Photochemical Reaction of 2,4,4,6-Tetraaryl-4*H*-Pyrans and -4*H*-Thiopyrans with Colour Change by a 1,5-Electrocyclic Reaction. X-Ray Molecular Structure of 4-Methyl-2,3,6-triphenyl-2*H*-thiopyran

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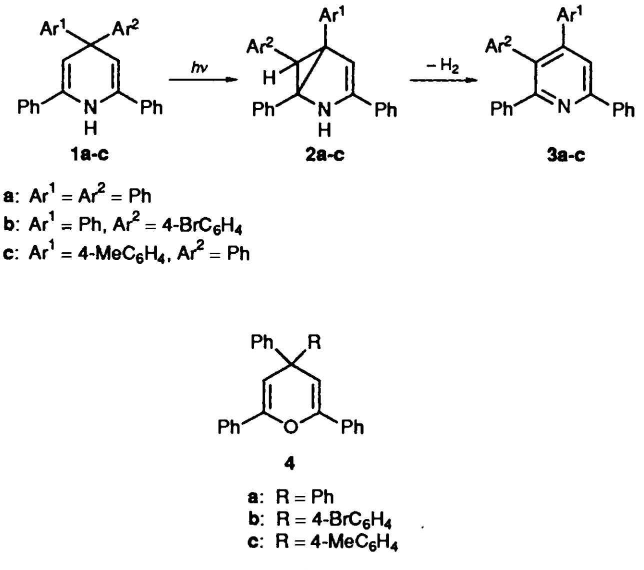
2,4,4,6-Tetraphenyl-4*H*-pyran and -4*H*-thiopyran exhibited a photochemical colour change in the solid state. On irradiation in solution, 2,4,4,6-tetraphenyl-4*H*-pyran gave 1,3,5,6-tetraphenyl-2-oxabicyclo[3.1.0]hex-3-ene, while the 4*H*-thiopyran gave 1,3,5,6-tetraphenyl-2-thiabicyclo-[3.1.0]hex-3-ene as an initial photoproduct, followed by further transformation into 2,3,4,6-tetraphenyl-2*H*-thiopyran. 4-(4-Bromophenyl)-2,4,6-triphenyl-4*H*-pyran, 4-(4-methylphenyl)-2,4,6-triphenyl-4*H*-pyran, and 4-(4-bromophenyl)-2,4,6-triphenyl-4*H*-thiopyran also showed photochemical colour changes and finally gave both the phenyl-migrated and the (substituted phenyl)-migrated products in comparable yields in each case. 4-Methyl-2,4,6-triphenyl-4*H*-thiopyran showed no photochemical colour change in the solid state, but in solution it afforded 4-methyl-2,3,6-triphenyl-2*H*-thiopyran, whose structure was confirmed by X-ray analysis. Based on comparison with the photochemical behaviour of 2,4,4,6-tetraphenyl-1,4-dihydropyridine and 2,2,4,6-tetraphenyl-1,2-dihydro-1,3,5-triazine, a six-membered ylide was proposed as the coloured photochemical intermediate.

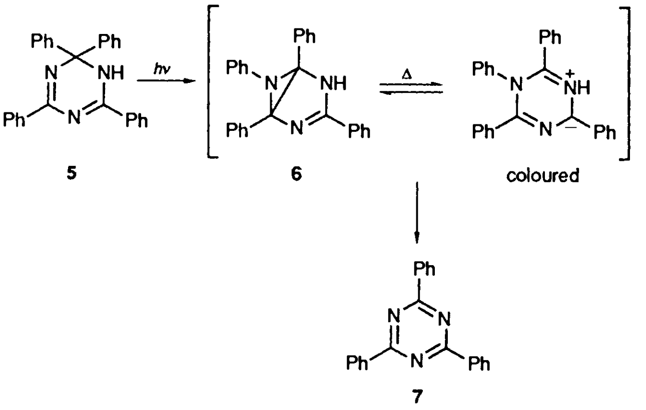
2,4,4,6-Tetraphenyl-1,4-dihydropyridine **1a** was reported to show photochromism both in the solid state and in oxygen-free solutions.[1,2] Recently one of us revealed that the colour change undergone by compound **1a** is not reversible; after prolonged irradiation compound **1a** gave 2,3,4,6-tetraphenylpyridine **3a** as a main photoproduct which was formed through a bicyclic intermediate **2a** by a di-π-methane rearrangement, followed by dehydrogenation (Scheme 1).[3] 2,4,4,6-Tetraphenyl-4*H*-pyran **4a**, which is the oxygen analogue of compound **1a**, has also been known to show photocolouration and bleaching in the solid state,[4] although its photochemical behaviour has not been fully investigated. The structure of the coloured species formed from compound **1a** is also still unknown. 2,2,4,6-Tetraphenyl-1,2-dihydro-1,3,5-triazine **5** has been known to exhibit a photochemical colour change in the solid state;[5] this substrate has a structure which is similar to that of compound **1a** or **4a**. In our previous paper we proposed a mechanism for the formation of the coloured species from compound **5** involving di-π-methane rearrangement to give a bicyclic intermediate **6** followed by a 1,5-electrocyclic ring-opening reaction (Scheme 2).[6] Based on the above proposals we expected that other heterocycles, *e.g.* 2,4,4,6-tetraaryl-4*H*-thiopyrans **8** and 2,4,4,6-tetraphenyl-4*H*-1,3-oxazine **9**, having a similar structure to that of compounds **1a**, **4a** and also **5**, can exhibit a photochemical colour change probably by a similar reaction pathway. This paper deals with spectroscopic studies of the photochemical behaviour of substrates **4**, **8**, and **9** both in the solid state and in solution, and proposes the structure of the coloured species derived from substrates **4**, **8** and **1**.



a: $Ar^1 = Ar^2 = Ph$
b: $Ar^1 = Ph, Ar^2 = 4\text{-}BrC_6H_4$
c: $Ar^1 = 4\text{-}MeC_6H_4, Ar^2 = Ph$

a: $R = Ph$
b: $R = 4\text{-}BrC_6H_4$
c: $R = 4\text{-}MeC_6H_4$

Scheme 1



Scheme 2

Results and Discussion

Photochemical Colour Change in the Solid State.—Colourless crystals of **4a** turned violet in a few minutes when irradiated with UV light. The UV spectrum of the coloured crystals recorded in a KBr pellet showed a broad absorption band around 590 nm. The violet colour gradually faded in the dark. Other 4*H*-pyrans (**4b,c**) and 4*H*-thiopyrans (**8a,b**) also exhibited a similar colour change (from colourless to violet) in the solid state, but 4-methylthiopyran **8d** and the oxazine **9** remained colourless on exposure to UV light. Although compounds **1a–c**

Table 1 Photochemical behaviour of compounds **1**, **4**, **5**, **8** and **9** in solution and in the solid state

Substrate	Colour change		Photoproducts		
	Solution	Solid	Bicyclic	Secondary	Solid-state
1a[a]	+	+	**2a**	**3a**	**3a**
1b[a]	+	+	**2b**	**3b**	
1c[a]	+	+	**2c**	**3c**	
4a	−	+	**10a**		
4b	−	+	**10b**, **10b′**		
4c	−	+	**10c**, **10c′**		
5[b]	−	+	**6**	**7**	**7**
8a	−	+	**11a**	**12a**	**12a**
8b	−	+	**11b**, **11b′**	**12b**, **12b′**	**12b**, **12b′**
8d	−	−	**11d**	**12d**	
9	−	−	**13**		

[a] Ref. 3. [b] Ref. 6.

Table 2 Chemical shifts of the characteristic ^1H NMR signals for the bicyclic products **2**, **10**, **11** and **13** and the starting heterocycles **1**, **4**, **8** and **9** in $[^2H_6]$acetone

Compound	Bicyclic product			Heterocycles
	Cyclopropyl (6-H)	Olefinic (4-H)	Ratio A:B	Olefinic (3-, 5-H)
2a[a]	3.11			**1a** 5.25
10a	3.70	5.80		**4a** 6.00
10b or	A 3.68	5.82		**4b** 6.01
10b′	B 3.74	5.81	1.5:1	
10c or	A 3.63	5.79		**4c** 5.98
10c′	B 3.66	5.76	1.3:1	
11a	3.81	6.25		**8a** 6.35
11b or	A 3.79	6.26		**8b** 6.34
11b′	B 3.82	6.25	1.4:1	
13	4.00			**9** 6.41

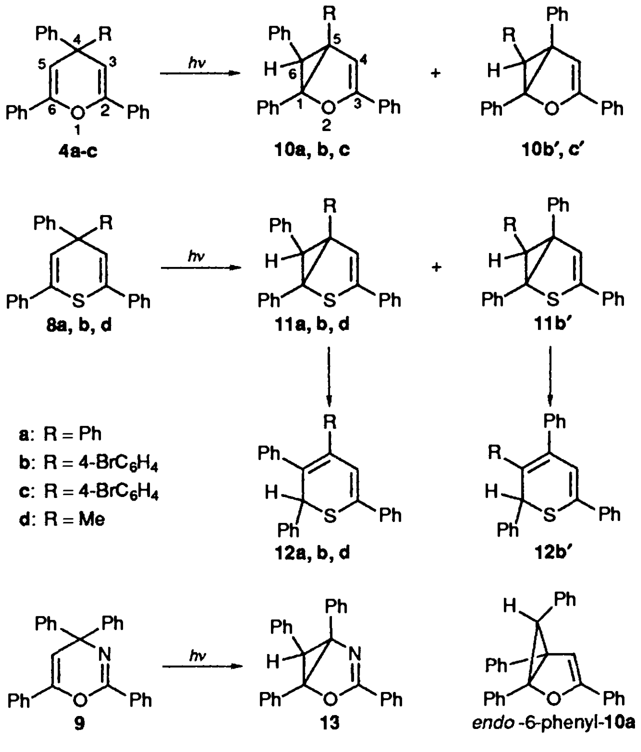
[a] Ref. 3; solvent C_6D_6.

exhibited a photochemical colour change in solution, none of the compounds **4**, **8** and **9** showed such a change even at low temperature (Table 1).

Photochemical Reactions of Compounds **4**, **8** *and* **9** *in Solution.*—All the compounds investigated, **4**, **8** and **9**, have a di-π-methane moiety composed of an aryl group at the 4-position and an olefinic group in the heterocycle. In order to characterize photoproducts by means of NMR spectroscopy, photolyses of substrates **4**, **8** and **9** were carried out in $[^2H_6]$acetone and variation of ^1H NMR spectra with repeated irradiation was recorded. On irradiation of a solution of compound **4a** the signal of the olefinic protons 3-, 5-H at δ 6.0 decreased with the appearance of two singlets at δ 3.7 and 5.8, which were assigned to compound **10a**. After irradiation for 6 h compound **4a** was no longer detected in the ^1H and ^{13}C NMR spectra and the resulting spectra suggested that the bicyclic compound **10a** was produced as a sole product. These facts indicated the occurrence of the same type of di-π-methane rearrangement as that reported for substrates **1a–c**. Isolation of the photoproduct was attempted, but was unsuccessful. Gravel *et al.* reported that 4,4-diphenyl-4*H*-pyran underwent di-π-methane rearrangement to give *trans-endo*-5,6-diphenyl-2-oxabicyclo[3.1.0]hex-3-ene and the *trans-endo* relationship of the phenyl groups is characteristic for this type of rearrangement.[7] In the case of compound **10a**, although the stereochemistry of the cyclopropyl ring could not be unambiguously determined it is reasonable to assign it to the 6-*endo* isomer based on the close similarity of the rearrangement process to that reported by Gravel *et al.* The observation that the olefinic proton 4-H in compound **10a** (δ 5.80) resonates at higher field than 3-, 5-H in compound **4a** (δ 6.00) may be due to the anisotropic shielding effect by the *endo*-phenyl group.

The *para*-substituted derivatives **4b** and **4c** gave two photoproducts in each case. These two products were separately observed in the ^1H NMR spectra and their ratio could be estimated from the relative signal intensities (Table 2). Although unambiguous structural assignments are not possible from the NMR data alone, it is likely that one of the two products was **10b** from **4b** (**10c** from **4c**), which was formed by migration of the phenyl group at the 4-position, and another one was **10b′** from **4b** (**10c′** from **4c**), which was an aryl-migrated product.

On irradiation of the 4*H*-thiopyran **8a** in $[^2H_6]$acetone the formation of the corresponding bicyclic product **11a** was revealed by the ^1H NMR spectrum. Under prolonged irradiation, however, two signals (δ 3.81, 6.25) due to compound **11a** decreased and the other two singlets appeared at δ 5.07 and 6.85, indicating that a secondary product was formed at the expense of the primary product **11a**. Although the secondary product could not be isolated with satisfactory purity, it was identified as 2,3,4,6-tetraphenyl-2*H*-thiopyran **12a** on the basis of similarities in the ^1H and ^{13}C NMR spectra with those of compound **12d** (*vide infra*). From an analogy with the photochemical reactions of compound **4b**, the *p*-bromo derivative **8b** was expected to give both the phenyl-migrated and the (*p*-bromophenyl)-migrated products. In fact, irradiation of **8b** in $[^2H_6]$acetone yielded compounds **11b** and **11b′** as primary products. When irradiation was continued the NMR signals due to **11b** and **11b′** decreased and two new sets of singlets appeared at δ 5.08 and 5.07, and δ 6.85 and 6.83 (*ca.* 7:5 respectively), indicating that primary products **11b** and **11b′** were transformed into the corresponding 2*H*-thiopyrans **12b** and **12b′**, respectively (Scheme 3).



Scheme 3

Although compound **8d** did not exhibit a photochemical colour change in the solid state, photolysis *did* occur in $[^2H_6]$acetone. In the ^1H NMR spectrum of the irradiated solution no signal assignable to a cyclopropyl proton of a

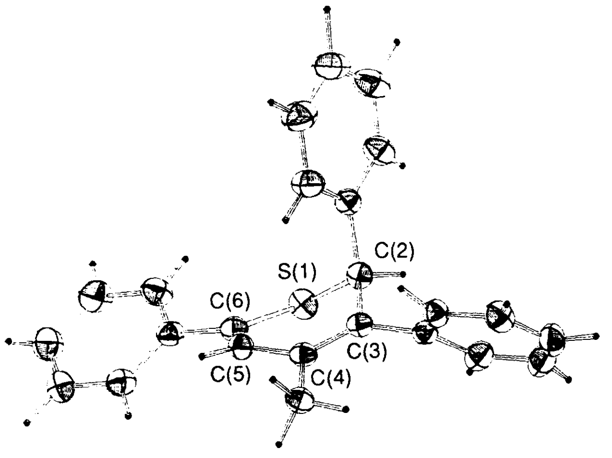


Fig. 1 ORTEP plot[8] of compound **12d**. Thermal ellipsoids enclose the 30% probability level

bicyclic intermediate similar to compound **11a** or **11b** was detected. Instead, two signals appeared at δ 4.87 and 6.73 accompanying a decrease of the signal due to the olefinic protons (δ 6.06) of the substrate **8d**. After irradiation had been continued until the starting material was completely consumed, the photoproduct was isolated as colourless crystals and unequivocally identified as 4-methyl-2,3,6-triphenyl-2*H*-thiopyran **12d** by means of X-ray crystal structure analysis (Fig. 1). On the basis of the observed photochemical processes of compounds **8a** and **8b** it is reasonable to think that compound **8d** also underwent di-π-methane rearrangement to give the bicyclic intermediate **11d** at an early stage of irradiation. It was, however, rapidly transformed into compound **12d** under the present experimental conditions.

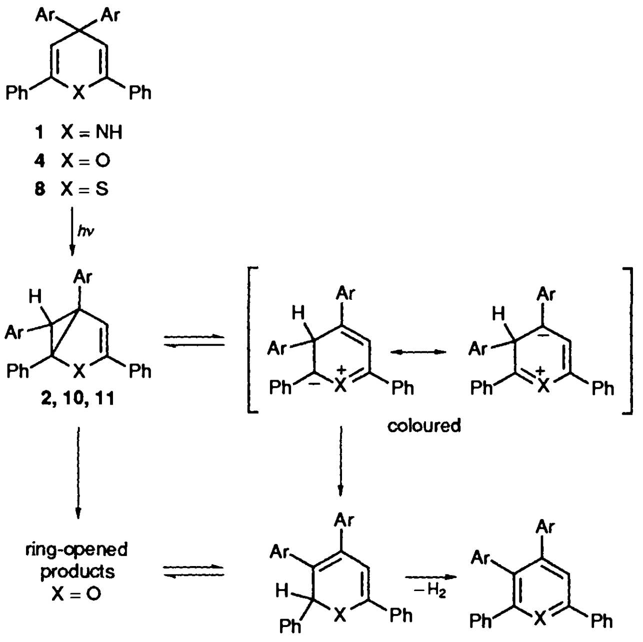
Irradiation of the oxazine **9** in [$^2H_6$]acetone yielded the corresponding bicyclic product **13**, which was characterized by an ^1H NMR signal at δ 4.0 assignable to the cyclopropyl proton. The structure of compound **13** was further supported by ^{13}C NMR and IR data (see Experimental section). During the photolysis no other products were detected in the ^1H NMR spectrum up to *ca.* 90% conversion, but prolonged irradiation led to decomposition of compound **13**. Preparative photolysis of compound **9** was carried out in acetone solution, and compound **13** was isolated as fine crystals in 92% yield based on consumed substrate **9**.

Photochemical Reactions in the Solid State.—Since compounds **4a–c** and **8a, b** exhibited a photochemical colour change only in the solid state and not in solution, their photochemical behaviour in the solid state was also investigated to compare with those in acetone solution. 4*H*-Pyrans **4a–c** were substantially photostable in the crystalline state. When irradiated with a xenon lamp or a low-pressure mercury lamp for more than 30 h, no photoproducts were detected by TLC or NMR spectroscopy, although a photochemical colour change was observed. This result suggests that the photochemical reactions accompanied by a colour change may happen only in the surface of the crystals.

Irradiation of the 4*H*-thiopyran **8a** with a low-pressure mercury lamp gave the same product as that in [$^2H_6$]acetone, namely compound **12a**, in a much lower yield (< 10%). It has been known that when two or more reaction paths can proceed competitively, a higher selectivity will be expected to be obtained in the solid state than in solution owing to the lattice-controlled nature of solid-state reactions.[9] In the case of compound **8b** we had expected selective formation of one of the two regioisomers, phenyl-migrated or aryl-migrated. Irradiation of compound **8b** in the solid state, however, gave a mixture of the two isomers **12b** and **12b′** in a ratio almost equal to that obtained in the acetone solution, indicating that the photochemical reaction of compound **8b** was little controlled by the crystal lattice.

Structure of the Photocoloured Species and the Photochemical Reaction Pathway.—Table 1 summarizes the photochemical behaviour of substrates **1a–c**, **4a–c**, **5**, **8a**, **b**, **d** and **9** both in solution and in the solid state. All the compounds investigated in this study, **4**, **8** and **9** were found to undergo di-π-methane rearrangement and gave bicyclic systems, cyclopyrans **10a–c** from **4a–c**, and cyclothiopyrans **11a**, **b** from **8a,b** in solution, just as substrates **1a–c** gave products **4a–c**. In the solid state compounds **4a–c** and **8a,b** showed photocolouration as did compounds **1a–c** and **5**.

Based on the above mentioned observations in this study and an analogy with the photochemical behaviour of compound **5** (Scheme 2) we have proposed a mechanism involving an ylide-type coloured species, which is illustrated in Scheme 4.



Scheme 4

Photoproduced bicycles **2a–c**, **10a–c** and **11a,b** undergo thermal 1,5-electrocyclic reaction to give six-membered ylides as coloured species. This suggestion is supported by the report of Klärner and Schröer[10] that 2-heterobicyclo[3.1.0]hex-3-ene systems with oxygen, sulphur or nitrogen can undergo thermal 1,5-electrocyclic ring opening to form six-membered ylide species. Although a small amount of a coloured species was formed only on the solid surface and it is difficult to detect the bicyclic species in the solid state, the photochemical colour change of species **1a–c**, **4a–c** and **8a,b** as well as that of compound **5** can be explained in terms of the same type of mechanism. In solution the ylides, except for those derived from substrates **1a–c**, are probably too unstable to exhibit the colouration and proceed to successive transformations. We consider that the mechanism summarized in Scheme 4 accounts for the results obtained to date for substrates **1**, **4**, **5** and **8**, but there is another possibility* that cannot be ruled out. That is that the six-membered ylide species is formed directly from the starting heterocycles by a 1,2-aryl shift and then either 1,5-bond formation of the ylide to give the bicyclic compounds or hydrogen migration occurs. It seems impossible to discriminate

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* We wish to thank a referee for pointing out this possibility.

between these reaction pathways on the basis of our results for the photochemical behaviour of compounds **1**, **4**, **5** and **8**, though a number of electrocyclic ring-opening reactions of bicycloheterocyclic systems to form coloured ylides or zwitterionic species have been reported.[11] If isolation of the unstable bicyclic species **2**, **10**, and **11** and irradiation of these in the solid state are possible, the results will serve to elucidate this problem.

As shown in Table 1, the bicycles **2a–c**, **6**, **10a–c**, **11a,b** and **13** showed rather different behaviour from each other, although they have a closely related isoelectronic structure, namely a 1,3,5,6-tetraaryl-2-heterobicyclo[3.1.0]hex-3-ene system. This complex behaviour can be explained based on Scheme 4. Klärner and Schröer[10] reported that the relative rates of the reactions from the parent bicyclic compounds cyclopyridine, cyclothiopyran and cyclopyran to the corresponding ylides are influenced very much by the nature of the heteroatoms. That is, the thermal ring-opening of the cyclothiopyran and cyclopyridine occur 63 100- and 72-times faster, respectively, than that of the cyclopyran. Such influences of the heteroatoms are considered to be reflected in the relative stability of the present bicyclic compounds **2a–c**, **6**, **10a–c** and **11a,b**, and also in the ease of formation of the ylide-type coloured species.

As is shown in Scheme 4, the bicycles **11a,b** rearranged irreversibly into monocycles **12a,b** probably by a sigmatropic 1,6-H shift *via* ylide intermediates. Although compounds **2a–c** are considered to give the corresponding dihydro-type heterocycles *via* ylide-type intermediates, it is likely that such 1,2-dihydropyridine derivatives are easily transformed into the stable pyridines **3a–c** by dehydrogenation. On the other hand compounds **10a–c**, which are more stable than species **2a–c** or **11a,b**, probably occurred *via* ring opening into acyclic dienones competing with the H-shift. These observations are quite similar to the results seen[10] when the cyclopyridine underwent irreversible rearrangement into the dihydro-type product such as **12** by a sigmatropic H-shift, whereas the cyclopyran was mostly transformed into the ring-opened products by cleavage of the C(1)–X and C(5)–C(6) bonds in preference to H-shift. As is shown in Table 1, only compounds **1a–c** exhibited photochemical colour change also in solution (oxygen-free), and furthermore the coloured species were stable at 77 K as well as in the solid state in oxygen-free medium.[3] These facts suggest that the coloured species formed from substrates **2a–c** are more stable than those from compounds **11a,b**.

Successful isolation of compound **13** from substrate **9** indicated that the ring system was the most stable among the bicycles examined in this study and there was no colour change on photolysis of compound **9**. This result seems to suggest that such a heterocyclic compound which affords a stable bicyclic species does not exhibit photocolouration in the solid state.

Furthermore the bicyclic systems containing four aryl groups may be stabilized by the aryl group at the 5-position, since in the case of the 4-methylthiopyran **8d** the corresponding bicyclic intermediate **11d** could not be detected by NMR spectroscopy.

Experimental

IR and UV spectra were taken on a JASCO A-302 spectrometer and a Shimadzu UV 240 spectrophotometer, respectively. ^{1}H (270 MHz) and ^{13}C (67.8 MHz) NMR spectra were recorded on a JEOL JNM-GX 270 spectrometer with Me$_4$Si as internal standard. *J*-Values are given in Hz. Mass spectra were recorded on a JEOL DX-300 mass spectrometer. M.p.s were obtained with a Yanagimoto micro apparatus and are uncorrected.

4*H*-Pyrans **4a–c** were synthesized from the corresponding diketones[3] by the method of Carvalho.[1] 4*H*-Thiopyrans **8a,b,d** were obtained by the method of Suld and Price.[12] M.p. and spectral data for known compounds **4a**,[1] **8a**,[12] and **8d**[12] coincided with those in the literature.

4-(4-*Bromophenyl*)-2,4,6-*triphenyl*-4H-*pyran* **4b**.—Yield 18.5%; needles, m.p. 135.5–137 °C (from EtOH); ν_{max}(KBr)/cm^{-1} 1680 and 1640; λ_{max}(hexane)/nm 250 (ε 35 000 dm^3 mol^{-1} cm^{-1}) and 227 (35 000); δ(CDCl$_3$) 5.71 (2 H, s, 3-, 5-H), 7.2–7.5 (15 H, m) and 7.75 (4 H, d, *J* 8); *m/z* 466 (M$^+$, 25%), 464 (M$^+$, 25), 389 (23), 387 (24), 309 (42), 280 (22) and 105 (100) (Found: *m/z* 464.0802. C$_{29}$H$_{21}$BrO requires M, 464.0776).

4-(4-*Methylphenyl*)-2,4,6-*triphenyl*-4H-*pyran* **4c**.—Yield 52%; needles, m.p. 115.5–117 °C (from EtOH); ν_{max}(KBr)/cm^{-1} 1680 and 1640; λ_{max}(hexane)/nm 250 (ε 29 000) and 230 (29 000); δ(CDCl$_3$) 2.33 (3 H, s, CH$_3$), 5.75 (2 H, s, 3-, 5-H), 7.1–7.4 (15 H, m) and 7.76 (4 H, d, *J* 8); *m/z* 400 (*M*$^+$, 56%), 323 (69), 309 (55), 295 (42) and 105 (100) (Found: M$^+$ 400.1796. C$_{30}$H$_{24}$O requires *M*, 400.1827).

4-(4-*Bromophenyl*)-2,4,6-*triphenyl*-4H-*thiopyran* **8b**.—Yield 35%; needles, m.p. 161–162 °C (from EtOH); λ_{max}(hexane)/nm 236 (ε 36 000); δ(CDCl$_3$) 6.17 (2 H, s, 3-, 5-H) and 7.2–7.6 (19 H, m); *m/z* 482 (*M*$^+$, 84%), 405 (64), 403 (63), 325 (100), 165 (33) and 121 (43) (Found: M$^+$ 480.0504. C$_{29}$H$_{21}$BrS requires *M*, 480.0548).

2,4,4,6-*Tetraphenyl*-4H-1,3-*oxazine* **9**.[13]—To a stirred mixture of β-phenylchalcone (0.85 g, 3 mmol) and benzonitrile (3.1 g, 30 mmol) under nitrogen at 0 °C was added aluminium chloride (0.40 g, 3 mmol). The mixture was stirred for 6 h at 80 °C and was then hydrolysed with 0.5 mol dm^{-3} H$_2$SO$_4$ and extracted with diethyl ether. The extract was washed with water and dried (Na$_2$SO$_4$). The solvent was removed under reduced pressure and the resultant residue was separated by silica gel column chromatography (eluent benzene) to give 2,4,4,6-tetraphenyl-4*H*-1,3-oxazine **9** (228 mg, 20%) as plates, m.p. 169.0–170.5 °C (from EtOH); λ_{max}(hexane)/nm 243 (ε 31 000); ν_{max}(KBr)/cm^{-1} 1683 and 1640; δ(CDCl$_3$) 6.02 (1 H, s), 7.2–7.5 (16 H, m), 7.76 (2 H, m) and 8.22 (2 H, m); *m/z* 387 (M$^+$, 5%), 310 (17), 283 (100), 207 (22), 178 (32) and 105 (55). (Found: M$^+$ 387.1583. Calc. for C$_{28}$H$_{21}$NO: *M*, 387.1623).

Photolyses of Compounds **4** *and* **8** *in* [^{2}H$_6$]*Acetone*.—Sample solutions were degassed and sealed. Irradiation was carried out with a 400 W high-pressure mercury lamp at room temperature and the progress of the photochemical reactions was monitored by NMR spectroscopy. Photoproducts **10a** and **12a** were characterized by their ^{1}H and ^{13}C NMR spectra, although they could not be isolated.

1,3,5,6-*Tetraphenyl*-2-*oxabicyclo*[3.1.0]*hex*-3-*ene* **10a** δ_H(CD$_3$COCD$_3$) 3.70 (1 H, s, 6-H), 5.80 (1 H, s, 4-H) and 7.0–7.5 (20 H, m); δ_C(CD$_3$COCD$_3$) 53.3, 80.9, 103.8, 104.5, 126.0, 127.7, 127.9, 128.3, 128.8, 129.1, 129.4, 129.5, 129.6, 129.9, 131.7, 132.1, 135.9, 139.5 and 156.5.

2,3,4,6-*Tetraphenyl*-2H-*thiopyran* **12a**. δ_H(CD$_3$COCD$_3$) 5.07 (1 H, s, 2-H), 6.85 (1 H, s, 5-H), 7.0–7.4 (16 H, m) and 7.5–7.6 (4 H, m); δ_C(CD$_3$COCD$_3$) 48.6, 124.2, 126.9, 128.2, 128.4, 128.7, 128.9, 129.0, 129.2, 129.6, 129.7, 129.9, 130.2, 130.8, 131.3, 134.0, 138.6, 139.1, 142.5, 142.9 and 143.0.

Formation of 1,3,5,6-*Tetraphenyl*-2-*oxa*-4-*azabicyclo*-[3.1.0]*hex*-3-*ene* **13** *by Preparative Photolysis of the Oxazine* **9**.—A solution of compound **9** (83 mg) in acetone (120 cm^3) was flushed with nitrogen for 40 min and then irradiated with a 400 W high-pressure mercury lamp under a gentle stream of nitrogen at room temperature. After 15 h irradiation the solvent was removed under reduced pressure and the resultant residue

Table 3 Final atom co-ordinates (× 10^4) for compound **12d**

Atom	x	y	z
S(1)[a]	63 271(6)	36 456(5)	52 170(5)
C(2)	6 691(2)	4 619(2)	6 846(2)
C(3)	8 162(2)	5 193(2)	7 076(2)
C(4)	9 231(2)	4 480(2)	6 817(2)
C(5)	9 002(2)	3 186(2)	6 137(2)
C(6)	7 830(2)	2 731(2)	5 353(2)
C(21)	6 267(2)	3 858(2)	8 119(2)
C(22)	4 899(3)	3 901(3)	8 359(3)
C(23)	4 487(3)	3 239(3)	9 527(3)
C(24)	5 402(4)	2 516(3)	10 436(3)
C(25)	6 765(4)	2 459(3)	10 213(3)
C(26)	7 190(3)	3 139(3)	9 060(3)
C(31)	8 291(2)	6 546(2)	7 713(2)
C(32)	7 583(3)	7 611(2)	7 014(3)
C(33)	7 635(3)	8 836(3)	7 634(4)
C(34)	8 399(3)	9 039(2)	8 977(3)
C(35)	9 102(3)	8 019(3)	9 668(3)
C(36)	9 064(3)	6 780(2)	9 053(2)
C(41)	10 729(2)	4 973(2)	7 134(2)
C(61)	7 698(2)	1 513(2)	4 468(2)
C(62)	6 473(3)	772(3)	4 155(3)
C(63)	6 370(3)	−367(3)	3 342(3)
C(64)	7 528(3)	−766(3)	2 815(3)
C(65)	8 747(3)	−30(2)	3 098(3)
C(66)	8 856(3)	1 099(2)	3 910(2)

[a] × 10^5.

was charged on a silica gel column. Elution with benzene gave the unchanged substrate **9** (6.2 mg recovery) and compound **13** (70.8 mg, 92% based on the consumed oxazine), m.p. 76–77 °C (from hexane–diethyl ether); ν_{max}(KBr)/cm^{-1} 1640 (C=N); δ_H($CDCl_3$) 3.70 (1 H, s), 7.1–7.5 (18 H, m) and 7.8 (2 H, d, J 7); δ_C($CDCl_3$) 28.8, 67.6, 78.2 and 162.0; m/z 387 (M^+, 9%), 282 (38), 179 (51) and 105 (100) (Found: M^+ 387.1600. $C_{28}H_{21}NO$ requires M, 387.1623).

Photolyses in the Solid State.—Solid-state photolyses of substrates **4** and **8** were carried out in KBr pellets. A pellet containing the sample crystals (2% w/w) was irradiated with a xenon lamp or a low-pressure mercury lamp at room temperature. The reaction mixture was extracted with $CDCl_3$ and analysed by ^1H NMR spectra.

X-*Ray Structure Analysis of* 4-*Methyl*-2,3,6-*triphenyl*-2H-*thiopyran* **12d**.—Plate-like crystals were obtained from ethanol; $C_{24}H_{20}S$, M = 340.5, triclinic, $P\bar{1}$, a = 9.772(3), b = 10.030(2), c = 9.505(2) Å, α = 88.85(4), β = 98.94(3), γ = 92.46(2)°, V = 919.4(4) Å^3, Z = 2, D_x = 1.230 g cm^{-3}, μ = 14.6 cm^{-1}. Intensity data were collected on a Rigaku AFC-4 diffractometer with graphite-monochromated Cu-Kα radiation and the ω–2θ scan technique up to 2θ = 125°, scan speed 4° min^{-1} in θ, scan width (1.0 + 0.15 tan θ)°. 2651 reflections were measured and 2503 with $|F_o| > 3\sigma(|F_o|)$ were considered as observed and used for the structure determination. The structure was solved by direct methods (MULTAN78[14]) and refined by full-matrix least-squares (SHELX76[15]). The methyl group was treated as a rigid group. The final refinement with anisotropic thermal parameters for non-H atoms and isotropic ones for H atoms converged at R = 0.048 and R_w = 0.060 for 2503 observed reflections.* Calculations were carried out on an IBM 4381-R24 computer at Ochanomizu University. Non-H atom co-ordinates are given in Table 3, and bond lengths and angles in Table 4.

Table 4 Bond distances/Å and bond angles/° for compound **12d**

S(1)–C(2)	1.826(2)	C(24)–C(25)	1.384(5)
S(1)–C(6)	1.752(2)	C(25)–C(26)	1.388(5)
C(2)–C(3)	1.511(3)	C(31)–C(32)	1.398(3)
C(2)–C(21)	1.520(3)	C(31)–C(36)	1.395(3)
C(3)–C(4)	1.347(3)	C(32)–C(33)	1.369(5)
C(3)–C(31)	1.490(3)	C(33)–C(34)	1.388(5)
C(4)–C(5)	1.455(3)	C(34)–C(35)	1.358(4)
C(4)–C(41)	1.512(3)	C(35)–C(36)	1.381(4)
C(5)–C(6)	1.334(3)	C(61)–C(62)	1.377(4)
C(6)–C(61)	1.487(3)	C(61)–C(66)	1.404(4)
C(21)–C(22)	1.393(4)	C(62)–C(63)	1.384(4)
C(21)–C(26)	1.383(4)	C(63)–C(64)	1.383(5)
C(22)–C(23)	1.386(4)	C(64)–C(65)	1.367(4)
C(23)–C(24)	1.364(5)	C(65)–C(66)	1.373(4)
C(6)–S(1)–C(2)	101.0(1)	C(23)–C(24)–C(25)	120.0(3)
S(1)–C(2)–C(3)	111.4(2)	C(24)–C(25)–C(26)	119.5(3)
S(1)–C(2)–C(21)	112.1(2)	C(21)–C(26)–C(25)	120.9(3)
C(3)–C(2)–C(21)	114.7(2)	C(3)–C(31)–C(32)	120.9(2)
C(2)–C(3)–C(4)	121.7(2)	C(3)–C(31)–C(36)	121.3(2)
C(2)–C(3)–C(31)	113.1(2)	C(32)–C(31)–C(36)	117.7(2)
C(4)–C(3)–C(31)	125.1(2)	C(31)–C(32)–C(33)	121.0(3)
C(3)–C(4)–C(5)	121.3(2)	C(32)–C(33)–C(34)	120.2(3)
C(3)–C(4)–C(41)	123.5(2)	C(33)–C(34)–C(35)	119.7(3)
C(5)–C(4)–C(41)	115.2(2)	C(34)–C(35)–C(36)	120.7(3)
C(4)–C(5)–C(6)	126.2(2)	C(31)–C(36)–C(35)	120.7(2)
S(1)–C(6)–C(5)	120.1(2)	C(6)–C(61)–C(62)	122.6(2)
S(1)–C(6)–C(61)	115.0(2)	C(6)–C(61)–C(66)	119.3(2)
C(5)–C(6)–C(61)	124.8(2)	C(62)–C(61)–C(66)	118.1(2)
C(2)–C(21)–C(22)	118.7(2)	C(61)–C(62)–C(63)	121.9(3)
C(2)–C(21)–C(26)	122.6(2)	C(62)–C(63)–C(64)	119.1(3)
C(22)–C(21)–C(26)	118.7(2)	C(63)–C(64)–C(65)	119.7(3)
C(21)–C(22)–C(23)	120.1(3)	C(64)–C(65)–C(66)	121.4(3)
C(22)–C(23)–C(24)	120.7(3)	C(61)–C(66)–C(65)	119.8(2)

Acknowledgements

We thank Prof. Y. Ohashi, Tokyo Institute of Technology, for his help with the X-ray study. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture (No 63628505). Y. M. thanks the Hayashi Memorial Foundation for Female Natural Scientists for financial support.

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* *Supplementary material* (see Instructions for Authors, section 5.6.3, January issue): Tables of hydrogen atom co-ordinates, atom co-ordinates and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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Paper 1/01019K
Received 5th March 1991
Accepted 5th September 1991