caused an extrusion of sulfur dioxide to give the corresponding β-phenyl enone and bis-enones in moderate yields, respectively, and that of di-β-ketovinyl sulfide and sulfoxide was also examined.

Keywords——photochemical extrusion of sulfur dioxide; mono-β-ketovinyl sulfone; homolytic cleavage of carbon-sulfur bond; di-β-ketovinyl sulfoxide; formation of bis-enone; di-β-ketovinyl sulfide

Although the photochemistry of β-ketovinyl hetero compounds having arylamino,[3] allylamino,[4] acylamino,[4,5] hydrazino,[6] acyloxy,[7] allyloxy,[4] azido,[8] alkoxy[9] or mercapto group[10] has been extensively studied by us and others and well established, the behavior of β-ketovinyl sulfones is quite unknown. We have now investigated the photochemistry of heretofore unknown mono-(I—III) and di-β-ketovinyl sulfones (VIa, b), and found that irradiation of (I—III) in benzene solution gave β-phenyl enone (V) in 19—50% yields, while that of di-β-ketovinyl sulfones (VIa, b) gave bis-enones (VIIa, b) in 35—47% yields. The present paper deals with these transformations and some photolyses of the related sulfur compounds (VIII and X).

Compounds (I—III) were prepared from 3-chloro-2-cyclohexen-1-one (IVa) by reaction with sodium salt of the corresponding thiol followed by oxidation with *m*-chloroperbenzoic acid (*m*-CPBA). Compounds (VIa, b) were synthesized by reaction of (IVa, b) with sodium sulfide nonahydrate followed by oxidation with *m*-CPBA (see Experimental section). Irradiation of a benzene solution of 5,5-dimethyl-3-phenylsulfonyl-2-cyclohexen-1-one (I) with a 350 W high-pressure mercury lamp in a Pyrex vessel for 30 hr afforded 5,5-dimethyl-3-phen-

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1) Part of this work was reported at the 95th Annual Meeting of Pharmaceutical Society of Japan, Kobe, April 1975.

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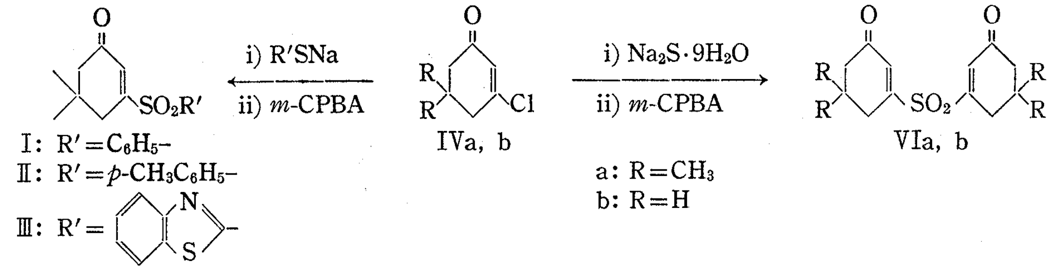

Chart 1

yl-2-cyclohexen-1-one (V) in 19% yield accompanied with a 10% yield of diphenyl. The structure (V) was assigned from the spectral analyses, and identified with an authentic specimen prepared by phenylation of 5,5-dimethyl-3-ethoxy-2-cyclohexen-1-one.[11] Similarly, other mono-β-ketovinyl sulfones (II and III) on irradiation in benzene solution gave the same compound (V) in 17 and 50% yields, respectively. The formation of V from (I—III) seems to occur by homolytic cleavage of carbon-sulfur bond followed by a combination with solvent used as proposed in the case of the photolysis of di-(p-tolyl)-sulfone in benzene or pyridine solution.[12]

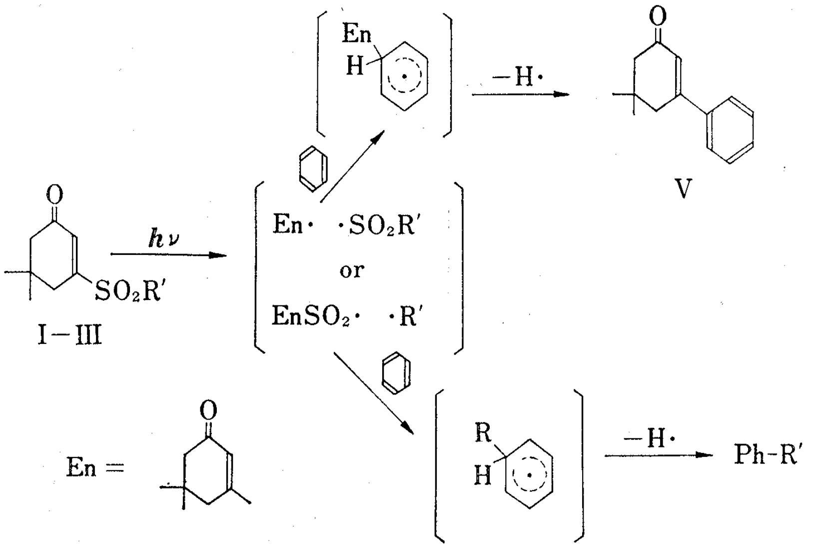

Chart 2

Next, we examined the photolysis of di-β-ketovinyl sulfones (VIa, b). A benzene solution of bis(5,5-dimethyl-2-cyclohexen-1-on-3-yl)-sulfone (VIa) was irradiated under the same conditions for 1 hr to give a 47% yield of bis-5,5-dimethyl-2-cyclohexen-1-on-3-yl (VIIa) accompanied with a small amount of (V). The isomeric structures (VIIa' and VIIa") are readily eliminated by consideration of nuclear magnetic resonance (NMR), ultraviolet (UV) and infrared (IR) spectral data: Two enone moieties should be combined symmetrically each other from the datum of NMR [$\delta(CDCl_3)$: 6.34 (2H, bs, $2\times CH=$), 2.41 (4H, bs, $2\times CH_2C=$), 2.31 (4H, s, $2\times CH_2CO$), and 1.10 (12H, s, $4\times CH_3$)] (VIIa' is eliminated), and one enone moiety might be conjugated with another double bond because of the large bathchromic shift in UV spectrum [λ_{max} (EtOH): 286 nm (log ε 4.39)] (VIIa" is eliminated) and all spectral data including IR absorption [$\nu_{max}^{CHCl_3}$ cm^{-1}: 1665 and 1580] are in good accordance with the assigned structure (VIIa). The photolysis of bis(2-cyclohexen-1-on-3-yl)-sulfone (VIb) pro-

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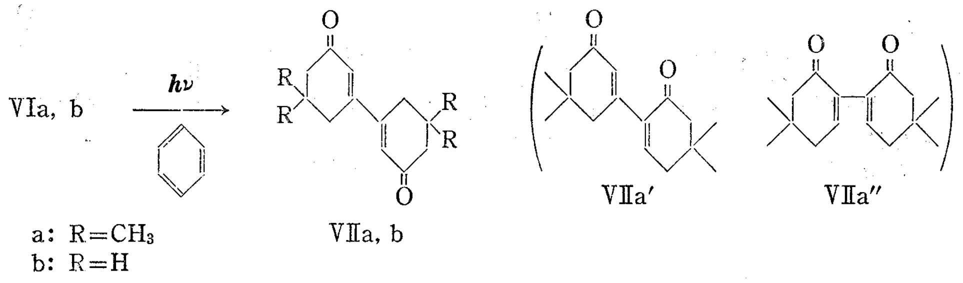

Chart 3

ceeded similarly to give bis-2-cyclohexen-1-on-3-yl (VIIb) in 35% yield. The transformation of (VIa, b) to (VIIa, b) was proved to have a practical utility because the production of the bis-enones had been feared to be troublesome thermochemically.[13] In view of the high selective formation of the bis-enones, the reaction may be explained by the mechanism as shown in Chart 4. Thus, an intramolecular $[2\pi+2\pi]$ photocycloaddition[14] may occur faster than the carbon-sulfur bond cleavage to afford an intermediate (A), which gives (VII) by extrusion of sulfur dioxide, however a concerted loss of sulfur dioxide or a radical recombination in a solvent cage could not be eliminated completely.

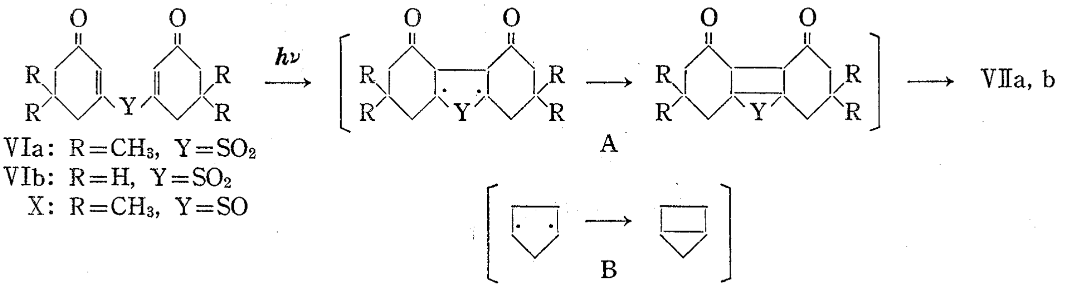

Chart 4

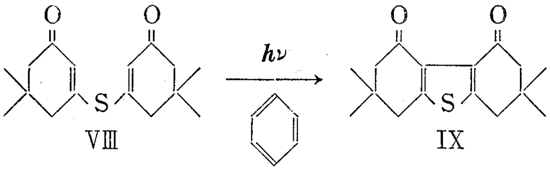

Chart 5

The result with di-β-ketovinyl sulfones led us to investigate the photolysis of the corresponding sulfide (VIII) and sulfoxide (X). The sulfide (VIII) caused the expected[10a,15] photocyclization-oxidation reaction to give the octahydrodibenzothiophene (IX) in 56% yield, and the corresponding sulfoxide (X), prepared by careful oxidation of (VIII) with one molar equivalent of *m*-CPBA, gave the bis-enone (VIIa) in 64% yield. That the yield of (VIIa) did not decrease even when the reaction was carried out under degassed condition (64% yield) or in the presence of 1,4-diazabicyclo(2,2,2)octane (DABCO) (68% yield) suggests that the formation of (VIIa) from (X) does not proceed through the sulfone (VIa) but through a similar intermediate (A) as proposed in the case of (VI). This is a novel behavior in sulfoxide photochemistry: The reported photochemistry of sulfoxide has been limited to the photosensitized oxidation to sulfones,[16] rearrangement of 2,2-dimethyl-thiochromane-1-oxide[17] and dibenzoylepisul-

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foxide,[18] racemization,[19] photodesulfurization,[12] and deoxygenation to sulfide,[12,20] and homolytic cleavage of C-SO bond.[12]

Experimental

All melting points are uncorrected. The IR spectra were recorded on a Hitachi-G2 spectrometer, UV spectra on a Hitachi EPS-3T spectrophotometer, and NMR spectra on a Hitachi R-20A spectrometer (tetramethylsilane as internal standard). Mass spectra were obtained with a Hitachi RMU-6M instrument with a direct inlet system operating at 70 eV. Preparative thin-layer chromatography (TLC) was carried out on Merck Silica gel GF_{254} (Type 60) or Merck Alumina PF_{254}.

General Procedure for Mono-β-ketovinyl Sulfones (I—III)——A suspension of sodium salt of the corresponding thiol and 3-chloro-5,5-dimethyl-2-cyclohexen-1-one (IVb) in benzene was stirred at room temperature for 10—15 hr. The reaction mixture was poured into water and extracted with benzene. The extract was washed with saturated aqueous sodium chloride, dried over $MgSO_4$ and evaporated *in vacuo* to give the corresponding sulfide. The sulfide was reacted with two or three molar equivalents of *m*-CPBA in methylene chloride at room temperature for 3 hr. After addition of a small amount of methylene chloride, the solution was washed with saturated aqueous sodium chloride, and dried over $MgSO_4$. Removal of the solvent *in vacuo* followed by recrystallization of the residue gave the corresponding sulfone (I—III).

5,5-Dimethyl-3-phenylsulfonyl-2-cyclohexen-1-one (I)——From 5,5-dimethyl-3-phenylthio-2-cyclohexen-1-one[10a] (0.232 g), the sulfone (I) (0.230 g, 87%) was obtained and recrystallized from benzene to give colorless crystals, mp 79.5—80.5°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1680, 1320, 1310, and 1150. NMR ($CDCl_3$) δ: 0.94 (6H, s, $2\times CH_3$), 2.26 (2H, s, CH_2CO), 2.36 (2H, d, $J=1.8$ Hz, $CH_2C=$), 6.72 (1H, t, $J=1.8$ Hz, CH=), and 7.5—8.0 (5H, m, ArH). UV λ_{max}^{EtOH} nm: 238 (log ε 4.08). The mass spectrum shows the molecular ion at *m/e* 264 (Calcd. 264). *Anal.* Calcd. for $C_{14}H_{16}O_3S$: C, 63.61; H, 6.10. Found: C, 63.68; H, 6.10.

5,5-Dimethyl-3-(*p*-tolyl)sulfonyl-2-cyclohexen-1-one (II)——From sodium salt of *p*-thiocresol (1.05 g) and 3-chloro-5,5-dimethyl-2-cyclohexen-1-one (IVa) (1.0 g), the sulfide (0.70 g, 45%) was obtained and recrystallized from pet. ether to give colorless crystals, mp 95—97°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1640 and 1580. NMR ($CDCl_3$) δ: 1.08 (6H, s, $2\times CH_3$), 2.22 (2H, s, CH_2CO), 2.38 (3H, s, $ArCH_3$, and 2H, s, $CH_2C=C$), 5.47 (1H, t, $J=1.5$ Hz, CH=C), and 7.1—7.5 (4H, m, ArH). UV λ_{max}^{EtOH} nm: 220 (log ε 4.08) and 291 (4.21). *Anal.* Calcd. for $C_{15}H_{18}OS$: C, 73.13; H, 7.36. Found: C, 73.19; H, 7.51.

The sulfide (0.150 g) was reacted with 70% *m*-CPBA (0.330 g) to give the sulfone (II) (0.155 g, 91%), which was recrystallized from benzene *n*-hexane to give colorless crystals, mp 86.5—88°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1685, 1595, 1325, 1310, and 1155. NMR ($CDCl_3$) δ: 0.97 (6H, s, $2\times CH_3$), 2.27 (2H, s, CH_2CO), 2.39 (2H, d, $J=1.3$ Hz, $CH_2C=$), 2.47 (3H, s, $ArCH_3$), 6.71 (1H, t, $J=1.3$ Hz, CH=), and 7.4—7.9 (4H, m, ArH). *Anal.* Calcd. for $C_{15}H_{18}O_3S$: C, 64.71; H, 6.52. Found: C, 64.74; H, 6.55.

5,5-Dimethyl-3-(2-benzothiazolyl)sulfonyl-2-cyclohexen-1-one (III)——From sodium salt of 2-mercaptobenzothiazole (2.94 g) and 3-chloro-5,5-dimethyl-2-cyclohexen-1-one (IVa) (2.37 g), the sulfide (3.85 g, 88%) was obtained and recrystallized from *n*-hexane to give yellow crystals, mp 80.5—81.5°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1650 and 1580. NMR ($CDCl_3$) δ: 1.11 (6H, s, $2\times CH_3$), 2.29 (2H, s, CH_2CO), 2.49 (2H, d, $J=1.3$ Hz, $CH_2C=$), 6.19 (1H, t, $J=1.3$ Hz, CHC=), 7.4—7.7 (2H, m, ArH), and 7.8—8.2 (2H, m, ArH). UV λ_{max}^{EtOH} nm: 238 (log ε 4.02), 270 (4.11), and 295 (4.03). *Anal.* Calcd. for $C_{15}H_{15}NOS_2$: C, 62.25; H, 5.22; N, 4.84. Found: C, 62.50; H, 5.34; N, 4.81.

The sulfide (0.145 g) was reacted with 70% *m*-CPBA (0.272 g) to give the sulfone (0.161 g, 99%), which was recrystallized from benzene *n*-hexane to give pale yellow crystals, mp 138—139°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1685, 1340, and 1150. NMR ($CDCl_3$) δ: 1.04 (6H, s, $2\times CH_3$), 2.33 (2H, s, CH_2CO), 2.67 (2H, bs, $CH_2C=$), 6.97 (1H, bs, CH=), 7.4—7.8 (2H, m, ArH), and 7.8—8.4 (2H, m, ArH). UV λ_{max}^{EtOH} nm: 246 (log ε 4.09). The mass spectrum shows the molecular ion at *m/e* 321 (Calcd. 321). *Anal.* Calcd. for $C_{15}H_{15}NO_2S_2$: C, 56.05; H, 4.70; N, 4.36. Found: C, 56.23; H, 4.76; N, 4.32.

Photolysis of (I)——A solution of the sulfone (I) (80 mg) in benzene (10 ml) was irradiated with a 350 W high pressure mercury lamp in a Pyrex vessel at room temperature for 30 hr. Removal of the solvent *in vacuo* followed by preparative TLC (alumina; *n*-hexane: acetone = 10: 1) gave 5,5-dimethyl-3-phenyl-2-cyclohexen-

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1-one (V) (12 mg, 19%). Recrystallization from pet. ether gave colorless crystals, mp 48.5—50.5° [lit. 51—52.5°13)]. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1655, 1610, and 1575. NMR ($CDCl_3$) δ: 1.15 (6H, s, $2\times CH_3$), 2.34 (2H, s, CH_2CO), 2.65 (2H, d, J=1.5 Hz, CH_2C=), 6.43 (1H, t, J=1.5 Hz, CH=), and 7.3—7.7 (5H, m, ArH). UV $\lambda_{max}^{CHCl_3}$ nm: 220 (log ε 3.92), and 282 (4.19).

Photolysis of (II)——A solution of (II) (91 mg) in benzene (10 ml) was irradiated for 9 hr. Work-up as described for the photolysis of (I) gave the enone (V) (11 mg, 17%), identical with an authentic specimen (mp and spectral data).

Photolysis of (III)——A solution of (III) (77 mg) in benzene (10 ml) was irradiated for 12 hr. Work-up as described for the photolysis of (I) gave the enone (V) (24 mg, 50%), identical with an authentic specimen (mp and spectral data).

Bis(5,5-dimethyl-2-cyclohexen-1-on-3-yl)sulfone (VIa)——A solution of the sulfide (VIII) (0.158 g) and 70% *m*-CPBA (0.310 g) in methylene chloride (10 ml) was stirred at room temperature for 3 hr. Work-up as described for (I) gave the sulfone (VIa) (0.137 g, 77%), which was recrystallized from benzene–*n*-hexane to give colorless crystals, mp 155—157°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1690, 1325, 1145, and 1135. NMR ($CDCl_3$) δ: 1.11 (12H, s, $4\times CH_3$), 2.36 (4H, s, $2\times CH_2CO$), 2.41 (4H, d, J=2.1 Hz, $2\times CH_2C$=), and 6.82 (2H, t, J=2.1 Hz, $2\times$CH=). UV λ_{max}^{EtOH} nm: 238 (log ε 4.24) and 285 (3.08). *Anal.* Calcd. for $C_{16}H_{22}O_4S$: C, 61.91; H, 7.15. Found: C, 61.78; H, 7.15.

Photolysis of (VIa)——A solution of (VIa) (40 mg) in benzene (10 ml) was irradiated for 1 hr. Removal of the solvent *in vacuo* followed by preparative TLC (alumina; *n*-hexane: acetone=5: 1) gave the bis-enone (VIIa) (15 mg, 47%) and a small amount of V (1.3 mg, 5%). Recrystallization of the bis-enone (VIIa) from *n*–hexane gave yellow crystals, mp 184.5—185.5°. The mass spectrum shows the molecular ion at *m/e* 246 (Calcd. 246). *Anal.* Calcd. for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 77.81; H, 8.90.

Bis(2-cyclohexen-1-on-3-yl)sulfone (VIb)——A mixture of 3-chloro-2-cyclohexen-1-one (IVb) (1.3 g) and sodium sulfide nonahydrate (1.2 g) was stirred at 40—50° for 10 hr. The mixture was extracted with methylene chloride, washed with saturated aqueous sodium chloride, and dried over $MgSO_4$. Removal of the solvent *in vacuo* gave bis(3-oxo-1-cyclohexen-1-yl)sulfide (1.6 g, 72%), which was recrystallized from pet. ether to give pale yellow crystals, mp 58.0—59.0°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1660 and 1580. NMR ($CDCl_3$) δ: 1.9—2.8 (12H, m, $6\times CH_2$) and 6.16 (2H, t, J=1.3 Hz, $2\times$CH=). The mass spectrum shows the molecular ion at *m/e* 222 (Calcd. 222). *Anal.* Calcd. for $C_{12}H_{14}O_2S$: C, 64.84; H, 6.35. Found: C, 64.72; H, 6.38.

The sulfide (95 mg) was reacted with 70% *m*-CPBA (0.230 g) in methylene chloride (10 ml) at room temperature for 3 hr. Work-up as described for the preparation of mono-β-ketovinyl sulfones (I—III) gave the sulfone (VIb) (61 mg, 56%). Recrystallization from n–hexane gave colorless crystals, mp 140.5—141.5°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1690, 1330, and 1150. NMR ($CDCl_3$) δ: 2.0—2.80 (12H, m, $6\times CH_2$) and 6.77 (2H, t, J=1.2 Hz, $2\times$CH=). UV λ_{max}^{EtOH} nm: 236 (log ε 4.17) and 284 (3.63). The mass spectrum shows the molecular ion at *m/e* 254 (Calcd. 254). *Anal.* Calcd. for $C_{12}H_{14}O_4S$: C, 56.68; H, 5.55. Found: C, 56.64; H, 5.59.

Photolysis of (VIb)——A solution of (VIb) (50 mg) in benzene (6 ml) was irradiated for 5 hr. Work-up as described for the photolysis of (VIa) gave the bis-enone (VIIb) (13.3 mg, 35%) and 3-phenyl-2-cyclohexen-1-one (4.1 mg, 12%). Recrystallization of the bis-enone (VIIb) from *n*-hexane gave colorless crystals, mp 100.5—102°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1665 and 1580. NMR ($CDCl_3$) δ: 1.8—2.7 (12H, m, $6\times CH_2$) and 6.34 (2H, bs, $2\times$CH=). UV λ_{max}^{EtOH} nm: 284 (log ε 4.10). The mass spectrum shows the molecular ion at *m/e* 190 (Calcd. 190). *Anal.* Calcd. for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.89; H, 7.52.

Bis(5,5-dimethyl-2-cyclohexen-1-on-3-yl)sulfide (VIII)——A mixture of 3-chloro-5,5-dimethyl-2-cyclohexen-1-one (IVa) (3.16 g) and sodium sulfide nonahydrate (2.64 g) was stirred at 50° for 10 hr. The mixture was partitioned with water (5 ml) and benzene (50 ml). The benzene layer was washed with saturated aqueous sodium chloride and dried over $MgSO_4$. Removal of the solvent *in vacuo* followed by column chromatography of the residue on Silica gel (CH_2Cl_2) gave the sulfide (VIII) (4.14 g, 74%), which was recrystallized from *n*-hexane to give pale yellow crystals, mp 81.5—83°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1650 and 1580. NMR (CCl_4) δ: 1.13 (12H, s, $4\times CH_3$), 2.20 (4H, s, $2\times CH_2CO$), 2.38 (4H, d, J=1.5 Hz, $2\times CH_2$=C), and 6.07 (2H, t, $2\times$ CH=C). UV λ_{max}^{EtOH} nm: 228 (log ε 3.99), 276 (4.00), and 311 (3.97). The mass spectrum shows the molecular ion at *m/e* 278 (Calcd. 278). *Anal.* Calcd. for $C_{16}H_{22}O_2S$: C, 69.03; H, 7.97. Found: C, 69.20; H, 8.02.

Photolysis of (VIII)——A solution of (VIII) (40 mg) in benzene (6 ml) was irradiated with a 350 W high pressure mercury lamp in Pyrex vessel at room temperature for 2.5 hr. Removal of the solvent *in vacuo* followed by preparative TLC (silica; *n*-hexane: acetone=5: 1) gave the octahydrodibenzothiophene (IX) (22 mg, 56%). Recrystallization from *n*-hexane gave yellow crystals, mp 155—156.5°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1695. NMR ($CDCl_3$) δ: 1.13 (12H, s, $4\times CH_3$), 2.37 (4H, s, $2\times CH_2CO$), and 2.80 (4H, s, $2\times CH_2C$=). UV λ_{max}^{EtOH} nm: 233 (log ε 4.27) and 280 (3.37). The mass spectrum shows the molecular ion at *m/e* 276 (Calcd. 276). *Anal.* Calcd. for $C_{16}H_{20}O_2S$: C, 69.53; H, 7.29. Found: C, 69.33; H, 7.27.

Bis(5,5-dimethyl-2-cyclohexen-1-on-3-yl)sulfoxide (X)——To a stirred solution of (VIII) (0.232 g) in methylene chloride (10 ml), 70% *m*-CPBA (247 mg) was added in portions during 1 hr. The mixture was stirred at room temperature for additional 2 hr. The mixture was washed with 10% aqueous sodium carbonate and saturated aqueous sodium chloride, and dried over $MgSO_4$. Removal of the solvent *in vacuo* followed by preparative TLC (alumina: *n*-hexane: acetone=5: 1) gave the sulfoxide (X) (232 mg, 91%). Recrystallization from benzene–*n*-hexane gave colorless crystals, mp 139—140°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1685, 1610, and 1080.

NMR ($CDCl_3$) δ: 1.10 (12H, s, 4 × CH_3), 2.23 (4H, s, 2 × CH_2CO), 2.36 (4H, bs, 2 × CH_2C=), and 6.64 (2H, bs, 2 × CH=). The mass spectrum shows the molecular ion at *m/e* 294 (Calcd. 294). *Anal.* Calcd. for $C_{16}H_{22}O_3S$: C, 65.27; H, 7.53. Found: C, 65.30; H, 7.53.

Photolysis of (X)——A solution of (X) (30 mg) in benzene (6 ml) was irradiated with a 350 W high pressure mercury lamp in a Pyrex vessel at room temperature for 1 hr. Work-up as described for the photolysis of (VIa) gave the yellow bis-enone (VIIa) (16.2 mg, 64%), identical with an authentic specimen (mp and spectral data) obtained by the photolysis of (VIa).