Photoconversion of 2,6-Bis(alkylthio)-3,5-diphenyl-4*H*-thiopyran-4-ones into 3,4-Bis(alkylthio)-2,5-diphenylcyclopentadienones

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The irradiation of 2,6-bis(alkylthio)-3,5-diphenyl-4*H*-thiopyran-4-ones (2) with a medium-pressure mercury arc lamp through a Pyrex filter produced 3,4-bis(alkylthio)-2,5-diphenylcyclopentadienones. The quantum efficiency for formation of cyclopentadienone derivatives was very low (Φ = 0·0002). Sensitization and quenching studies indicate that the reaction involves the triplet state of compounds (2). Cycloadditions of the photoproduct with some dienophiles were studied. The mechanism of the photochemical rearrangement of compounds (2) is discussed.

THE photochemistry of cyclic keto-sulphides has been recently subjected to extensive study [1] because of the occurrence of charge-transfer interactions in many of these compounds.[2] Most of the cyclic keto-sulphides studied bear an sp^3 carbon atom α to the sulphur atom, and on irradiation give ring-contracted, ring-expanded, and isomerized products.[3-6] On the other hand, irradiation of 4*H*-thiopyran-4-ones (1) which have an sp^2 carbon atom adjacent to the sulphur atom, yields dimers containing a cyclobutane ring [7] or 'head-to-tail' cage dimers.[8] The absence of charge-transfer inter-

action in compounds (1) [9] is reflected in their photo-dimerization. The formation of photodimers from compounds (1) has only been observed for unhindered 4*H*-thiopyran-4-ones [*i.e.* 2,6-disubstituted 3,5-unsub-stituted (1a—c)]. Although there is no charge-transfer interaction in structure (1), phenyl groups in the 3- and 5-positions would be expected to prevent the formation of the photodimer by their steric effect. The photo-chemistry of 2,6-bis(alkylthio)-3,5-diphenyl-4*H*-thio-pyran-4-ones and the related systems has been studied with this in mind.[10]

[1] For a review of photochemical reactions of keto-sulphides, see E. Block, *Quart. Reports Sulphur Chem.*, 1969, **4**, 256.

[2] N. J. Lonard, T. L. Brown, and T. W. Milligan, *J. Amer. Chem. Soc.*, 1959, **81**, 504; 1960, **82**, 4075; G. Bergson, G. Gleason, and L. Schotte, *Acta Chem. Scand.*, 1962, **16**, 1159.

[3] C. Ganter and J. F. Moser, *Helv. Chim. Acta*, 1968, **51**, 300; 1969, **52**, 967.

[4] P. Y. Johnson and G. A. Berchtold, *J. Org. Chem.*, 1970, **35**, 584; W. C. Lumma and G. A. Berchtold, *ibid.*, 1969, **34**, 1566.

[5] J. G. Pacifici and C. Diebert, *J. Amer. Chem. Soc.*, 1969, **91**, 4595.

[6] A. Padwa, A. Battisti, and E. Shefter, *J. Amer. Chem. Soc.*, 1969, **91**, 4000; A. Padwa and A. Battisti, *ibid.*, 1971, **93**, 1304.

[7] N. Sugiyama, Y. Sato, H. Kataoka, C. Kashima, and K. Yamada, *Bull. Chem. Soc. Japan*, 1969, **42**, 3005.

[8] N. Ishibe and M. Odani, *J. Org. Chem.*, 1971, **36**, 3142; N. Sugiyama, Y. Sato, and C. Kashima, *Bull. Chem. Soc. Japan*, 1970, **43**, 3205.

[9] E. Mayer, W. Broy, and R. Zahradnik, *Adv. Heterocyclic Chem.*, 1967, **8**, 238.

[10] Preliminary report, N. Ishibe and M. Odani, *Chem. Comm.*, 1971, 702.

RESULTS AND DISCUSSION

Irradiation of 2,6-bis(methylthio)-3,5-diphenyl-4H-thiopyran-4-one (2a) in methanol–methylene dichloride (1 : 1 v/v) (medium-pressure mercury arc lamp; Pyrex filter; nitrogen atmosphere) gave 2,5-diphenyl-3,4-bis-(methylthio)cyclopentadienone (3a), in nearly quantitative yield, and sulphur. Similar results were obtained with methylene dichloride, chloroform, or benzene as solvent. Under the same conditions the ethyl and benzyl analogues (2b and c) gave the cyclopentadienones (3b) (77%) and (3c) (30%).† The products were identified from the following spectral and chemical evidence.

(1)
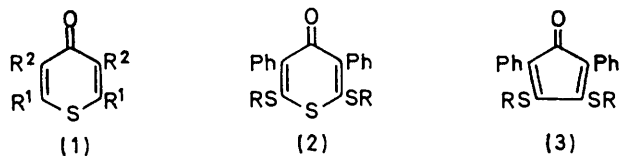
a; $R^1 = H$, $R^2 = H$
b; $R^1 = Me$, $R^2 = H$
c; $R^1 = Ph$, $R^2 = H$
d; $R^1 = SMe$, $R^2 = Me$
e; $R^1 = H$, $R^2 = Ph$

(2)

a; R = Me
b; R = Et
c; R = CH_2Ph

(3)

a; R = Me
b; R = Et
c; R = CH_2Ph

The mass spectra of the cyclopentadienones (3) showed parent peaks at m/e 324 (3a), 352 (3b), and 476 (3c), indicating that a sulphur atom had been eliminated from structure (2). The electronic spectra (Table 1) showed intense absorptions at 270 and 340 nm and broad absorption at 510—575 nm, characteristic of cyclopentadienones.[11-13] The spectrum of 2,3,4,5-tetraphenylcyclopentadienone (Table 1) is similar. The

TABLE 1

U.v. spectra of the photoproducts (3) in chloroform

| Compound	$\lambda_{max.}/nm$ (log ε)
(3a)	269 (4·27), 336 (4·04), 519 (3·69)
(3b)	270 (4·27), 340 (4·04), 510 (2·67)
(3c)	268 (5·22), 340 (4·91), 438 (2·99), 575 (2·45)
Tetraphenylcyclopentadienone	250 (4·40), 335 (32·7), 510 (3·18)

335 nm band observed for tetraphenylcyclopentadienone is shifted to shorter wavelength in 2-methyl-3,4,5-triphenylcyclopentadienone and 2,5-diethyl-3,4-diphenylcyclopentadienone.[14] This suggests an important contribution from the resonance structure (4).[11] The molecular extinction coefficients of the 340 nm band for compounds (3) are *ca.* ten times greater than those of tetracyclone derivatives.[12,13] This can be explained if the phenyl group is coplanar with the five-membered ring ketone system; tetraphenylcyclopentadienone exists as a nonplanar structure owing to steric interaction with the *ortho*-hydrogen atom of the phenyl

† T.l.c. of the mixture showed at least one other product, which was not identified.

[11] For a review of the chemistry of cyclopentadienones, see M. A. Ogliaruso, M. G. Romanelli, and E. I. Becker, *Chem. Rev.*, 1965, **65**, 261.

[12] S. B. Coan, D. E. Trucker, and E. I. Becker, *J. Amer. Chem. Soc.*, 1953, **75**, 900; 1955, **77**, 60.

ring.[15] This planar structure for (3) is supported by the strong i.r. carbonyl absorption at 5·95 μm, in agreement with that of phencyclone,[15] which exists as a planar structure (*cf.* tetraphenylcyclopentadienone, ν_{OO} 5·87 μm [15]). The n.m.r. spectra of the photoproducts (3) showed multiplets at δ 7·30—7·50 p.p.m. typical of 2,5-diphenyl substitution in cyclopentadienones.[16]

(4)

(3)

(4')
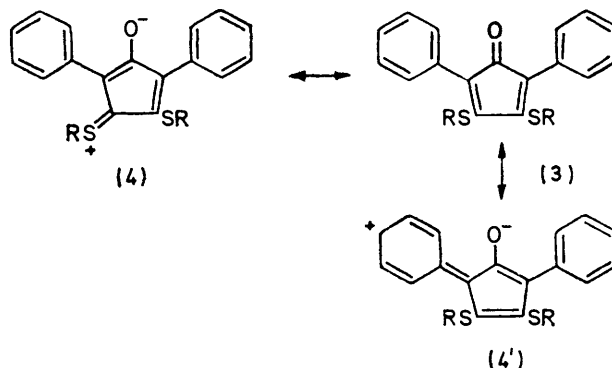
Diels–Alder reactions with some dienophiles were carried out to confirm the structures of the photoproducts. When compound (3a or b) in bromobenzene was heated with dimethyl acetylenedicarboxylate, the dimethyl 5',6'-bis(alkylthio)-*p*-terphenyl-2',3'-dicarboxylate (5a or b) was formed in high yield. Structure (5a) was confirmed by desulphurization with Raney nickel. The product was identical with an authentic sample of dimethyl *p*-terphenyl-2',3'-dicarboxylate.[17] Treatment of (3a or b) with benzyne generated from diphenyliodonium-2-carboxylate gave 1,4-diphenyl-2,3-bis(alkylthio)naphthalene (6a or b). Maleic anhydride also

(5)

a; R = Me
b; R = Et

(6)
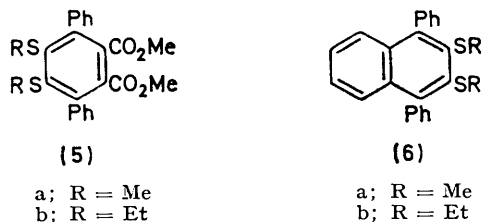
a; R = Me
b; R = Et

added to (3a) to give the dihydrophthalic anhydride (7). The n.m.r. spectrum of compound (7) showed signals at δ 8·03 (s) and 7·69 (s) (2 × Me), 4·59 and 4·37 (q, J 8·0 Hz, 2 × CH), and 2·69 (s) and 2·50 (s) p.p.m. (2 × Ph). The nonequivalence of the two sets of apparently similar protons can be explained on the basis of a preferred conformation in which the methyl groups of the methylthio-substituents are in a *trans*-relationship (7a). A Dreiding model of this adduct indicates that steric interaction between the methyl protons and the phenyl protons prevents the existence

[13] V. F. D. Agostino, M. J. Dunn, A. E. Ehrlich, and E. I. Becker, *J. Org. Chem.*, 1958, **23**, 1539.
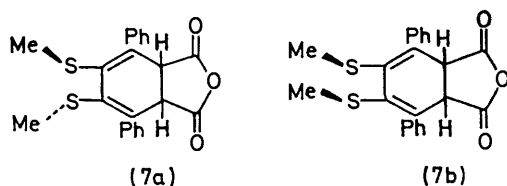
[14] C. F. H. Allen and J. A. VanAllan, *J. Org. Chem.*, 1953, **18**, 882.

[15] C. F. H. Allen and R. Y. Ning, *Canad. J. Chem.*, 1964, **42**, 2151.

[16] Ref. 11, p. 361.

[17] K. Alder and M. Schumacher, *Annalen*, 1950, **571**, 87.

of a *cis*-conformer (7b). Chemical evidence for structure (7) was obtained from the following reaction.

(7a) (7b)

Aromatization with bromine yielded the phthalic anhydride (8), whose n.m.r. spectrum showed signals at δ 2·09 (s, 2 × Me) and 7·30—7·60 p.p.m. (m, 2 × Ph). Esterification of the product with acidic methanol gave the diester (5a), which was identical with an

(7) $\xrightarrow[-HBr]{Br_2}$ (8) $\xrightarrow{MeOH, H^+}$ (5a)

SCHEME 1
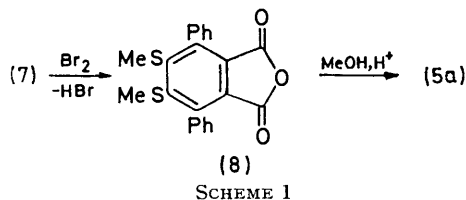
authentic sample synthesized from the addition reaction of (3a) with dimethyl acetylenedicarboxylate. These Diels–Alder reactions, in which 1,4-adducts are decarbonylated to yield benzene, naphthalene, and dihydrophthalic anhydride derivatives, are characteristic of the cyclopentadienone system.[18]

Quantum yields for the formation of the cyclopentadienone (3a) in various solvents were determined by use of a rotating photochemical assembly. Benzophenone–diphenylmethanol actinometry [19] was used throughout. Reactions were carried out to low conversions to prevent appreciable light absorption by the products, and yields were determined by u.v. spectroscopy (at $\lambda_{max.}$ 519 nm). The results (Table 2) show the

TABLE 2

Quantum yields for photolysis of the thiopyranone (2a) [a]

Added reagent	Solvent	Quantum yield ($\times 10^3$) [c]
None	PhH	0·15
None	CH₂Cl₂	0·22
None	CH₂Cl₂–MeOH(1 : 1)	0·19
None	CHCl₃	0·25
None	CHCl₃–MeOH(1 : 1)	0·20
None	CH₂Br₂	0·31
None	CH₂Br₂–MeOH(1 : 1)	0·21
Benzophenone (0·05M) [b]	CH₂Cl₂	0·19
Bis(dimethylamino)benzo-phenone (0·002M) [b]	CH₂Cl₂	0·21

[a] Concentration *ca.* 10⁻³M. [b] Absorbing over 95% of incident light. [c] Average of cyclopentadienone formation for three runs.

quantum yield for cyclopentadienone formation to be very low (average 0·0002).

[18] Ref. 11, p. 303
[19] W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Amer. Chem. Soc.*, 1961, **83**, 2789.
[20] Ref. 9, p. 249.

The u.v. absorption spectra of the thiopyranone (2a) in several solvents showed an intense band at 280 nm with a shoulder at 308 nm (see Table 3), presumably

TABLE 3

U.v. spectra of 4*H*-thiopyran-4-one derivatives

Compd.	Solvent	$\lambda_{max.}$/nm (log ε)
(2a)	CHCl₃	280 (4·39), 308sh (4·19)
(2a)	MeCN	277 (4·32), 313sh (4·13)
(2a)	MeCN–MeOH(98 : 2)	277 (4·32), 313sh (4·13)
(2a)	Chx ‡	280 (4·93), 315sh (4·70)
(2b)	CHCl₃	281 (4·17), 314sh (4·30)
(2c)	CHCl₃	281 (4·35), 317sh (4·23)
(1a) †	Chx ‡	280 (4·19), 318 (1·72)
(1d)	CHCl₃	253 (4·16), 312 (4·14)
(1e)	CHCl₃	309 (4·35)

† Ref. 20. ‡ Cyclohexane.

derived from the π–π* transition. Attempts to observe the n–π* band were unsuccessful because of the poor solubility of (2a) in nonpolar solvents [4*H*-thiopyran-4-one (1a) in cyclohexane shows an n–π* band of low intensity at 318 nm [20]].

To elucidate the multiplicity of the excited state of compound (2a), quantum yields for reactions sensitized by benzophenone (E_T 68·8 kcal mol⁻¹) [21] and 4,4'-bis-(dimethylamino)benzophenone (E_T 61·0 kcal mol⁻¹) [21] were determined in methylene dichloride, in which these sensitizers show a rapid decay rate and efficient intersystem crossing.[21] The concentrations were adjusted so that the sensitizer absorbed more than 95% of the incident light. The results are collected in Table 2. The formation of (3a) from preformed triplet (*i.e.* in the sensitized runs) indicates that rearrangement *via* the triplet state is possible. More interesting is that the quantum yields for the formation of (3a) in the sensitized runs are the same within experimental error as in the direct photolysis. Zimmerman and his group have pointed out that identical product distributions

(11)
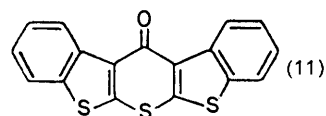
and similar quantum efficiencies under both triplet sensitization and direct irradiation conditions provide a 'fingerprint'.[22] In our case (3a) is the sole photoproduct. Our observation on the quantum yields indicates that the triplet state of (2) is the excited state responsible for the rearrangement in the direct irradiation. This conclusion is supported by effective quenching of the photoreaction of (2a). An attempt to determine the quantum efficiencies for appearance of (3a) in the presence of *cis*-penta-1,3-diene did not give reproducible quantum yields because of the low quantum efficiency of the photoreaction. In the photolysis of

[21] W. G. Herktroter, A. A. Lamola, and G. S. Hammond, *J. Amer. Chem. Soc.*, 1964, **86**, 4537.
[22] H. E. Zimmerman and K. G. Hancock, *J. Amer. Chem. Soc.*, 1968, **90**, 3749; H. E. Zimmerman and R. L. Morse, *ibid.*, p. 954; H. E. Zimmermann, K. G. Hancock, and G. C. Licke, *ibid.*, p. 4892.

(2a) on a preparative scale, however, the formation of (3a) was quenched effectively by cis-penta-1,3-diene, a good triplet quencher at the concentrations used [23] (see Experimental section). Both the high quenching efficiency of excited (2a) and the similarity in quantum efficiencies under both triplet sensitization and direct irradiation conditions clearly indicate that the photochemical reaction of (2) proceeds via the excited triplet state. While the triplet excitation energy of (2a) is not known, a lower limit of ca. 55 kcal mol^{-1} can be assumed, since the photoreaction of (2a) is effectively quenched by cis-penta-1,3-diene (E_T 56·9 kcal mol^{-1}).[24] Bis(dimethylamino)benzophenone, possessing a triplet excitation energy of 61·0 kcal mol^{-1} (ref. 21) effectively brings about the photoconversion (2a) $\longrightarrow$ (3a). These results suggest that the triplet excitation energy is in the range 55—61 kcal mol^{-1}.

As already described the u.v. spectra of compounds (2) did not show an n–π^* band. To elucidate whether the n–π^* of the π–π^* triplet state is the state responsible for the rearrangement of (2), the heavy-atom effect on the quantum yield for the appearance of (3a) was studied. The results (Table 2) show that heavy-atom solvents do not exert a noticeable effect on the formation of (3a). The quantum yield in methylene dibromide is only twice that in benzene. If the photoreaction of (2) were to proceed via the π–π^* triplet state, the heavy-atom perturbation should show a marked increase on the quantum yield, as observed in the photodimerization of acenaphthylene.[25] The n–π^* excited state is expected to be relatively insensitive to heavy-atom perturbation since the spin–orbit coupling inherent in the carbonyl function is comparable to or greater than that due to a heavy atom.[26] This has been confirmed in a study of singlet–triplet absorption in halogen-substituted benzophenones [27] and in the photochemical processes of aliphatic ketones [28] and of coumarin.[29] Insensitivity of the quantum yield to heavy-atom perturbation suggests that the n–π^* excited triplet state of (2) is responsible for the photoreaction of (2).

As outlined in Scheme 2, two mechanisms can be considered. The first involves C–S bond homolysis followed by diradical reorganization (path a). The second involves excitation to the n–π^* singlet state; this is then converted into the triplet state which in turn forms a species which may be represented by the polar structure (9). The latter may then rearrange to (10) (cf. 4,4-diphenylcyclohexa-2,5-dienone [30]). The intermediate (9) or (10) is then desulphurised, to give structure (3). An attempt to obtain clear evidence

for the intermediacy of structure (10) was unsuccessful. Irradiation of (2a) in the presence of triphenylphosphine produced both (3a) and triphenylphosphine sulphide. However, though triphenylphosphine is a good reagent for eliminating the sulphur atom from an episulphide,[31] irradiation of triphenylphosphine in the presence of sulphur also yielded triphenylphosphine sulphide. Recently unstable bicyclic episulphides have been isolated from the photolysis of 2,5-dihydrothiophens.[32]
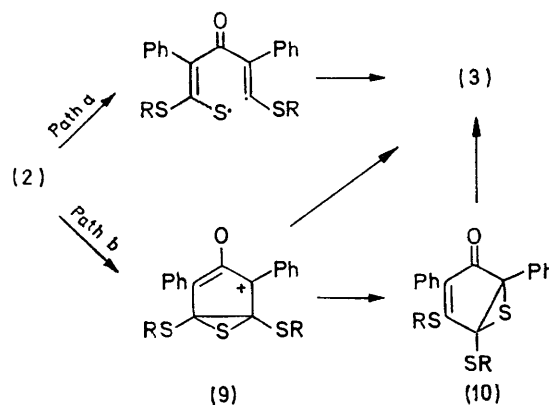
SCHEME 2

These results led us to irradiate compound (2a) at low temperature. Photolysis in methylene dichloride at $-50°$ resulted in the formation of (3a), obtained after removal of the solvent under vacuum at this temperature. This suggests that the sulphur atom is eliminated photochemically.[32,33] While we cannot exclude the possibility of path a, we believe that path b is the mechanism responsible for formation of (3). The photorearrangement of (2) is effectively quenched by cis-penta-1,3-diene, although the photochemical rearrangement of 4,4-diphenylcyclohexa-2,5-dienone was not quenched by the triplet quencher, which indicates that the triplet reaction rate, k_r, is greater than 10^{10} s^{-1}.[34] This suggests that k_r for rearrangement is small compared with that of 4,4-diphenylcyclohexa-2,5-dienone.

To investigate the scope of the photoreaction, the photolysis of 2,6-bis(methylthio)-3,5-dimethyl-4H-thiopyran-4-one (1d) was carried out. Both direct and benzophenone-sensitized irradiation in methylene dichloride did not affect the starting material. Phenyl

[23] G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, J. Amer. Chem. Soc., 1964, 86, 3197.

[24] A. A. Lamola, 'Energy Transfer and Organic Photochemistry,' ed. A. A. Lamola and N. J. Turro, Interscience, New York, 1969, p. 102.

[25] D. O. Cowan and R. L. E. Drisko, J. Amer. Chem. Soc., 1967, 89, 3068; 1970, 92, 6281, 6286.

[26] M. A. El-Sayed, J. Chem. Phys., 1964, 41, 2462.

[27] R. F. Brockman and D. R. Kearns, J. Chem. Phys., 1967, 46, 2333.

[28] P. J. Wagner, J. Chem. Phys., 1966, 45, 2335.

[29] H. Morrison, H. Curtis, and T. McDowell, J. Amer. Chem. Soc., 1966, 88, 5415; H. Morrison and R. Hoffman, Chem. Comm., 1968, 453; R. Hoffman, P. Wells, and H. Morrison, J. Org. Chem., 1971, 36, 102.

[30] For a review, see P. J. Kropp, Org. Photochem., 1967, 1, 1; K. Schaffner, Adv. Photochem., 1966, 4, 81.

[31] N. P. Nemeiter and F. G. Bordwell, J. Amer. Chem. Soc., 1959, 81, 578; D. E. Bissing and A. J. Speziale, ibid., 1965, 87, 2683; B. M. Trost and S. Ziman, Chem. Comm., 1969, 181.

[32] R. M. Kellog, J. Amer. Chem. Soc., 1971, 93, 2344.

[33] A. Padwa and E. S. Hand, Chem. Comm., 1965, 506; A. Padwa, D. Crumrine, and S. Shubber, J. Amer. Chem. Soc., 1964, 88, 3064.

[34] H. E. Zimmerman and J. S. Swenton, J. Amer. Chem. Soc., 1967, 89, 906.

groups on the 3- and 5-positions of 4*H*-thiopyran-4-one would be expected to stabilize the intermediate (9) more effectively than the methyl group. This effect is apparently important, but is not always sufficient for the photoconversion, since irradiation of 3,5-diphenyl-4*H*-thiopyran-4-one (1e) had no effect. A Dreiding model indicates that in structure (2) coplanarity of the phenyl ring with the heterocyclic ring is prevented by steric repulsion between a phenyl proton and a thiomethyl proton, whereas in (1d) and (1e) there is no steric crowding of the substituents. This steric crowding must be important for the photorearrangement of 4*H*-thiopyran-4-one derivatives. We have recently reported that 2,6-disubstituted 3,5-diphenyl-4*H*-pyran-4-ones rearranged photochemically to 2*H*-pyran-2-ones.[35] Irradiation of (11) (a coplanar compound) in methylene dichloride did not affect the starting material. The u.v. spectra of compounds (2) and (1) show similar patterns. To clarify these observations, a study of the emission spectroscopic properties of compounds (2) and (1) is planned.

Structure (3) is apparently the first reported example of a cyclopentadienone with two phenyl substituents which exists as a monomer at room temperature; only cyclopentadienone derivatives substituted with at least three phenyl groups have previously been reported to exist as monomers.[11]

EXPERIMENTAL

M.p.s were taken with a hot-stage apparatus. U.v. spectra were measured with a Hitachi 124 spectrophotometer, i.r. spectra with a JASCO-402G spectrophotometer, and n.m.r. spectra for solutions in [²H]chloroform with a JEOLCO PS-100 spectrometer (tetramethylsilane as internal standard). Mass spectra were obtained with a Hitachi spectrometer (RMU6L).

*2,6-Dimercapto-3,5-diphenyl-*4H-*thiopyran-4-one.*— The method reported by Apitzsch[36] and Tucker,[37] slightly modified, was used for this preparation. A solution of dibenzyl ketone (25 g) in carbon disulphide (37 g) was added to powdered potassium hydroxide (26·6 g) with vigorous stirring during 10 min at such a rate as to maintain the vigorous evolution of heat. The mixture was then stirred for 30 min at room temperature. The resultant dark red solid was heated for 2 h at 50—60°, then hydrolysed with water (300 ml). Unchanged dibenzyl ketone and excess of carbon disulphide were removed by extraction with ether. The crude product was obtained by acidification of the cold aqueous solution with dilute hydrochloric acid. Precipitation of the oily brown mass was accompanied by evolution of hydrogen sulphide. The oil slowly crystallized; recrystallization from chloroform gave an orange solid (63%), m.p. 163—165° (lit.,[36,37] 164°); δ 2·16 (2H, s), and 7·2—7·6 p.p.m. (10H, m).

*2,6-Bis(alkylthio)-3,5-diphenyl-*4H-*thiopyran-4-ones* (2).[36] —The m.p.s of these products were consistent with those reported.[36,37] I.r. and n.m.r. spectral data are given in Table 4.

[35] N. Ishibe, M. Odani, and M. Sunami, *Chem. Comm.*, 1971, 1034.

[36] H. Apitzsch, *Ber.*, 1905, **38**, 2888.

*2,6-Bis(methylthio)-3,5-dimethyl-*4H-*thiopyran-4-one* (1d).[36]—This material had m.p. 122—123° (lit.,[36] 123°); spectral properties are shown in Tables 3 and 4.

TABLE 4
I.r. and n.m.r. spectral data

Compound	$v_{max.}$ (C=O)/ cm^{-1}	δ(p.p.m.)
(2a)	1575	2·44 (6H, s), 7·2—7·4 (10H, m)
(2b)	1580	1·29 (6H, t, *J* 6·0 Hz), 2·91 (4H, q, *J* 5·5 Hz), 7·15—7·5 (10H, m)
(2c)	1558	4·07 (4H, s), 7·1—7·4 (20H, m)
(3a)	1686	2·23 (6H, s), 7·3—7·55 (10H, m)
(3b)	1688	1·11 (6H, t, *J* 6·0 Hz), 2·68 (4H, q, *J* 5·5 Hz), 7·25—7·6 (10H, m)
(3c)	1676	3·88 (4H, s), 7·0—7·5 (20H, m)
(1a)	1560	2·24 (3H, s), 2·65 (3H, s)
(1e)	1580	7·25—7·6 (10H, m), 7·78 (2H, s)

*3,5-Diphenyl-*4H-*thiopyran-4-one* (1e).—A mixture of 2,6-dimercapto-3,5-diphenyl-4*H*-thiopyran-4-one (1 g) and Raney nickel (15 g) in 70% aqueous ethanol (150 ml) was refluxed for 24 h. After filtration and evaporation of the ethanol under vacuum, the aqueous solution was extracted with ether. Evaporation of the extract left compound (1e) (41%), m.p. 168—169° (from ethanol) (lit.,[38] 167°). Spectral properties are given in Tables 3 and 4.

12H-Bis[1]benzothieno[2,3-b:3′,2′-e]thiopyran-12-one (11).[38]—This material had m.p. 228—229° (lit.,[38] 232°).

*Irradiation of 2,6-Bis(alkylthio)-3,5-diphenyl-*4H-*thiopyran-4-ones.*—A solution of compound (2a) (1·5 g) in methanol–methylene dichloride (1 : 1 v/v; 200 ml) was irradiated under nitrogen with a Taika medium-pressure mercury arc lamp through a Pyrex filter for 50 h. After 5 h the solution had become red. The solvent was evaporated and the residual dark brown solid was chromatographed on silica gel with benzene–chloroform (7 : 3) as eluant to afford sulphur (26 mg), the cyclopentadienone (3a) (380 mg), and starting material (950 mg). The crude photoproduct was recrystallized from methanol to give dark red *needles*, m.p. 123—124°. Spectral properties are given in Tables 1 and 4; *m/e* 324 (M$^+$) (Found: C, 69·55; H, 4·9; O, 5·5; S, 19·9. C$_{19}$H$_{18}$OS$_2$ requires C, 70·3; H, 5·0; O, 4·9; S, 19·8%).

Compound (2b) was similarly irradiated. Chromatography on silica gel with benzene–chloroform (6 : 4) gave the cyclopentadienone (3b) (280 mg) and sulphur (25 mg). Recrystallization from ether yielded dark red *needles*, m.p. 94—95° (spectral properties in Tables 1 and 4), *m/e* 352 (M$^+$) (Found: C, 71·3; H, 5·85; O, 4·5. C$_{21}$H$_{20}$OS$_2$ requires C, 71·55; H, 5·7; O, 4·55%).

After similar photolysis of (2c), silica gel chromatography with benzene–chloroform (7 : 3) gave a reddish brown solid (80 mg). Recrystallization from ether gave brown *crystals* (3c), m.p. 178—181°, *m/e* 476 (M$^+$) (spectral properties in Tables 1 and 4) (Found: C, 83·6; H, 5·35; O, 3·3. C$_{31}$H$_{24}$OS$_2$ requires C, 83·75; H, 5·45; O, 3·6%).

Irradiation of Compounds (1d), (1e), *and* (11).—A solution of the thiopyranone (1·5 g) in acetonitrile (200 ml) was irradiated with a Taika 100 W medium-pressure mercury arc lamp (Pyrex or quarz filter) under nitrogen for 60 h. The usual work-up gave only starting material.

[37] H. J. Teague and W. P. Tucker, *J. Org. Chem.*, 1967, **32**, 3140.

[38] A. Schönberg and R. von Ardenne, *Chem. Ber.*, 1966, **99**, 3316.

Quenching of the Photoreaction of the Thiopyranone (2a).— A mixture of compound (2a) (1·5 g) and *cis*-penta-1,3-diene (0·3—0·8 g) in methylene dichloride (200 ml) was irradiated under nitrogen with a Taika medium-pressure mercury arc lamp for 50 h. The concentrations of photoproduct (3a) were determined spectrometrically by recording the absorbance at 519 nm. The yield of (3a) decreased to 5—15%.

Quantum Yield Determinations.—All quantitative measurements were made by use of a rotating assembly with a central light source [internal water-cooled mercury lamp (Taika 100 W)]. Samples in 13 mm Pyrex ampoules were placed in holders on the assembly *ca.* 5 cm from the immersion well. The light of λ 312 nm was isolated with a filter solution of $NiSO_4,6H_2O$–$CoSO_4,7H_2O$–biphthalate [39] in water circulated through the inner jacket. All studies were carried out at room temperature. Samples in Pyrex ampoules were degassed to 10^{-3} mmHg in three freeze–thaw cycles and then sealed under vacuum. Benzophenone–diphenylmethanol actinometry was used for quantum yield determinations. An actinometer quantum yield of 0·69 was used when the concentration of benzophenone and diphenylmethanol in benzene was 0·1M.[19] Reliably reproducible output rates of $1·89 \times 10^{15}$ quanta s^{-1} were recorded. After the irradiation the degree of reaction was determined by quantitative u.v. spectroscopy. The conversions of (2a) were taken to 2% or less.

Dimethyl 5′,6′-Bis(alkylthio)-p-terphenyl-2′,3′-dicarboxylates (5a *and* b).—A mixture of the cyclopentadienone (3a) (150 mg) and dimethyl acetylenedicarboxylate (68 mg) in bromobenzene (2 ml) was refluxed until the characteristic red colour of (3a) had disappeared. The mixture was cooled in ice–salt and light petroleum (20 ml) was added to give a pale yellow precipitate. Recrystallization from cyclohexane yielded colourless *crystals* (5a) (70%), m.p. 194—195°; $\nu_{max.}$ (KBr) 1742 and 1722 cm^{-1} (CO); δ 2·12 (6H, s), 3·45 (6H, s), and 7·3—7·5 p.p.m. (10H, m); *m/e* 438 (M^+) (Found: C, 65·8; H, 5·15; O, 14·3; S, 14·5. $C_{24}H_{22}O_4S_2$ requires C, 65·8; H, 5·05; O, 14·6; S, 14·6%).

The *diester* (5b) was similarly obtained (84%) from (3b); m.p. 106—109°; $\nu_{max.}$ (KBr) 1723 cm^{-1} (CO); δ 0·98 (6H, t, *J* 6·0 Hz), 2·57 (4H, q, *J* 5·5 Hz), and 7·25—7·5 p.p.m. (10H, m); *m/e* 466 (M^+) (Found: C, 65·65; H, 5·35; O, 13·5. $C_{26}H_{26}O_4S_2$ requires C, 66·95; H, 5·65; O, 13·7%).

2,3-Bis(alkylthio)-1,4-diphenylnaphthalenes (6a *and* b).— A mixture of the cyclopentadienone (3a) (326 mg) and 2-phenyliodoniobenzoate [40] (diphenyliodonium-2-carboxylate) (425 mg) in diethylbenzene (2·5 ml) was heated with a microburner until it acquired an amber colour. Diethylbenzene was carefully distilled off and 95% ethanol (10 ml) was added to the residual oil. The solution was refluxed for 1 h, then stored at 0° to yield colourless crystals which afforded *compound* (6a) (38%), m.p. 172—173° (from ethanol); $\lambda_{max.}$ (CHCl$_3$) 247 (log ϵ 4·59) and 292 nm (4·13); δ 2·25 (6H, s) and 7·3—7·5 p.p.m. (14H, m); *m/e* 372 (M^+) (Found: C, 77·15; H, 5·55; S, 17·3. $C_{24}H_{20}S_2$ requires C, 77·4; H, 5·4; S, 17·2%).

Compound (6b) similarly prepared from (3b) in 46% yield had m.p. 123—124°; $\lambda_{max.}$ (CHCl$_3$) 247 (log ϵ 4·64) and 294 nm (4·16); δ 1·04 (6H, t, *J* 6·0 Hz), 2·75 (4H, q, *J* 5·5 Hz), and 7·25—7·6 p.p.m. (14H, m); *m/e* 400 (M^+) (Found: C, 78·2; H, 6·15. $C_{26}H_{24}S_2$ requires C, 77·95; H, 6·05%).

Dimethyl p-*Terphenyl-2′,3′-dicarboxylate.*—A solution of the diester (5a) (150 mg) in 70% aqueous ethanol (100 ml) was refluxed with Raney nickel (15 g) for 60 h, cooled to room temperature, and filtered. The filtrate was concentrated *in vacuo* to give a solid, which afforded dimethyl *p*-terphenyl-2′,3′-dicarboxylate (89 mg), m.p. 190—191° (from ethanol) (lit.,[17] 180°); $\lambda_{max.}$ (CHCl$_3$) 261 nm (log ϵ 4·40); δ 3·60 (6H, s), 7·40 (10H, s), and 7·51 p.p.m. (s, 2H); *m/e* 346 (M^+) (Found: C, 76·0; H, 5·2. Calc. for $C_{22}H_{18}O_4$: C, 76·3; H, 5·25%).

1,2-Dihydro-4,5-bis(methylthio)-3,6-diphenylphthalic Anhydride (7a).—A mixture of the cyclopentadienone (3a) (40 mg) and maleic anhydride (13 mg) in bromobenzene (2 ml) was refluxed for 4 h until the characteristic colour of (3a) had disappeared. The solvent was removed and the residual solid afforded yellow *crystals* (7a) (93%), m.p. 223—226° (from benzene–light petroleum); $\nu_{max.}$ (KBr) 1820 and 1750 cm^{-1} (CO); δ 8·08 (3H, s), 7·69 (3H, s), 4·59 and 4·37 (2H, q, *J* 8·0 Hz), 2·69 (5H, s), and 2·50 p.p.m. (5H, s); *m/e* 394 (M^+) (Found: C, 67·15; H, 4·65; O, 11·9; S, 16·0. $C_{22}H_{18}O_3S_2$ requires C, 67·0; H, 4·6; O, 12·15; S, 16·25%).

4,5-Bis(methylthio)-3,6-diphenylphthalic Anhydride (8).— A mixture of the anhydride (7a) (169 mg) and bromine (0·2 ml) in bromobenzene (1 ml) was refluxed for 1 h. After removal of bromobenzene, the residual solid was crystallized from benzene–light petroleum to yield yellow *crystals* (8) (82%), m.p. 196—197°; $\lambda_{max.}$ (CHCl$_3$) 271 (log ϵ 4·13), 319 (3·85), and 361 nm (3·81); δ 2·09 (6H, s) and 7·3—7·6 p.p.m. (10H, m); *m/e* 392 (M^+) (Found: C, 67·2; H, 4·4; O, 12·3. $C_{22}H_{16}O_3S_2$ requires C, 67·3; H, 4·1; O, 12·25%).

Methanolysis of the Anhydride (8).—A solution of the anhydride (8) (80 mg) and concentrated sulphuric acid (0·1 ml) in methanol was refluxed for 90 min. After evaporation of the methanol, benzene (1 ml) was added. The benzene was distilled off and water (20 ml) was added; the mixture was then neutralized with aqueous potassium hydroxide and extracted with chloroform. After concentration of the extract, the diester (5a) was isolated by preparative t.l.c. with benzene–chloroform (1 : 1) as eluant. The product was identical with an authentic sample prepared from the reaction of (3a) with dimethyl acetylenedicarboxylate.

[39] M. Koizumi, M. Shida, S. Kato, N. Mataga, and A. Imamura, 'Zikken Kagaku Koza,' ed. M. Kotake, Maruzen, Tokyo, 1956, vol. 6, p. 272
[40] L. F. Fieser and M. J. Haddadin, *Org. Synth.*, 1966, **46**, 107.