

Registry No.—1a, 51416-11-6; 1b, 58735-17-4; 2a, 58735-18-5; 2b, 58735-19-6; 3a, 58735-20-9; 3b, 58735-21-0; 4a, 58735-22-1; 4b, 58735-23-2; 5a, 58735-24-3; 5b, 58735-25-4; 6a, 58735-26-5; 6b, 58735-27-6; 7a, 58735-28-7; 7b, 58735-29-8; methyl 6-phthalimido-2β-chloromethyl-2α-methylpenam-3-carboxylate, 51415-59-9; 2-mercaptobenzothiazole, 149-30-4; *p*-nitrobenzyl 6-phthalimido-2β-chloromethyl-2α-methylpenam-3-carboxylate, 56446-37-8.

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Photochemical Reaction of 4-Diphenylmethylene-4*H*-thiopyrans

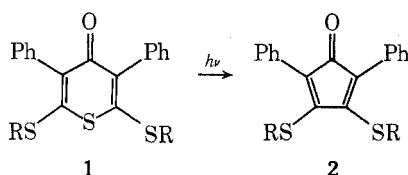
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Ultraviolet irradiation of 4-diphenylmethylene-2,6-bis(methylthio)-3,5-diphenyl-4*H*-thiopyran affords 2-diphenylmethylene-4,5-bis(methylthio)-3,6-diphenyl-2*H*-thiopyran via the triplet state of the former. Photolysis of 4-diphenylmethylene-4*H*-thiopyran, 4-diphenylmethylene-2,6-bis(methylthio)-3,5-dimethyl-4*H*-thiopyran, and 4-diphenylmethylene-3,5-diphenyl-4*H*-thiopyran resulted in the recovery of the starting materials. All of these 4-diphenylmethylene-4*H*-thiopyrans fluoresce at room temperature, but do not phosphoresce at 77 K.

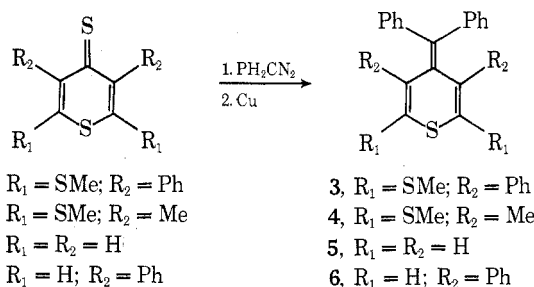
The photochemistry of 4-thiopyrones has been the subject of study in this and other laboratories. Under the influence of ultraviolet light, unhindered 4*H*-thiopyran-4-ones undergo dimerization,² whereas hindered 4*H*-thiopyran-4-ones lead to elimination of sulfur atom.³ In this photochemical rearrangement of 2,6-bis(alkylthio)-3,5-diphenyl-4*H*-thiopyran-4-ones (1) to 3,4-bis(alkylthio)-2,5-diphenylcyclopentadienones (2), evidence in favor of the mechanism



involving its n, π^* triplet state was given.³ It seemed of considerable import to inspect the photochemistry of a system lacking n, π^* excitation but having a similar π system. Such a molecule would have available only π, π^* excited state and its photochemistry would define the behavior of these states. Accordingly the diphenylmethylene analogues were selected for the present study. Specifically, 4-diphenylmethylene-2,6-bis(methylthio)-3,5-diphenyl-4*H*-thiopyran was chosen for study of the photochemical reaction in detail.⁴

Results and Discussion

4-Diphenylmethylene-4*H*-thiopyrans (3–6) were most conveniently prepared by the reaction of corresponding 4*H*-thiopyran-4-thiones (7–10) with diphenyldiazomethane, followed by treatment with copper powder according to the established procedure.^{5,6} The structure assigned to 4-diphenylmethylene-4*H*-thiopyrans rests on their elemental analysis and spectral data. Their mass spectra showed an intense peak correspondent with their parent ion. The ir spectra exhibited a stretching vibration of the exocyclic double bond at 1605–1620 cm^{-1} . The NMR spectra of 3 and 4 showed the equivalent thiomethyl protons at δ 2.2–2.3 and those of 5 and

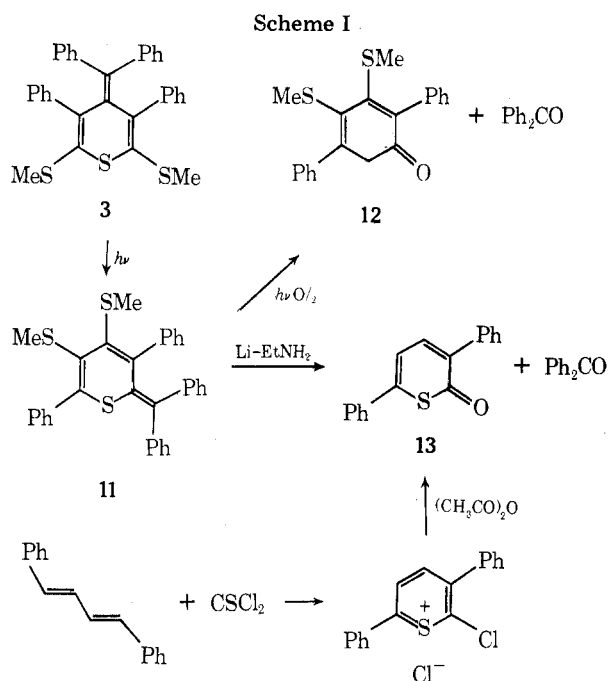


6 displayed the olefinic protons at δ 6.2–6.9. These spectral data were in complete agreement with the structure and are given in the Experimental Section.

Irradiation of 4-diphenylmethylene-2,6-bis(methylthio)-3,5-diphenyl-4*H*-thiopyran (3) in benzene with a medium-pressure mercury lamp through a Pyrex filter gave an almost quantitative yield of a product isomeric with the starting material. This is assigned structure 11 on the basis of chemical reaction outlined in Scheme I. Photooxygenation of the photoproduct yielded 4,5-bis(methylthio)-3,6-diphenyl-2*H*-thiopyran-2-one (12). Upon addition to Li-EtNH₂ the photoproduct was desulfurized⁷ to give 3,6-diphenyl-2*H*-thiopyran-2-one (13),^{8,9} identical with an authentic sample^{11,12} in ir and NMR spectra. The irradiation of 3 in methylene chloride under similar conditions also afforded 11 in excellent yield.

Irradiation of 4 or 5 or 6 in benzene with a medium-pressure mercury lamp equipped with a Pyrex filter or a 313–436-nm solution filter¹³ produced no reaction. Prolonged irradiation of 4, 5, or 6 also resulted in the recovery of the starting materials. When photolysis was sensitized by acetophenone which absorbed more than 95% of the incident light, 5 was also recovered unchanged.

Ultraviolet absorption spectra of the 4-diphenylmethylene-4*H*-thiopyran in ethanol are given in Figure 1, which shows two broad intense bands at 230–240 and 340–380 nm, whereas the corresponding 4*H*-thiopyran-4-ones exhibit two



intense bands at 230–280 and 300–310 nm.¹⁴ Hypsochromic shifts were observed for 3, 4, and 6 relative to the spectrum of 5, whereas a bathochromic shift was observed for 4-diphenylmethylene-2,6-diphenyl-4H-thiopyran. This hypsochromic shift might be caused by steric factors which significantly reduce electron interaction between the thiopyran ring and the substituents at the C-3 and C-5 positions. This steric hindrance was also reflected into the ultraviolet spectra of the corresponding 4H-thiopyran-4-ones.¹⁴

The 4-diphenylmethylene-4H-thiopyrans 3–6 fluoresce in ethanol at room temperature. No evidence of phosphorescence was obtained at least at 77 K. The observed luminescence is diagnosed as fluorescence from the overlap of excitation and emission bands in the 0–0 band region (Figure 1) and from the short luminescence lifetimes which allowed complete suppression of the emission when the phosphoroscope was used. Observation of emission spectra at room temperature also indicates that the obtained emission indeed is fluorescence. It is worthy to note that the 4-diphenylmethylene-4H-thiopyrans studied fluoresce in solution at room temperature but do not phosphoresce at 77 K, whereas the corresponding ketone analogues, 4H-thiopyran-4-ones,¹⁴ do not fluoresce in solution at both room and low temperature (77 K) but phosphoresce at 77 K.

Quantum yields for appearance of 11 in benzene or methylene chloride were determined using potassium ferrioxalate actinometry.¹⁵ The deaerated samples were irradiated with the 360-nm light.¹³ Reactions were carried out in 2–3% conversion and the yield of product was determined by the ultraviolet spectrophotometric method. The results of these run (Table I) showed the average quantum yield to be very high (1.00), as has been obtained in the photorearrangement of 4,4-diphenyl-2,5-cyclohexadienone.¹⁶

Thioxanthone ($E_T = 65.6$ kcal/mol) and acridine ($E_T = 45.3$ kcal/mol) were selected for sensitization studies because of their high molecular extinction coefficients at 360 nm. Quantum efficiency for the formation of 11 on thioxanthone sensitization absorbing over 90% of incident light did not give a reproducible value. This would be due to the self-quenching reaction of thioxanthone¹⁷ at the high concentration used. Under preparative conditions, however, 3 was rearranged to 11 in the thioxanthone-sensitized run as effectively as in the direct run. On the other hand, sensitization by acridine did not lead to the formation of photoproduct. Cyclooctatetraene

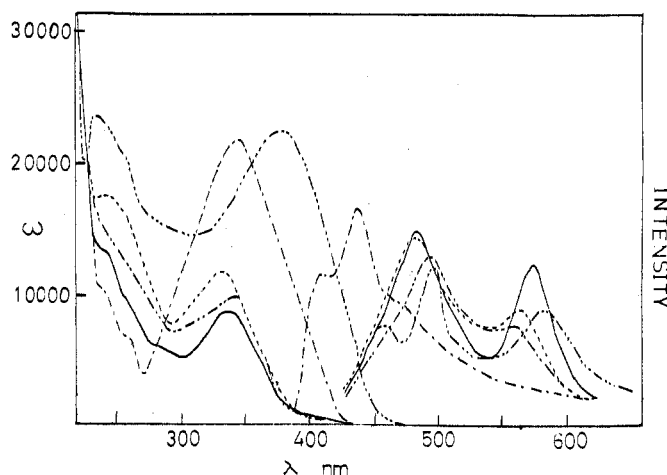


Figure 1. Electronic absorption and fluorescence spectra of 4-diphenylmethylene-4H-thiopyrans in ethanol: 3, —; 4, - - -; 5, - · - ·; 6, · · · ·; 4-diphenylmethylene-2,6-diphenyl-4H-thiopyran, - - - -.

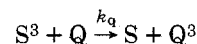
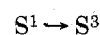
Table I. Quantum Yield for the Formation of 11^a

Solvent	Additive	ϕ
Benzene	None	0.99
Methylene chloride	None	1.01
Benzene	<i>cis</i> -Piperylene, 0.1 M	0.97
Benzene	Cyclooctatetraene, 0.26 M	0.074

^a The concentration of 3 was $1.0\text{--}6.0 \times 10^{-3}$ M.

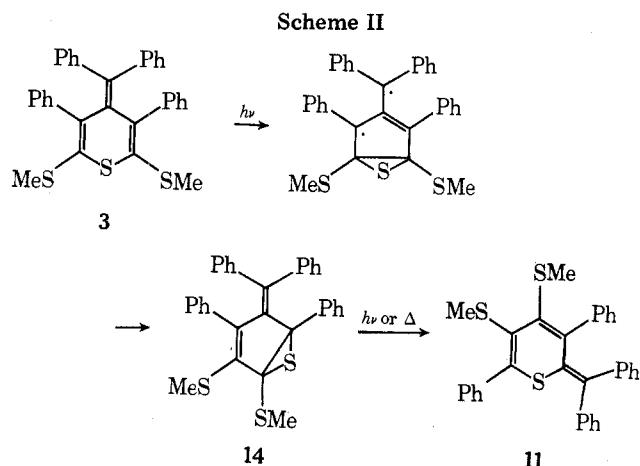
($E_T > 40$ kcal/mol¹⁸) quenched in part the photoisomerization of 3 to 11, whereas *cis*-piperylene ($E_T = 56.9$ kcal/mol) did not quench this photorearrangement (Table I). These results, together with the sensitization experiment, suggest that the π, π^* triplet might mainly be responsible for the photoisomerization of 3 to 11¹⁹ and that the triplet energy lies between 45 and 57 kcal/mol.

Stern–Volmer analyses were undertaken in benzene using cyclooctatetraene as the quencher. The result is shown in Figure 2. The rationale for the Stern–Volmer plot can be seen in the following scheme and in eq 1



$$1/\phi = \frac{k_r + k_d}{k_r} + \frac{k_q}{k_r} [Q] \quad (1)$$

where S, S¹, and S³ are the ground state, first excited singlet state, and lowest triplet state, respectively, of 3; P is product; [Q] is the concentration of quencher; k_d is the unimolecular rate of triplet decay of 3, k_q is the bimolecular rate of quenching, and k_r is the desired unimolecular rate of triplet rearrangement. When we assumed that quenching of triplet is diffusion controlled with a bimolecular rate of 3.2×10^9 M⁻¹ s⁻¹,²¹ solution of eq 1 indicates $k_r = 7.3 \times 10^7$ s⁻¹. The reaction rate of photorearrangement of 3 to 11 is fast but slower by $1/100$ th order of magnitude than the rate of photorearrange-



ment of 4,4-diphenyl-2,5-cyclohexadienone,¹⁶ which is diffusion controlled.

A proposed mechanism consistent with the observed rearrangement is depicted in Scheme II. In contrast to the photoisomerization of 1-methylenecyclohexa-2,5-dienes to 2-methylenebicyclo[3.1.0]hex-2-enes via their π, π^* singlet^{22,23} the compound 14, a possible intermediate, was not isolated in the photorearrangement of 3 and attempts to trap the intermediate in the presence of excess of triphenylphosphine have been unsuccessful. As pointed out previously⁴ this differing behavior might derive from both a heavy-atom effect of a sulfur atom²⁴ and π electron conjugation of the triene through a sulfur atom in the heterocyclic ring. A very low quantum yield and elimination of a sulfur atom were observed in the photoreaction of 1 in contrast to the diphenylmethylene analogue 3. However, it has been noted previously³ that these reactions proceed via n, π^* triplet. Hence, the difference between the rearrangement of diphenylmethylene-4*H*-thiopyran and that of 4*H*-thiopyran-4-ones might be ascribed to the role of the nonbonding electron promoted to the π system in the excited state.¹⁹

Most of 4-diphenylmethylene-4*H*-thiopyrans (4, 5, and 6) were not affected by ultraviolet irradiation, although their absorption and emission spectra are similar to those of 3. Steric repulsion between phenyl protons on C-3 and those on an exo-methylene carbon might prevent free rotation of an exo-methylene moiety which provides a mechanism for excited energy dissipation in the 1-methylene-2,5-cyclohexadienes.²⁵ On the other hand, the 4*H*-thiopyrans, 4, 5, and 6, seem to be capable of dissipating excited energy because of free rotation of an exo-methylene bond. The photoreactivity of these 4-diphenylmethylene-4*H*-thiopyrans is, therefore, sensitive to the extent of substituents in the 4*H*-thiopyran ring and similar sensitivity to the extent of substituents was observed in the photoreaction of 4*H*-thiopyran-4-ones,³ 4*H*-pyran-4-ones,²⁶ and 4-pyridones.²⁷

Experimental Section

Melting points were taken on a Yanagimoto melting point apparatus and are uncorrected. Ultraviolet spectra were recorded on a Hitachi 323 spectrophotometer. Infrared spectra were determined on a Jasco DS-402G grating spectrophotometer. Nuclear magnetic resonance spectra were obtained with a Varian T-60A or HA-100 spectrometer and with a JEOL PS 100 spectrometer using tetramethylsilane as an internal standard. Mass spectral analyses were obtained on a Hitachi RMU-6L mass spectrometer. Microanalyses were performed at the Microanalytical Laboratory of Kyoto University, Kyoto, Japan.

4-Diphenylmethylene-2,6-bis(methylthio)-3,5-diphenyl-4*H*-thiopyran (3) and 4-diphenylmethylene-2,6-diphenyl-4*H*-thiopyran were prepared according to the reported method.⁵

2,6-Bis(methylthio)-3,5-dimethyl-4*H*-thiopyran-4-thione (8). A mixture of 2.21 g of 2,6-bis(methylthio)-3,5-dimethyl-4*H*-thiopyran-

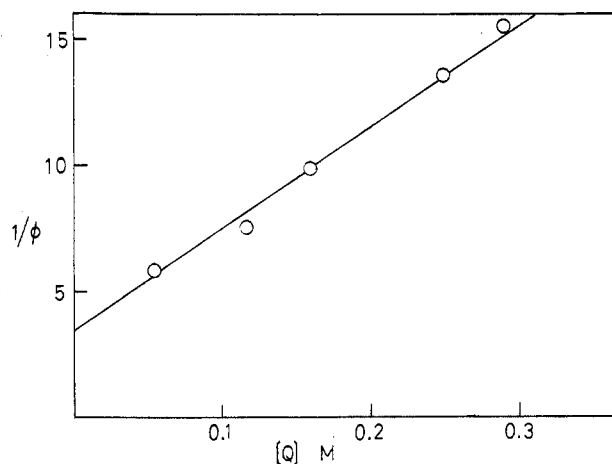


Figure 2. Plot of reciprocal of quantum yield for appearance of 11 vs. concentration of added cyclooctatetraene in the photorearrangement of 3.

ran-4-one²⁸ and 6 g of phosphorus pentasulfide in 100 ml of benzene was refluxed with stirring for 3 h. Aqueous ammonium sulfide was added to the reaction mixture. After separation of the organic layer, the aqueous solution was extracted with benzene. The combined benzene solution was dried over anhydrous sodium sulfate and concentrated under reduced pressure to give a green solid. Recrystallization from ethanol gave 1.78 g (75.6%) of 8; mp 183.0–184.5 °C; ir (KBr) 2970, 1480, 1420, 1365, 1340, 1305, 1235, 1120, 1020, 925, 750 cm^{-1} ; NMR (CDCl_3) δ 2.60 (s, 6 H), 2.66 (s, 6 H).

Anal. Calcd for $\text{C}_9\text{H}_{12}\text{S}_4$: C, 43.51; H, 4.87. Found: C, 43.47; H, 4.85.

3,5-Diphenyl-4*H*-thiopyran-4-thione (10). The procedure was the same as the one described for the preparation of 8. From 1.6 g of 3,5-diphenyl-4*H*-thiopyran-4-one^{3b} and 5 g of phosphorus pentasulfide in 100 ml of benzene there was obtained 1.33 g (78.2%) of 10 as a green solid; mp 171.5–174.0 °C; ir (KBr) 3040, 1600, 1540, 1440, 1320, 1310, 1120, 860, 830, 760, 695 cm^{-1} ; NMR (CDCl_3) δ of 7.32 (s, 10 H), 7.49 (s, 2 H).

Anal. Calcd for $\text{C}_{17}\text{H}_{12}\text{S}_2$: C, 72.82; H, 4.31. Found: C, 72.68; H, 4.28.

4-Diphenylmethylene-2,6-bis(methylthio)-3,5-dimethyl-4*H*-thiopyran (4). A solution of 1.3 g of 8 and 1.1 g of diphenyldiazomethane in 100 ml of benzene was refluxed for 4 h. After addition of 300 ml of petroleum ether to the reaction mixture at room temperature a white solid was obtained. A mixture of this solid and 10 g of copper powder in 100 ml of xylene was refluxed for 8 h. After removal of unreacted copper powder by filtration and evaporation of the solvent in vacuo three fractional recrystallizations from benzene–ligroin gave 1.56 g (78%) of colorless crystals of 4; mp 121–124 °C; ir (KBr) 3040, 2970, 1615, 1600, 1445, 1435, 1320, 1030, 915, 910, 900, 890, 770, 755, 705 cm^{-1} ; NMR (CDCl_3) δ 1.61 (s, 6 H), 2.25 (s, 6 H), 7.25 (s, 10 H); mass spectrum m/e (rel intensity) 384 (17), 383 (26), 382 (100, M^+), 336 (9), 325 (20), 334 (38), 321 (9), 320 (20), 319 (37), 289 (12), 288 (35), 287 (21), 286 (12), 285 (10), 271 (14), 244 (20), 91 (34), 78 (56), 77 (18).

Anal. Calcd for $\text{C}_{22}\text{H}_{22}\text{S}_3$: C, 69.06; H, 5.80; S, 25.15. Found: C, 68.92; H, 5.78; S, 25.00.

4-Diphenylmethylene-4*H*-thiopyran (5). A similar procedure was employed to the one described in the preparation of 4. From 0.93 g of 4*H*-thiopyran-4-thione and 1.45 g of diphenyldiazomethane 1.3 g (76%) of yellow crystals of 5 was obtained; mp 128–130 °C; uv (CH_2Cl_2) λ_{max} 344 nm (ϵ 20 800); ir (KBr) 3040, 3010, 1615, 1595, 1490, 1455, 1370, 1030, 905, 785, 755, 700 cm^{-1} ; NMR (CDCl_3) δ 6.21 and 6.43 (d of q, 4 H, $J = 1.5, 11$ Hz), 7.0–7.3 (m, 10 H); mass spectrum m/e (rel intensity) 264 (6), 263 (22), 262 (100, M^+), 261 (6), 229 (7), 228 (17), 185 (9), 184 (8), 101 (8), 100 (11).

Anal. Calcd for $\text{C}_{18}\text{H}_{14}\text{S}$: C, 82.40; H, 5.38. Found: C, 82.32; H, 5.33.

4-Diphenylmethylene-3,5-diphenyl-4*H*-thiopyran (6). A mixture of 1.3 g of 3,5-diphenyl-4*H*-thiopyran-4-thione and 1.1 g of diphenyldiazomethane in 100 ml of benzene was refluxed for 4 h. After evaporation of the solvent in vacuo, the residual solid was recrystallized from ethanol to afford 1.44 g (75%) of pale yellow crystals of 6; mp 158–159 °C; uv (CH_2Cl_2) λ_{max} 334 nm (ϵ 13 200); ir (KBr) 3040, 1620, 1600, 1535, 1490, 1445, 1030, 800, 770, 760, 750, 735, 695 cm^{-1} ; NMR (CDCl_3) δ 6.60 (s, 2 H), 6.8–7.2 (m, 20 H); mass spectrum m/e

(rel intensity) 316 (9), 315 (34), 314 (100, M⁺), 313 (19), 237 (21), 236 (9), 203 (10), 202 (8), 128 (9).

Anal. Calcd for C₃₀H₂₂S: C, 86.92; H, 5.35. Found: C, 87.08; H, 5.55.

Irradiation of 4-Diphenylmethylene-2,6-bis(methylthio)-3,5-diphenyl-4H-thiopyran (3). A solution of 0.5 g of 2,6-bis(methylthio)-3,5-diphenyl-4-diphenylmethylene-4H-thiopyran in 700 ml of benzene was irradiated with a 500-W Ushio medium-pressure mercury lamp using a Pyrex filter. The progress of the reaction was followed by TLC (silica gel), using benzene-cyclohexane (1:1) as eluent. After 2 h, nearly 100% of the starting material had reacted and the irradiation was halted. After evaporation of the solvent in vacuo, the residual solid was recrystallized from benzene-*n*-hexane to give 0.46 g (92%) of 2-diphenylmethylene-3,6-diphenyl-4,5-bis(methylthio)-2H-thiopyran, mp 207–210 °C, as yellow crystals: uv (CH₂Cl₂) λ_{max} 285 nm (ε 11 900), 328 (11 000), 403 (6900); ir (KBr) 3060, 3020, 2920, 1605, 1580, 1490, 1460, 1310, 1180, 1160, 1075, 1035, 910, 895, 845, 800, 770, 735, 700 cm⁻¹; NMR (CDCl₃) δ 2.30 (s, 3 H), 2.32 (s, 3 H), 6.6–7.4 (m, 20 H); mass spectrum *m/e* (rel intensity) 508 (22), 507 (40), 506 (100, M⁺), 476 (34), 458 (47), 426 (44), 412 (73), 380 (30), 334 (31), 167 (28), 121 (33).

Anal. Calcd for C₃₂H₂₆S₂: C, 75.84; H, 5.17; S, 18.98. Found: C, 75.75; H, 5.35; S, 19.02.

Photooxygenation of 2-Diphenylmethylene-3,6-diphenyl-4,5-bis(methylthio)-2H-thiopyran. A solution of 0.4 g of 2-diphenylmethylene-4,5-bis(methylthio)-3,6-diphenyl-2H-thiopyran in 1000 ml of methylene chloride was irradiated with a Taika 300-W medium-pressure mercury lamp equipped with the filter system for 560-nm light described by Calvert and Pitts.²⁹ Oxygen was bubbled through the reaction solution while it was irradiated for 3 h. The residue obtained on evaporation was chromatographed on silica gel with benzene-cyclohexane (2:1) to give 0.075 g of benzophenone and 0.167 g of 4,5-bis(methylthio)-3,6-diphenyl-2H-thiopyran-2-one: mp 153.0–154.5 °C; ir (KBr) 3000, 1610, 1590, 1525, 1485, 1445, 1315, 1270, 1180, 980, 825, 725, 700 cm⁻¹; NMR (CDCl₃) δ 1.79 (s, 3 H), 2.13 (s, 3 H), 7.3–7.5 (m, 10 H); mass spectrum *m/e* (rel intensity) 358 (8), 357 (10), 356 (32, M⁺) 342 (14), 341 (48), 329 (25), 328 (100), 266 (52), 234 (32), 200 (22), 121 (33).

Anal. Calcd for C₁₉H₁₆O₂S₂: C, 64.01; H, 4.52; O, 4.49; S, 26.98. Found: C, 63.98; H, 4.43; O, 4.42; S, 27.17.

Desulfurization of 2-Diphenylmethylene-3,6-diphenyl-4,5-bis(methylthio)-2H-thiopyran. Redistilled anhydrous ethylamine (30 ml) was condensed into the reaction flask equipped with a dry ice condenser as designed by Truce.³⁰ When the lithium metal dissolved and a deep blue color developed, 0.6 g of 2-diphenylmethylene-4,5-bis(methylthio)-3,6-diphenyl-2H-thiopyran was added in portions under nitrogen atmosphere. After evaporation of ethylamine at room temperature, 50 ml of water was cautiously added with cooling. After neutralization this mixture was extracted with ether. The residue obtained on evaporation was separated by preparative thick layer chromatography on silica gel with benzene-cyclohexane (2:1) as eluent to give 0.008 g of benzophenone and 0.019 g of 3,6-diphenyl-2H-thiopyran-2-one, mp 182–183 °C (lit.¹¹ 183.5–184 °C). Its ir and NMR spectra were consistent with those of 13 prepared from *trans*-1,4-diphenylbutadiene and thiophosgene.¹¹

Irradiation of 4-Diphenylmethylene-2,6-bis(methylthio)-3,5-dimethyl-4H-thiopyran, 4-Diphenylmethylene-4H-thiopyran, or 4-Diphenylmethylene-3,5-diphenyl-4H-thiopyran. A solution of the 4-diphenylmethylene-4H-thiopyrans (0.2–0.5 g) in benzene or methylene chloride (700 ml) was irradiated under nitrogen atmosphere for 14–20 h using a Ushio 500-W medium-pressure mercury lamp equipped with a Pyrex filter or a 313–436-nm solution filter.¹³ The solution was concentrated to 10 ml. The reaction mixture showed only one spot on TLC (silica gel), the *R_f* value being the same as that of the starting material.

Quantum Yield Determinations. Solutions containing various weights of cyclooctatetraene and 3 were made up to 25 ml with Spectrograde benzene, and poured into the Pyrex tube. The tubes were degassed to a pressure of 10⁻³ Torr or less in three freeze-pump-thaw cycles, and then sealed. The samples were irradiated in a merry-go-round assembly using a 100-W medium-pressure mercury arc lamp as the central light source. The light source was filtered by a CoSO₄·7H₂O–CuSO₄·5H₂O filter solution to isolate 313–436-nm light.¹³ Potassium ferrioxalate actinometry¹⁵ was used to determine the lamp intensity. After irradiation the concentration of the photo-product 11 was determined at 403 nm by quantitative ultraviolet spectroscopy. The conversions of 3 were run 5% or less.

Measurement of Fluorescence Spectra. The fluorescence excitation and emission spectra were obtained on a Hitachi MPF-4 spectrofluorometer. The fluorescence spectra (uncorrected) were

measured at 298 K in absolute ethanol (Wako Chemical). The concentration of the samples ranged from 10⁻⁵ to 10⁻⁷ M. Attempts to measure the phosphorescence excitation and emission spectra were carried out on a Hitachi MPF-4 spectrofluorometer at 77 K using Hitachi phosphoroscope attachments. Concentrations of these compounds ranged from 10⁻⁶ to 10⁻⁴ M.

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Registry No.—3, 58944-29-9; 4, 58944-30-2; 5, 58944-31-3; 6, 58944-32-4; 7, 14172-81-7; 8, 24162-39-8; 9, 1120-94-1; 10, 21125-43-9; 2,6-bis(methylthio)-3,5-dimethyl-4H-thiopyran-4-one, 24215-64-3; phosphorus pentasulfide, 1314-80-3; 3,5-diphenyl-4H-thiopyran-4-one, 13700-75-9; diphenyldiazomethane, 883-40-9; 2-diphenylmethylene-3,6-diphenyl-4,5-bis(methylthio)-2H-thiopyran, 52680-68-9; 4,5-bis(methylthio)3,6-diphenyl-2H-thiopyran-2-one, 52577-73-8.

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- Raney Ni (W-2 and W-4) could not be used for desulfurization of the photoproduct, since the reaction mixture showed at least ten spots on silica gel TLC, along with a comparable amount of tarry material. The amount isolated from the reaction mixture was not sufficient for structure elucidation.
- It was anticipated to obtain 2-diphenylmethylene-3,6-diphenyl-2H-thiopyran⁹ and/or 1,4,6,6-tetraphenylhexa-1,3,5-triene in this reaction. These compounds, however, were not isolated from the reaction mixture.
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