

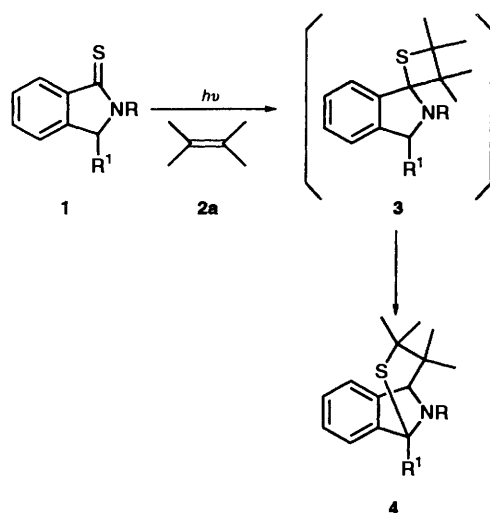
## Photoreactions of 1,3-Dihydroisobenzofuran-1-thiones and 1,3-Dihydro-2-benzothiophene-1-thiones with Alkenes

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The photoreactions of isobenzofuran-1-thiones **7** and 2-benzothiophene-1-thiones **11** in the presence of alkenes have been examined. Irradiation of thiones **7** and **11** in the presence of alkenes gave spiro-thietanes **15** and **21**, which are formed by [2 + 2] cycloaddition of the C=S bond of thiones and the C=C bond of alkenes. The spiro-thietanes **15a, b, d** and **e**, derived from 3-unsubstituted or 3-monosubstituted 1,3-dihydroisobenzofuran-1-thiones **7a, b, d** and **e** and alkenes, are somewhat labile and undergo thermal rearrangement to give the tricyclic isobenzofurans **16**. The formation of compounds **16** can be explained on the basis of ring-cleavage of the thietanes, assisted by the participation of the oxygen lone-pair electrons.

The photochemistry of thiocarbonyl compounds has received much attention from both synthetic and mechanistic viewpoints.<sup>1-6</sup> Some reports have dealt with photochemical reactions involving the C=S group of thioamides.<sup>7</sup> The majority of these reports deal with intra- and inter-molecular cycloaddition to alkenes. Aminothietanes are suggested to be intermediates in these reactions, although such products have not been isolated except for one example,<sup>7c</sup> probably because the nitrogen lone-pair-assisted cleavage of the C-S bond of the thietane ring facilitates further reactions. We recently reported that the photocycloaddition of isoindoline-1-thiones **1** with alkenes **2** yielded the unexpected tricyclic isoindolines **4** through the aminospirothietane intermediate **3**, formed by [2 + 2] photocycloaddition of the C=S double bond of **1** and the C=C double bond of **2** (Scheme 1).<sup>7r</sup>

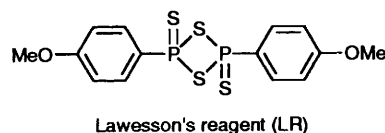
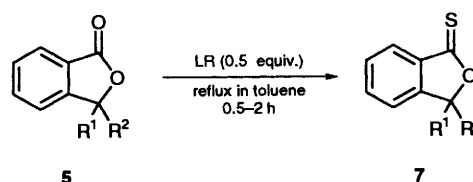


Scheme 1

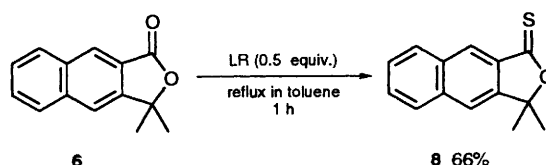
However, the formation of stable thietanes, which have heteroatoms such as oxygen and sulfur adjacent to the thietane ring, has been reported by several groups.<sup>8</sup> We set out to investigate the photocycloaddition of 1,3-dihydroisobenzofuran-1-thiones **7**, 1,3-dihydronaphtho[2,3-*c*]furan-1-thione **8** and 1,3-dihydro-2-benzothiophene-1-thiones **11** in order to discover the effect of a heteroatom adjacent to the thiocarbonyl function on the formation of a thietane ring and that of the heteroatom lone-pair electrons in the thietane ring cleavage. In the present paper, we describe the results of photochemical reactions of thiones **7**, **8** and **11** with alkenes **2**.

## Results and Discussion

**Preparation of 1,3-Dihydroisobenzofuran-1-thiones 7, 1,3-Dihydronaphtho[2,3-*c*]furan-1-thione 8 and 1,3-Dihydro-2-benzothiophene-1-thiones 11.**—1,3-Dihydroisobenzofuran-1-thiones **7**, 1,3-dihydronaphtho[2,3-*c*]furan-1-thione **8** and 1,3-dihydro-2-benzothiophene-1-thione **11a** were readily prepared by direct thionation of their oxygen analogues, **5**, **6** and **9**, with 2,4-bis(*p*-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-dithione (Lawesson's reagent; LR) in reasonable yields.



<b>5</b>	R <sup>1</sup>	R <sup>2</sup>	Yield of <b>7</b> (%)
<b>a</b>	H	H	50
<b>b</b>	Me	H	49
<b>c</b>	Me	Me	44
<b>d</b>	Ph	H	55
<b>e</b>	PhCH <sub>2</sub>	H	25
<b>f</b>	Ph	Ph	60
<b>g</b>	CH <sub>2</sub> =CHCH <sub>2</sub>	CH <sub>2</sub> CH=CH <sub>2</sub>	29



Preparation of 1,3-dihydroisobenzofuran-1-thiones **7** and 1,3-dihydronaphtho[2,3-*c*]furan-1-thione **8**

3-Methyl- and 3-phenyl-1,3-dihydro-2-benzothiophene-1-thiones, **11b** and **11c** were synthesized by the following procedure. Treatment of *o*-acetylbenzoic acid **10a** with 0.5 equiv. of LR in toluene under reflux yielded **11b** (trace), 3-methyl-3-sulfanyl-1,3-dihydro-2-benzothiophen-1-one **12** (27%), 3-methyl-3-sulfanyl-1,3-dihydroisobenzofuran-1-one **13**

(37%) and 3-methylideneisobenzofuran-1-one **14** (10%). By use of an equimolar amount of LR, the yield of **11b** increased to 21%. Thionation of **12** with LR also gave **11b**. Treatment of **13** with LR in dimethoxyethane (DME) under reflux yielded **11b** and **12** in 43 and 20% yields, respectively. The formation of 3-methyl-1,3-dihydro-2-benzothiophene-1-thione **11b** can be interpreted in terms of stepwise thionation (**10a** → **13** → **12** → **11b**) from *o*-acetylbenzoic acid **10a**. In a similar manner, thionation of *o*-benzoylbenzoic acid **10b** with LR yielded 3-phenyl-1,3-dihydro-2-benzothiophene-1-thione **11c** in 54% yield.

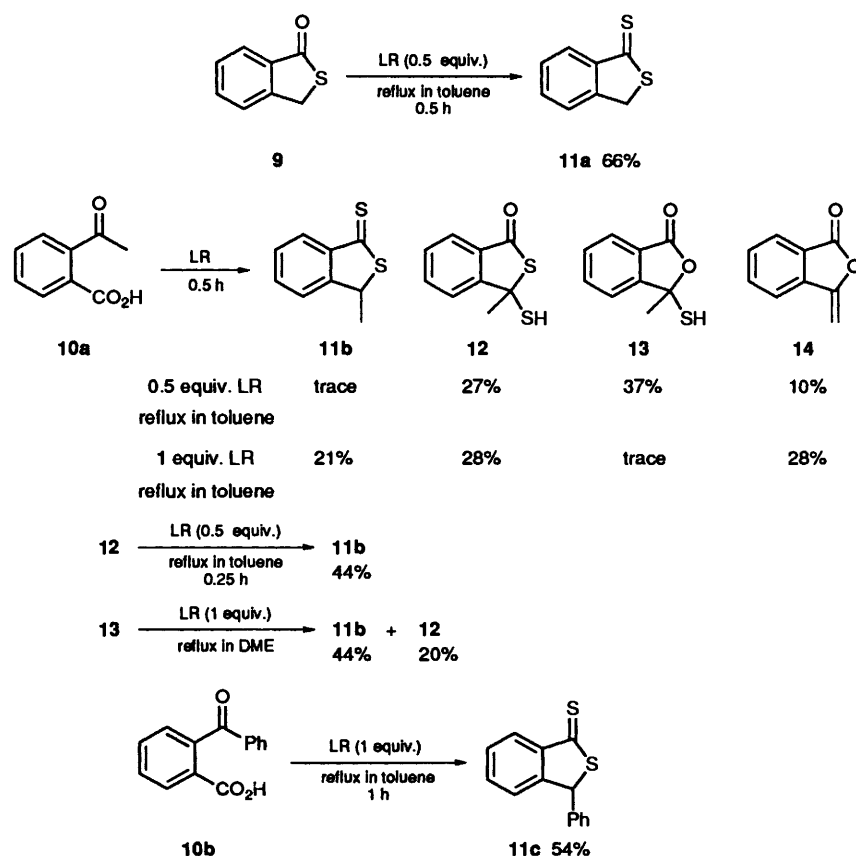
**Photochemical Reactions of 1,3-Dihydroisobenzofuran-1-thiones 7, 1,3-Dihydronaphtho[2,3-*c*]furan-1-thione 8 and 1,3-Dihydro-2-benzothiophene-1-thiones 11.**—Photolysis of 1,3-dihydroisobenzofuran-1-thione **7a** alone in benzene resulted in no change. However, irradiation of **7a** in benzene in the presence of an excess of 2,3-dimethylbut-2-ene **2a** with a high-pressure mercury lamp through a Pyrex filter under argon for 6 h at room temperature gave the expected product, spiro-thietane **15a**, formed by [2 + 2] cycloaddition of the C=S double bond of **7a** and the C=C double bond of **2a**, in 80% isolated yield. Similar results were obtained when MeOH and acetonitrile were used as solvent. The structure of **15a** was elucidated on the basis of spectroscopic data and elemental analysis. The <sup>1</sup>H NMR spectrum of **15a** showed four singlets assignable to methyl protons, an AB quartet assignable to methylene protons and aromatic proton signals. In the <sup>13</sup>C NMR spectrum of **15a**, four methyl carbon and three quaternary carbon signals newly appeared along with the methylene and aromatic carbon signals. The spiro-thietane **15a** thus formed was quite stable even when heated to reflux in benzene. However, at higher temperatures (reflux in toluene), **15a** rearranged to the tricyclic isobenzofuran **16a**. In a similar manner, 1,3-dihydroiso-

benzofuran-1-thiones **7b–g**, upon irradiation in the presence of 2,3-dimethylbut-2-ene **2a**, readily reacted to yield the spiro-thietanes **15b–g** in high yields. Generally, the spiro-thietanes **15b, d** and **e** resulting from 3-monosubstituted 1,3-dihydroisobenzofuran-1-thiones **7b, d** and **e** with **2a** were obtained as a mixture of two stereoisomers. These spiro-thietanes are thermally labile and can be easily converted into the rearranged products, tricyclic isobenzofurans **16b, d** and **e** (Table 1).

The structures of the spiro-thietanes **15b, d** and **e** were deduced from their <sup>1</sup>H NMR spectra. The photoaddition of 3-methyl-1,3-dihydroisobenzofuran **7b** to 2-methylpropene **2b** and 2-methylbut-2-ene **2c** gave the tricyclic isobenzofurans **16h** and **i**, respectively, and was regiospecific and in the latter case non-stereospecific. The regiospecificity is that expected with the formation of a more stable possible biradical intermediate (**B** in Scheme 2). Irradiation of the thione **7a** in the presence of electron-poor alkenes such as acrylonitrile **2d** and methacrylonitrile **2e** gave 2-alkylideneisobenzofurans **17** and **18**. 1,3-Dihydronaphtho[2,3-*c*]furan-1-thione **8** gave both spiro-thietane **19** and alkylidenenaphtho[2,3-*c*]furan **20**.

Photocycloaddition of 1,3-dihydro-2-benzothiophene-1-thiones **11a–c** in the presence of 2,3-dimethylbut-2-ene **2a** gave stable spiro-thietanes, **21a** as a sole stereoisomer and **21b** and **c** as a mixture of two stereoisomers. These photoproducts are stable even when heated to reflux in toluene for 15 h. The structures of these photoproducts were characterized from their spectral properties.

The stereochemistry of compounds **21b** and **c** was tentatively assigned as shown in Fig. 1 on the basis of NMR spectral data, although that of **21b** is as yet uncertain because of very close similarities between the NMR spectra of the two stereoisomers. The signals of the two methyl protons of isomer-2 of **21c** appeared as a singlet at higher field ( $\delta$  0.83 and 1.64) than those of isomer-1 ( $\delta$  1.33 and 1.80) because of the anisotropic shield-



ing effect of the phenyl group at the C-3 position of **21**. Irradiation of 1,3-dihydroisobenzofuran **7a** and 2,3-dimethylbut-2-ene **2a** in benzene in the  $n-\pi^*$  region using a halogen lamp gave the spiro-thietane **15a** (16%), but in low yield. Irradiation of **7a** and **2a** in benzene at 366 nm with or without a triplet sensitizer (thioxanthen-9-one:  $E_T$  65–66 kcal mol<sup>-1</sup>; 1 cal. = 4.184 J) showed no significant change in yield (ca. 80% in both cases). The formation of the spiro-thietane **15a** (30–40% yield) was slightly quenched by the addition of quenchers [2,5-dimethylhexadiene ( $E_T$  = 59 kcal mol<sup>-1</sup>) or cyclooctatetraene ( $E_T$  = 40 kcal mol<sup>-1</sup>)]. Although not identified, it appears plausible that the photocycloaddition proceeds mainly *via* the  $n-\pi^*$  triplet state. The formation of spiro-thietanes **15** and **21**, tricyclic isobenzofurans **16** and alkylideneisobenzofurans **17** and **18** could be explained according to the mechanisms depicted in Schemes 2 and 3.

The spiro-thietanes **15** and **21** are formed through the photochemical [2 + 2] cycloaddition of the C=S bond of **7** and **11** and the C=C bond of alkenes **2** in a regiospecific and non-stereospecific manner. The spiro-thietanes **21** derived from 2-benzothiophene-1-thiones **11** are stable, however those derived

from isobenzofuran-1-thiones **7** are somewhat labile and undergo thietane ring cleavage assisted by the lone-pair electrons on the oxygen atom to yield zwitterion **22**, which may be in equilibrium with **23** and **24**. Cyclization of **23** or **24** then yields the tricyclic isobenzofurans **16**. An attempt to trap the zwitterion intermediate with MeOH was unsuccessful. The spirothietane **15a** was also produced in 64% yield when a solution of **7a** in MeOH in the presence of **2a** was irradiated. Irradiation of 3-methyl-1,3-[3-<sup>2</sup>H]dihydroisobenzofuran-1-thione [3-<sup>2</sup>H]**7b** ( $R^1$  = Me,  $R^2$  = D, D content > 95%) in benzene in the presence of 2,3-dimethylbut-2-ene **2a** gave a mixture of two stereoisomers of deuteriated spiro-thietane [3-<sup>2</sup>H]**15b** (D content > 95%), which was converted into deuteriated tricyclic isobenzofuran [5-<sup>2</sup>H]**16b** (D content 45%) as shown in Fig. 2.

The deuteriated tricyclic isobenzofuran [5-<sup>2</sup>H]**16b** (D content 30%) was also obtained when a solution of spiro-thietane **15b** in methanol-[<sup>2</sup>H]chloroform was kept at room temperature for 15 h. These results suggest that partial 1,3-deuterium migration took place (**22** → **23**) and sulfanylethylisobenzofuran **24**, in

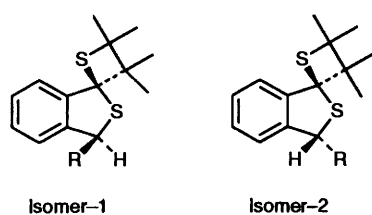


Fig. 1 Stereoisomers of spiro-thietanes **21b** and **c**

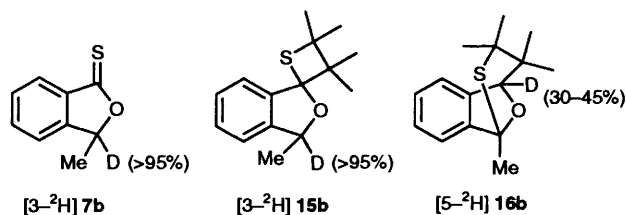
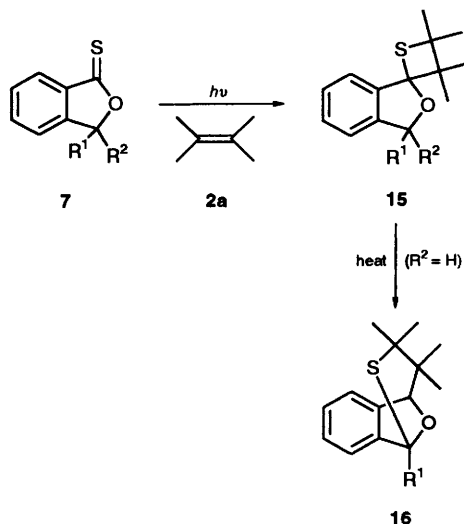


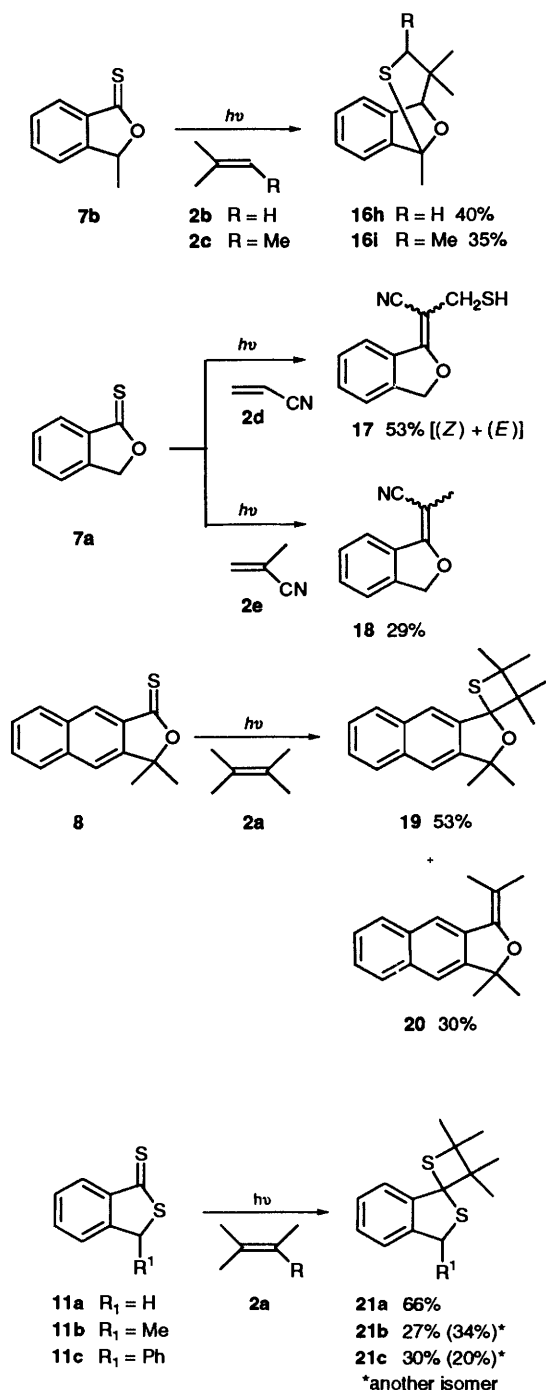
Fig. 2

Table 1 Yields<sup>a</sup> of photoproducts **15** and rearrangement products **16**



	R <sup>1</sup>	R <sup>2</sup>	Solvent	Irradiation t/h	Yield of <b>15</b> (%)	Yield of <b>16</b> (%)
<b>7a</b>	H	H	Benzene	6	<b>15a</b> 80	<b>16a</b> 20 <sup>c</sup>
<b>7a</b>			MeOH	6	<b>15a</b> 64	
<b>7a</b>			MeCN	6	<b>15a</b> 74	
<b>7a</b> <sup>b</sup>			Benzene	6	<b>15a</b> 16	
<b>7b</b>	Me	H	Benzene	7	<b>15b</b> 79	<b>16b</b> 100 <sup>d</sup>
[3- <sup>2</sup> H] <b>7b</b>	Me	D	Benzene	8	[3- <sup>2</sup> H] <b>15b</b> 85	[5- <sup>2</sup> H] <b>16b</b> 100 <sup>d</sup>
<b>7b</b>			MeOH	7	<b>15b</b> 95	
<b>7c</b>	Me	Me	Benzene	5	<b>15c</b> 83	
<b>7d</b>	Ph	H	Benzene	5	<b>15d</b> 73	<b>16d</b> 100 <sup>d</sup>
<b>7e</b>	PhCH <sub>2</sub>	H	Benzene	7	<b>15e</b> 80	<b>16e</b> 50 <sup>d</sup>
<b>7f</b>	Ph	Ph	Benzene	12	<b>15f</b> 67	
<b>7g</b>	Allyl	Allyl	Benzene	10	<b>15g</b> 49	

<sup>a</sup> Isolated yield. <sup>b</sup> Halogen lamp (> 400 nm) was used as an irradiation source. <sup>c</sup> Reflux in toluene for 15 h. Unchanged **15a** was recovered in 51% yield. <sup>d</sup> Room temperature in CDCl<sub>3</sub> or neat.



which the hydrogen of the sulfanyl function can be easily exchanged with deuterium, is the reactive intermediate. The low incorporation of deuterium in [5-<sup>2</sup>H]**16b** was probably due to D-H exchange in the equilibrium between these intermediates **22**, **23** and **24** by a trace of water in the benzene solution although dry solvent was used. The formation of alkylideneisobenzofurans **17** and **18** can be understood in terms of 1,3-hydrogen transfer or the elimination of thioaldehyde from zwitterion intermediate **27**. Homolytic cleavage of the spirothietane ring involving biradical **26** would also be possible. In the ring cleavage of thietanes adjacent to heteroatoms such as oxygen and sulfur, the participation of the oxygen lone-pair electrons is more effective than that of the sulfur lone-pair electrons. The effectiveness of the heteroatom lone-pair electrons parallels the electronic influence of heteroatom substituents on the rate and course of a reaction.<sup>9</sup>

## Experimental

Mps and bps are uncorrected. IR spectra were measured using a Hitachi 26-30 spectrophotometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on JEOL FX 90Q (90 MHz) and FX 100 (100 MHz) spectrometers using CDCl<sub>3</sub> as solvent and tetramethylsilane as an internal standard. *J* Values are given in Hz. UV spectra were recorded on a JASCO UVIDECE-505 spectrophotometer.

*General Procedure for the Thionation of 1,3-Dihydroisobenzofuran-1-ones 5, 1,3-Dihydronaphtho[2,3-c]furan-1-one 6 and 1,3-Dihydro-2-benzothiophen-1-one 9.*—A solution of the corresponding ketone **5**, **6** and **9** (10 mmol) and 2,4-bis(*p*-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-dithione (LR) (5.5 mmol) in toluene (70 cm<sup>3</sup>) was refluxed under argon for 0.5–2 h. After removal of the solvent, the residue was chromatographed on a silica gel column with benzene–hexane (4:1) to yield the thione analogues **7**, **8** and **11a**.

**1,3-Dihydroisobenzofuran-1-thione 7a.** Mp 114–115 °C (lit.,<sup>10</sup> 116–117 °C); λ<sub>max</sub>(EtOH)/nm 225 (ε/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 8400), 242 (5800), 291 (13 200) and 305 (14 600); λ<sub>max</sub>(hexane)/nm 222 (ε/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 7900), 228 (8800), 235 (7900), 288 (11 600) and 303 (12 700); ν<sub>max</sub>(KBr)/cm<sup>-1</sup> 1615, 1590, 1500, 1465, 1315, 1270, 1165, 765 and 715; δ<sub>H</sub> 5.57 (2 H, s), 7.28–7.80 (3 H, m) and 7.98–8.08 (1 H, m); δ<sub>C</sub> 77.8 (t), 121.4 (d), 126.7 (d), 129.2 (d), 133.8 (d), 136.7 (s), 144.7 (s) and 211.0 (s).

**3-Methyl-1,3-dihydroisobenzofuran-1-thione 7b.** Bp 145 °C/3 mmHg; mp 61–62 °C (Found: C, 65.5; H, 4.95. C<sub>9</sub>H<sub>8</sub>OS requires C, 65.8; H, 4.9%); ν<sub>max</sub>(KBr)/cm<sup>-1</sup> 1605, 1590, 1465, 1345, 1305, 1270, 1160, 770, 745 and 725; δ<sub>H</sub> 1.70 (3 H, d, *J* 6.8), 5.83 (1 H, q, *J* 6.8), 7.29–7.78 (3 H, m) and 8.04 (1 H, d, *J* 1.0); δ<sub>C</sub> 19.7 (q), 86.5 (d), 121.0 (d), 126.7 (d), 129.2 (d), 133.9 (d), 145.4 (s), 149.0 (s) and 210.1 (s).

**3-Methyl-1,3-[3-<sup>2</sup>H]dihydroisobenzofuran-1-thione [3-<sup>2</sup>H]-7b.** ν<sub>max</sub>(KBr)/cm<sup>-1</sup> 1610, 1585, 1465, 1335, 1325, 1260, 1205, 1060, 775, 740 and 730; δ<sub>H</sub> 1.69 (3 H, s), 7.39–7.78 (3 H, m) and 7.93–8.04 (1 H, m).

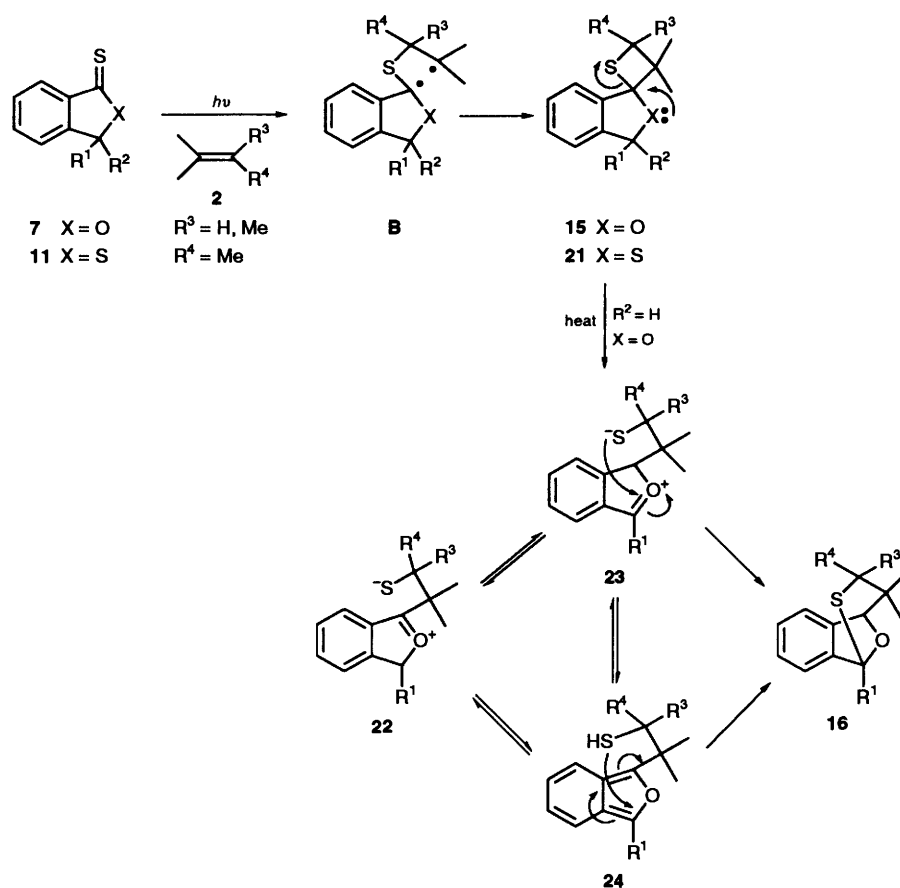
**3,3-Dimethyl-1,3-dihydroisobenzofuran-1-thione 7c.** Bp 130 °C/3 mmHg; mp 33–34 °C (Found: C, 67.1; H, 5.6. C<sub>10</sub>H<sub>10</sub>OS requires C, 67.4; H, 5.65%); ν<sub>max</sub>(KBr)/cm<sup>-1</sup> 1605, 1485, 1470, 1260, 1075, 835, 765 and 750; δ<sub>H</sub> 1.73 (6 H, s), 7.37–7.77 (3 H, m) and 7.95–8.01 (1 H, m); δ<sub>C</sub> 26.6 (q), 94.8 (s), 120.2 (d), 126.8 (d), 129.2 (d), 133.9 (d), 135.5 (s), 152.5 (s) and 190.8 (s).

**3-Phenyl-1,3-dihydroisobenzofuran-1-thione 7d.** Mp 99–100 °C (Found: C, 74.35; H, 4.55. C<sub>14</sub>H<sub>10</sub>OS requires C, 74.3; H, 4.45%); ν<sub>max</sub>(KBr)/cm<sup>-1</sup> 1590, 1320, 1265, 1165, 775 and 695; δ<sub>H</sub> 6.63 (1 H, s), 7.07–7.74 (8 H, m) and 8.08 (1 H, dd, *J* 1.5, 6.3); δ<sub>C</sub> 91.3 (d), 122.3 (d), 126.7 (d), 127.4 (d), 129.0 (d), 129.5 (d), 129.6 (d), 134.0 (d), 135.3 (s), 136.6 (s), 147.5 (s) and 210.0 (s).

**3-Benzyl-1,3-dihydroisobenzofuran-1-thione 7e.** Bp 185 °C/3 mmHg; mp 54–55 °C (Found: C, 74.85; H, 5.1. C<sub>15</sub>H<sub>12</sub>OS requires C, 74.95; H, 5.05%); ν<sub>max</sub>(KBr)/cm<sup>-1</sup> 1605, 1485, 1465, 1360, 1315, 1270, 1155, 765, 750, 735 and 695; δ<sub>H</sub> 3.14 (1 H, A of ABX, *J* 6.4, 14.2), 3.34 (1 H, B of ABX, *J* 6.4, 14.2), 5.90 (1 H, X of ABX, *J* 6.4), 7.06–7.74 (8 H, m) and 7.75–8.05 (1 H, m); δ<sub>C</sub> 40.1 (t), 89.5 (d), 121.6 (d), 126.5 (d), 127.0 (d), 128.4 (d), 129.2 (d), 129.5 (d), 133.3 (d), 134.4 (s), 136.5 (s), 146.8 (s) and 209.7 (s).

**3,3-Diphenyl-1,3-dihydroisobenzofuran-1-thione 7f.** Mp 133–134 °C (Found: C, 79.05; H, 4.65. C<sub>20</sub>H<sub>14</sub>OS requires C, 79.45; H, 4.65%); ν<sub>max</sub>(KBr)/cm<sup>-1</sup> 1585, 1485, 1460, 1335, 1315, 1260, 1200, 775, 755, 740 and 690; δ<sub>H</sub> 7.32 (11 H, s), 7.41–7.76 (2 H, m) and 8.01–8.11 (1 H, m); δ<sub>C</sub> 100.6 (s), 123.6 (d), 127.2 (d), 128.5 (d), 128.8 (d), 129.5 (d), 133.8 (d), 136.1 (s), 133.9 (s), 149.8 (s) and 208.9 (s).

**3,3-Diallyl-1,3-dihydroisobenzofuran-1-thione 7g.** Bp 160 °C/2 mmHg (Found: C, 73.05; H, 6.2. C<sub>14</sub>H<sub>14</sub>OS requires C, 73.0; H, 6.15%); ν<sub>max</sub>(film)/cm<sup>-1</sup> 1635, 1605, 1585, 1470, 1345, 1310, 1270,



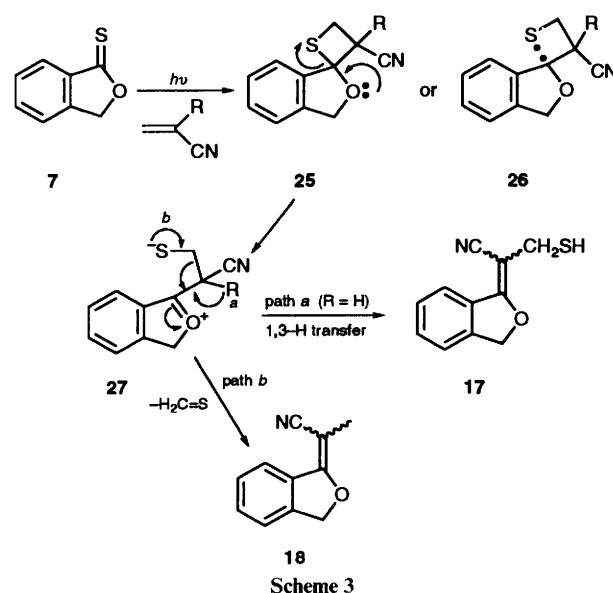
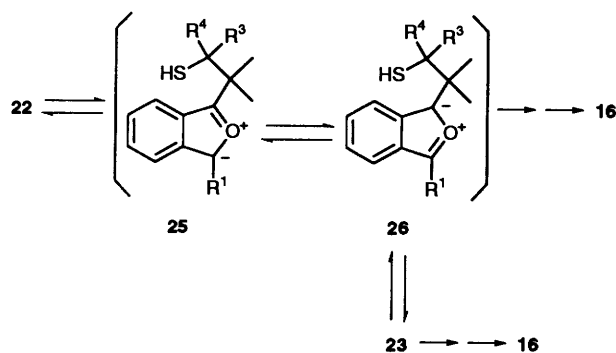
Scheme 2 †

1195, 920, 835, 765 and 695;  $\delta_{\text{H}}$  2.58–2.99 (4 H, m), 4.97–5.17 (4 H, m), 5.35–5.77 (2 H, m), 7.18–7.74 (3 H, m) and 7.99 (1 H, dd,  $J$  1.0, 6.9);  $\delta_{\text{C}}$  43.2 (t), 97.6 (s), 120.5 (t), 121.2 (d), 126.8 (d), 129.2 (d), 130.3 (d), 133.5 (d), 137.2 (s), 149.2 (s) and 209.4 (s).

3,3-Dimethyl-1,3-dihydronaphtho[2,3-c]furan-1-thione **8**. Mp 114–115 °C (Found: C, 73.3; H, 5.3. C<sub>14</sub>H<sub>12</sub>OS requires C, 73.65; H, 5.3%);  $\nu_{\text{max}}$ (KBr)/cm<sup>-1</sup> 1620, 1600, 1495, 1445, 1305, 1275, 1175, 1085, 820 and 750;  $\delta_{\text{H}}$  1.80 (6 H, s), 7.46–7.71 (2 H, m), 7.76 (1 H, s), 7.87–8.08 (2 H, m) and 8.57 (1 H, s);  $\delta_{\text{C}}$  27.4 (q), 94.6 (s), 118.9 (d), 126.9 (d), 128.0 (d), 128.2 (d), 129.1 (d), 130.0 (d), 133.2 (s), 133.9 (s), 135.9 (s), 147.0 (s) and 209.0 (s).

1,3-Dihydro-2-benzothiophene-1-thione **11a**. Mp 63–64 °C (Found: C, 57.9; H, 3.6. C<sub>8</sub>H<sub>6</sub>S<sub>2</sub> requires C, 57.85; H, 3.65%);  $\lambda_{\text{max}}$ (EtOH)/nm 225 ( $\epsilon$ /dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 6600), 292 (14 000) and 344 (10 300);  $\lambda_{\text{max}}$ (hexane) 225 ( $\epsilon$  6900), 284 (13 500) and 342

† One of the referees suggested that a carbonyl ylide species, **25** and **26**, which could be responsible for the equilibration of intermediates **22** and **23**, also might be considered as an intermediate in the conversion of **15** into **16**:



(9300);  $\nu_{\text{max}}$ (KBr)/cm<sup>-1</sup> 1590, 1565, 1465, 1400, 1260, 1205, 1125, 1040, 895, 755 and 700;  $\delta_{\text{H}}$  4.50 (2 H, s), 7.33–7.69 (3 H, m) and 8.02 (1 H, d,  $J$  7.3);  $\delta_{\text{C}}$  40.8 (t), 124.4 (d), 125.4 (d), 128.0 (d), 132.6 (d), 144.1 (s), 147.1 (s) and 228.4 (s).

Reaction of *o*-Acybenzoic Acid **10** with LR. —A solution of *o*-acybenzoic acid **10** (10 mmol) and LR (5.5–10 mmol) in toluene was refluxed under argon for 0.5–1 h. After removal of the solvent, the residue was chromatographed on a silica gel column with benzene–hexane (4:1) to yield products **11–14**.

**3-Methyl-1,3-dihydro-2-benzothiophene-1-thione 11b.** Bp 155 °C/3 mmHg (Found: C, 59.9; H, 4.45. C<sub>9</sub>H<sub>8</sub>S<sub>2</sub> requires C, 59.95; H, 4.45%;  $\nu_{\max}(\text{film})/\text{cm}^{-1}$  1600, 1465, 1260, 1050, 760 and 740;  $\delta_{\text{H}}$  1.72 (3 H, d, *J* 6.8), 4.88 (1 H, q, *J* 6.8), 7.03–7.70 (3 H, m) and 7.93–8.06 (1 H, m);  $\delta_{\text{C}}$  20.3 (q), 51.1 (d), 124.1 (d), 128.0 (d), 132.6 (d), 143.1 (s), 151.9 (s) and 227.4 (s).

**3-Phenyl-1,3-dihydro-2-benzothiophene-1-thione 11c.** Mp 93–94 °C (Found: C, 68.75; H, 4.85. C<sub>14</sub>H<sub>10</sub>S<sub>2</sub> requires C, 68.85; H, 4.95%;  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  1590, 1465, 1445, 1265, 1120, 1040, 895, 765, 750 and 720;  $\delta_{\text{H}}$  5.95 (1 H, s), 7.21–7.60 (8 H, m) and 8.15 (1 H, d, *J* 7.6);  $\delta_{\text{C}}$  60.6 (d), 124.5 (d), 126.0 (d), 128.3 (d), 128.5 (d), 128.6 (d), 129.2 (d), 133.0 (d), 137.5 (s), 143.6 (s), 151.2 (s) and 227.2 (s).

**3-Methyl-3-sulfanyl-1,3-dihydro-2-benzothiophen-1-one 12.** Mp 108–110 °C (Found: C, 55.1; H, 3.95. C<sub>9</sub>H<sub>8</sub>OS<sub>2</sub> requires C, 55.05; H, 4.1%;  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  2540 and 1660;  $\delta_{\text{H}}$  2.20 (3 H, d, *J* 1.0), 3.09 (1 H, d, *J* 1.0) and 7.32–7.85 (4 H, m);  $\delta_{\text{C}}$  34.3 (q), 60.2 (s), 123.4 (d), 124.1 (d), 128.8 (s), 128.8 (d), 133.2 (s), 134.3 (d), 156.0 (s) and 190.0 (s).

**3-Methyl-3-sulfanyl-1,3-dihydroisobenzofuran-1-one 13.** Mp 67–68 °C (Found: C, 59.95; H, 4.55; C<sub>9</sub>H<sub>8</sub>O<sub>2</sub>S requires C, 60.0; H, 4.45%;  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  2530 and 1750;  $\delta_{\text{H}}$  2.05 (3 H, s) 2.97 (1 H, s) and 7.47–7.97 (4 H, m);  $\delta_{\text{C}}$  30.7 (q), 89.9 (s), 121.7 (d), 124.3 (s), 125.4 (d), 129.8 (d), 134.7 (d), 153.1 (s) and 167.9 (s).

**3-Methylidene-1,3-dihydroisobenzofuran-1-one 14.** Mp 54–55 °C (lit.,<sup>11</sup> 53.5–54.5 °C);  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  1765 and 1645;  $\delta_{\text{H}}$  5.22 (2 H, s) and 7.34–7.93 (4 H, m);  $\delta_{\text{C}}$  91.3 (t), 120.5 (d), 125.3 (d), 130.5 (d), 134.5 (d), 139.0 (s), 151.9 (s) and 166.9 (s).

**Thionation of 3-Methyl-3-sulfanyl-1,3-dihydro-2-benzothiophen-1-one 12.**—A solution of **12** (1 mmol) and LR (0.55 mmol) in toluene (50 cm<sup>3</sup>) was heated to reflux under argon for 0.25 h. After removal of the solvent, the residue was chromatographed on a silica gel column with benzene–hexane (4:1) to give 3-methyl-1,3-dihydro-2-benzothiophene-1-thione **11b** in 44% yield. Similar treatment of 3-methyl-3-sulfanyl-1,3-dihydroisobenzofuran-1-one **13** (1 mmol) with LR (1 mmol) in DME (50 cm<sup>3</sup>) gave **11b** and **12**.

**General Procedure for the Photochemical Reactions of the Thiones 7, 8 and 11 with Alkenes 2.**—A solution of the thione (200 mg) and alkene **2** (ca. 1 cm<sup>3</sup>) in benzene (or MeOH or acetonitrile) (70 cm<sup>3</sup>) was irradiated in a Pyrex vessel with a high-pressure mercury lamp (300 W) under argon for 5–12 h. After removal of the solvent, the residual oil was chromatographed on a silica gel column with benzene–hexane (4:1–1:2) as eluent to give the corresponding photoproducts **15–21**. A solution of the spiro-thietane **15a** (100 mg) in toluene (30 cm<sup>3</sup>) was heated to reflux for 15 h and usual work-up gave the tricyclic isobenzofurans **16a** (20%) and unchanged starting material (51%). The photoproducts **15b** and **15d–e** were unstable at room temperature and easily rearranged to tricyclic isobenzofuran derivatives **16b** and **16d–e** in organic solvents such as CHCl<sub>3</sub> and benzene and even neat.

**3',3',4',4'-Tetramethylspiro[1,3-dihydroisobenzofuran-1,2'-thietane] 15a.** Mp 104–105 °C (Found: C, 71.8; H, 7.7. C<sub>14</sub>H<sub>18</sub>OS requires C, 71.75; H, 7.75%;  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  1460, 1440, 1030 and 755;  $\delta_{\text{H}}$  1.05 (3 H, s), 1.35 (3 H, s), 1.40 (3 H, s), 1.82 (3 H, s), 5.08 (2 H, ABq, *J* 12.7, 14.6), 7.10–7.40 (3 H, m) and 7.49–7.65 (1 H, m);  $\delta_{\text{C}}$  20.2 (q), 24.4 (q), 26.3 (q), 30.4 (q), 49.5 (s), 58.0 (s), 72.1 (t), 100.7 (s), 120.5 (d), 125.7 (d), 127.0 (d), 128.2 (d), 139.2 (s) and 139.8 (s); *m/z* 234 (M<sup>+</sup>) and 160 (M<sup>+</sup> – Me<sub>2</sub>C=S).

**3,3,4,4-Tetramethyl-1,3,4,5-tetrahydro-1,5-epoxy-2-benzothiepine 16a.** Bp 140 °C/3 mmHg (Found: C, 71.95; H, 7.8. C<sub>14</sub>H<sub>18</sub>OS requires C, 71.75; H, 7.75%;  $\nu_{\max}(\text{film})/\text{cm}^{-1}$  1460, 1395, 1375, 1365, 1120, 1015, 995, 755 and 740;  $\delta_{\text{H}}$  0.34 (3 H, s), 0.97 (3 H, s), 1.04 (3 H, s), 1.37 (3 H, s), 4.57 (1 H, s), 6.15 (1 H, s)

and 7.11–7.45 (4 H, m);  $\delta_{\text{C}}$  20.1 (q), 25.2 (q), 28.7 (q), 29.2 (q), 37.9 (s), 48.2 (s), 84.1 (d), 87.9 (d), 120.1 (d), 121.9 (d), 127.0 (d), 128.2 (d), 141.7 (s) and 143.5 (s).

**3,3',3',4',4'-Pentamethylspiro[1,3-dihydroisobenzofuran-1,2'-thietane] 15b.** (1:1 Mixture of two stereoisomers), oil (Found: C, 72.6; H, 8.05. C<sub>15</sub>H<sub>20</sub>OS requires C, 72.55; H, 8.1%;  $\nu_{\max}(\text{film})/\text{cm}^{-1}$  1455, 1365, 1110, 1075, 1015 and 745;  $\delta_{\text{H}}$  1.07 (s), 1.26 (s), 1.42 (s), 1.43 (d, *J* 6.6), 1.50 (d, *J* 6.8), 1.51 (s), 1.80 (s), 1.83 (s), 5.12–5.46 (m), 7.00–7.39 (m) and 7.44–7.67 (m).

**Deuteriated Spiro-thietane [3-<sup>2</sup>H]15b.** (1:1 Mixture of two stereoisomers);  $\delta_{\text{H}}$  1.07 (s), 1.26 (s), 1.43 (s), 1.47 (s), 1.48 (s), 1.50 (s), 1.80 (s), 1.93 (s), 7.00–7.38 (m) and 7.46–7.67 (m).

**1,3,3,4,4-Pentamethyl-1,3,4,5-tetrahydro-1,5-epoxy-2-benzothiepine 16b.** Bp 130 °C/3 mmHg (Found: C, 72.65; H, 8.35. C<sub>15</sub>H<sub>20</sub>OS requires C, 72.55; H, 8.1;  $\nu_{\max}(\text{film})/\text{cm}^{-1}$  1460, 1375, 1085, 1000, 755 and 705;  $\delta_{\text{H}}$  0.31 (3 H, s), 0.97 (3 H, s), 1.03 (3 H, s), 1.34 (3 H, s), 1.89 (3 H, s), 4.60 (1 H, s) and 7.03–7.35 (4 H, m);  $\delta_{\text{C}}$  19.9 (q), 24.0 (q), 25.0 (q), 28.5 (q), 36.3 (s), 48.9 (s), 88.4 (d), 90.5 (s), 119.0 (d), 121.8 (d), 126.7 (d), 128.2 (d), 142.0 (s) and 146.6 (s).

**Deuteriated tricyclic isobenzofuran [5-<sup>2</sup>H]16b.**  $\delta_{\text{H}}$  0.31 (3 H, s), 0.97 (3 H, s), 1.03 (3 H, s), 1.33 (3 H, s), 1.89 (3 H, s), 4.60 (0.6 H, s) and 7.09–7.35 (4 H, m).

**3,3,3',3',4',4'-Hexamethylspiro[1,3-dihydroisobenzofuran-1,2'-thietane] 15c.** Mp 78–79 °C (Found: C, 73.25; H, 8.55. C<sub>16</sub>H<sub>22</sub>OS requires C, 73.25; H, 8.45%;  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  1440, 1360, 1015, 820, 760 and 725;  $\delta_{\text{H}}$  1.08 (3 H, s), 1.40 (3 H, s), 1.44 (3 H, s), 1.49 (6 H, s), 1.78 (3 H, s), 6.99–7.14 (1 H, m), 7.19–7.37 (2 H, m) and 7.53–7.66 (1 H, m);  $\delta_{\text{C}}$  21.3 (q), 24.2 (q), 26.7 (q), 29.1 (q), 29.9 (q), 30.2 (q), 48.7 (s), 57.6 (s), 85.1 (s), 98.3 (s), 120.0 (d), 125.7 (d), 127.1 (d), 128.4 (d), 139.3 (s) and 147.8 (s).

**3',3',4',4'-Tetramethyl-3-phenylspiro[1,3-dihydroisobenzofuran-1,2'-thietane] 15d.** (1:2 Mixture of two stereoisomers), mp 103–105 °C (Found: C, 77.65; H, 6.95. C<sub>20</sub>H<sub>22</sub>OS requires C, 77.4; H, 7.15%;  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  1600, 1495, 1450, 1365, 1005, 755 and 695;  $\delta_{\text{H}}$  (minor isomer) 1.03 (s), 1.60 (s), 1.75 (s), 1.77 (s), 6.16 (s), 6.82–6.98 (m), 7.10 (m) and 7.64–7.88 (m);  $\delta_{\text{H}}$  (major isomer) 1.14 (s), 1.36 (s), 1.44 (s), 1.85 (s), 6.12 (s), 6.82–6.98 (m), 7.10–7.62 (m) and 7.64–7.88 (m).

**3,3,4,4-Tetramethyl-1-phenyl-1,3,4,5-tetrahydro-1,5-epoxy-2-benzothiepine 16d.** Bp 200 °C/3 mmHg (Found: C, 77.15; H, 7.15. C<sub>20</sub>H<sub>22</sub>OS requires C, 77.4; H, 7.15%;  $\nu_{\max}(\text{film})/\text{cm}^{-1}$  1600, 1495, 1460, 1450, 1380, 1365, 1120, 1020, 1000, 750 and 700;  $\delta_{\text{H}}$  0.41 (3 H, s), 1.02 (3 H, s), 1.09 (3 H, s), 1.40 (3 H, s), 4.81 (1 H, s), 7.03–7.51 (7 H, m) and 7.64–7.78 (2 H, m);  $\delta_{\text{C}}$  20.0 (q), 25.1 (q), 28.6 (q), 36.5 (s), 49.6 (s), 88.5 (d), 93.9 (s), 120.4 (d), 121.8 (d), 125.3 (d), 126.8 (d), 128.2 (d), 128.4 (d), 140.2 (s), 141.4 (s) and 146.3 (s).

**3',3',4',4'-Tetramethyl-3-benzylspiro[1,3-dihydroisobenzofuran-1,2'-thietane] 15e.** (1:1 Mixture of two stereoisomers), oil;  $\nu_{\max}(\text{film})/\text{cm}^{-1}$  1650, 1600, 1490, 1455, 1365, 1105, 1010, 745 and 695;  $\delta_{\text{H}}$  1.01 (s), 1.10 (s), 1.34 (s), 1.39 (s), 1.42 (s), 1.49 (s), 1.77 (s), 1.83 (s), 3.03 (d of q, *J* 2.4, 14.2), 3.09 (d of q, *J* 2.4, 13.7), 5.31–5.56 (m), 6.76–6.93 (m), 7.05–7.35 (m) and 7.51–7.65 (m).

**1-Benzyl-3,3,4,4-tetramethyl-1,3,4,5-tetrahydro-1,5-epoxy-2-benzothiepine 16e.** Mp 108–110 °C (Found: C, 77.75; H, 7.55. C<sub>21</sub>H<sub>24</sub>OS requires C, 77.75; H, 7.45%;  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  1450, 1390, 995, 975, 805, 750 and 700;  $\delta_{\text{H}}$  0.26 (3 H, m), 0.94 (3 H, s), 1.00 (3 H, s), 1.29 (3 H, s), 3.53 (2 H, ABq, *J* 14.7), 4.60 (1 H, s) and 7.04–7.43 (9 H, m);  $\delta_{\text{C}}$  20.0 (q), 25.0 (q), 28.6 (q), 28.9 (q), 36.5 (s), 43.3 (t), 49.2 (s), 88.2 (d), 93.3 (s), 120.1 (d), 121.9 (d), 126.6 (d), 126.7 (d), 127.8 (d), 128.1 (d), 130.8 (d), 135.4 (s), 142.2 (s) and 145.4 (s).

**3,3-Diphenyl-3',3',4',4'-tetramethylspiro[1,3-dihydroisobenzofuran-1,2'-thietane] 15f.** Mp 136.5–138 °C (Found: C, 80.45; H, 6.85. C<sub>26</sub>H<sub>26</sub>OS requires C, 80.8; H, 6.76%;  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  1595, 1485, 1440, 1365, 1005, 995, 975, 765, 740 and 695;  $\delta_{\text{H}}$  0.59 (3 H, s), 1.30 (3 H, s), 1.42 (3 H, s), 1.79 (3 H, s) and 7.00–7.70 (14

H, m);  $\delta_C$  21.3 (q), 24.3 (q), 26.6 (q), 30.3 (q), 49.0 (s), 57.7 (s), 93.8 (s), 100.1 (s), 123.7 (d), 126.0 (d), 127.0 (d), 127.5 (d), 127.7 (d), 127.9 (d), 128.2 (d), 140.1 (s), 143.6 (s), 144.9 (s) and 146.0 (s).

3,3-Diallyl-3',3',4',4'-tetramethylspiro[1,3-dihydroisobenzofuran-1,2'-thietane] **15g**. Bp 175 °C/2 mmHg (Found: C, 76.65; H, 8.35.  $C_{20}H_{26}OS$  requires C, 76.4; H, 8.35%);  $\nu_{max}(\text{film})/\text{cm}^{-1}$  1635, 1455, 1365, 1015, 910, 750, 740 and 720;  $\delta_H$  1.13 (3 H, s), 1.39 (3 H, s), 1.45 (3 H, s), 1.76 (3 H, s), 2.44–2.59 (4 H, m), 4.81–5.16 (4 H, m), 5.47–6.07 (2 H, m), 6.92–7.15 (1 H, m), 7.17–7.39 (m, 2 H) and 7.45–7.67 (1 H, m);  $\delta_C$  21.6 (q), 24.2 (q), 27.0 (q), 30.8 (q), 44.1 (t), 44.5 (t), 48.2 (s), 57.8 (s), 89.0 (s), 98.9 (s), 118.1 (t), 118.2 (t), 121.0 (d), 125.5 (d), 127.4 (d), 128.1 (d), 133.6 (d), 140.7 (s) and 144.7 (s).

1,4,4-Trimethyl-1,3,4,5-tetrahydro-1,5-epoxy-2-benzothiepine **16h**. Bp 125 °C/3 mmHg; mp 80–81 °C (Found: C, 70.95; H, 7.35.  $C_{13}H_{16}OS$  requires C, 70.85; H, 7.3%);  $\nu_{max}(\text{KBr})/\text{cm}^{-1}$  1460, 1375, 1315, 1095, 990, 755 and 695;  $\delta_H$  0.95 (3 H, s), 1.41 (3 H, s), 1.90 (3 H, s), 2.07 (2 H, s), 4.58 (1 H, s) and 7.11–7.43 (4 H, m);  $\delta_C$  22.7 (q), 23.7 (q), 25.7 (q), 29.8 (s), 36.5 (t), 87.5 (d), 90.1 (s), 118.8 (d), 121.3 (d), 126.6 (d), 128.1 (d), 141.3 (s) and 143.7 (s).

1,3,4,4-Tetramethyl-1,3,4,5-tetrahydro-1,5-epoxy-2-benzothiepine **16i**. (1:1 Mixture of two stereoisomers), bp 135 °C/3 mmHg (Found: C, 72.0; H, 7.75.  $C_{14}H_{18}OS$  requires C, 71.75; H, 7.75%);  $\nu_{max}(\text{film})/\text{cm}^{-1}$  1455, 1370, 1095, 1065, 1000 and 745;  $\delta_H$  0.35 (d, *J* 7.8), 0.96 (3 H, *J* 6.8), 0.98 (s), 1.03 (s), 1.23 (s), 1.46 (s), 1.89 (s), 2.17 (q, *J* 6.8), 2.63 (q, *J* 7.8), 4.60 (br s) and 7.10–7.49 (m);  $\delta_C$  14.1 (q), 17.9 (q), 20.3 (q), 22.6 (q), 23.5 (q), 23.6 (q), 24.1 (q), 27.9 (q), 32.0 (s), 34.1 (s), 42.1 (d), 45.1 (d), 86.7 (d), 88.5 (d), 89.7 (s), 91.0 (s), 118.4 (d), 118.9 (d), 121.3 (d), 121.9 (d), 126.4 (d), 126.7 (d), 128.1 (d), 128.2 (d), 140.6 (s), 141.6 (s), 144.7 (s) and 146.4 (s).

1-(1-Cyano-2-sulfanylethylidene)-1,3-dihydroisobenzofuran **17**. Although two (*E/Z*)-geometrical isomers of **17** were isolated, their configurations could not be clarified because of the close similarity between the NMR spectra of the two isomers. The configuration of **18** is also unclear. *Isomer A*, mp 67–68 °C (Found: C, 65.25; H, 4.45; N, 7.05.  $C_{11}H_9NOS$  requires C, 65.0; H, 4.45; N, 6.9%);  $\nu_{max}(\text{KBr})/\text{cm}^{-1}$  2550, 2180 and 1625;  $\delta_H$  1.96 (1 H, t, *J* 6.8), 3.72 (2 H, d, *J* 6.8), 5.50 (2 H, s), 7.40–7.66 (3 H, m) and 7.70–7.84 (1 H, m);  $\delta_C$  22.5 (t), 75.2 (t), 82.8 (s), 118.6 (s), 121.9 (d), 124.8 (d), 129.1 (d), 130.2 (s), 131.7 (d), 143.5 (s) and 168.5 (s).

*Isomer B*; mp 97–98 °C (Found: C, 64.9; H, 4.35; N, 6.75.  $C_{11}H_9NOS$  requires C, 65.0; H, 4.45; N, 6.9%);  $\nu_{max}(\text{KBr})/\text{cm}^{-1}$  2550, 2190 and 1625;  $\delta_H$  1.99 (1 H, t, *J* 8.3), 3.57 (2 H, d, *J* 8.3), 5.48 (2 H, s), 7.29–7.64 (3 H, m) and 8.21–8.43 (1 H, m);  $\delta_C$  22.9 (t), 75.8 (t), 82.3 (s), 119.2 (s), 121.2 (d), 124.4 (d), 128.9 (d), 130.3 (s), 131.6 (d), 142.2 (s) and 167.3 (s).

1-(1-Cyanoethylidene)-1,3-dihydroisobenzofuran **18**. Mp 95–96 °C (Found: C, 77.1; H, 5.35; N, 8.1.  $C_{11}H_9NO$  requires C, 77.15; H, 5.3; N, 8.2%);  $\nu_{max}(\text{KBr})/\text{cm}^{-1}$  2180 and 1635;  $\delta_H$  2.00 (3 H, s), 5.40 (2 H, s), 7.26–7.57 (3 H, m) and 8.20–8.33 (1 H, m);  $\delta_C$  13.5 (q), 74.8 (t), 121.1 (d), 124.0 (d), 128.7 (d), 130.8 (d), 141.8 (s) and 167.0 (s).

3,3,3',3',4',4'-Hexamethylspiro[1,3-dihydronaphtho[2,3-c]furan-1,2'-thietane] **19**. Mp 144–146 °C (Found: C, 76.7; H, 7.85.  $C_{20}H_{24}OS$  requires C, 76.9; H, 7.75%);  $\nu_{max}(\text{KBr})/\text{cm}^{-1}$  1460, 1370, 1285, 1005, 895 and 750;  $\delta_H$  1.11 (3 H, s), 1.50 (6 H, s), 1.57 (3 H, s), 1.59 (3 H, s), 1.82 (3 H, s), 7.34–7.52 (3 H, m), 7.72–7.95 (2 H, m) and 8.07 (1 H, s);  $\delta_C$  21.3 (q), 24.3 (q), 26.7 (q), 29.3 (q), 30.2 (q), 30.4 (q), 48.9 (s), 57.8 (s), 84.6 (s), 97.6 (s), 118.1 (d), 124.9 (d), 125.5 (d), 126.2 (d), 127.5 (d), 128.6 (d), 133.0 (s), 133.6 (s), 138.8 (s) and 146.5 (s).

1-Isopropylidene-1,3-dihydronaphtho[2,3-c]furan **20**. Mp 117–118 °C (Found: C, 85.6; H, 7.6.  $C_{17}H_{18}O$  requires C, 85.65; H, 7.6%);  $\nu_{max}(\text{KBr})/\text{cm}^{-1}$  1655, 1600, 1495, 1440, 1375, 1360, 1290, 1115, 880 and 755;  $\delta_H$  1.60 (6 H, s), 1.96 (3 H, s), 2.13 (3 H, s),

7.33–7.53 (3 H, m) and 7.69–7.96 (3 H, m);  $\delta_C$  18.8 (q), 19.8 (q), 29.1 (q), 83.3 (s), 104.8 (s), 118.6 (d), 121.3 (d), 125.7 (d), 125.8 (d), 127.5 (d), 128.5 (d), 132.5 (s), 132.7 (s), 133.5 (s), 147.1 (s) and 147.9 (s).

3',3',4',4'-Tetramethylspiro[1,3-dihydro-2-benzothiophene-1,2'-thietane] **21a**. Bp 165 °C/2 mmHg (Found: C, 67.2; H, 7.3.  $C_{14}H_{18}S_2$  requires C, 67.15; H, 7.25%);  $\nu_{max}(\text{film})/\text{cm}^{-1}$  1475, 1450, 1370, 1125, 820, 750 and 720;  $\delta_H$  1.08 (3 H, s), 1.36 (3 H, s), 1.49 (3 H, s), 1.81 (3 H, s), 3.80 (1 H, d, *J* 14.2), 4.17 (1 H, d, *J* 14.2), 7.15–7.36 (3 H, m) and 7.55–7.69 (1 H, m);  $\delta_C$  23.8 (q), 25.0 (q), 26.3 (q), 30.2 (q), 37.3 (t), 49.7 (s), 56.7 (s), 72.3 (s), 124.4 (d), 125.8 (d), 127.1 (d), 127.5 (d), 141.1 (s) and 142.7 (s).

3,3',3',4',4'-Pentamethylspiro[1,3-dihydro-2-benzothiophene-1,2'-thietane] **21b**. (Isomer-1), mp 53–54 °C (Found: C, 67.95; H, 7.65.  $C_{15}H_{20}S_2$  requires C, 68.15; H, 7.6%);  $\nu_{max}(\text{KBr})/\text{cm}^{-1}$  1475, 1445, 1365, 910, 815 and 755;  $\delta_H$  1.08 (3 H, s), 1.24 (3 H, s), 1.35 (3 H, s), 1.54 (3 H, d, *J* 6.6), 1.80 (3 H, s), 4.50 (1 H, q, *J* 6.6), 7.13–7.29 (3 H, m) and 7.61–7.67 (1 H, m);  $\delta_C$  20.3 (q), 24.0 (q), 25.0 (q), 26.3 (q), 30.2 (q), 45.8 (d), 49.5 (s), 56.6 (s), 71.7 (s), 122.8 (d), 125.8 (d), 127.4 (d), 143.1 (s) and 145.8 (s). (Isomer-2), mp 71–72 °C (Found: C, 67.8; H, 7.45.  $C_{15}H_{20}S_2$  requires C, 68.15; H, 7.6%);  $\nu_{max}(\text{KBr})/\text{cm}^{-1}$  1470, 1445, 1365, 910, 810 and 750;  $\delta_H$  1.14 (3 H, s), 1.24 (3 H, s), 1.42 (3 H, s), 1.58 (3 H, d, *J* 6.9), 1.72 (3 H, s), 4.43 (1 H, q, *J* 6.9), 7.11–7.35 (3 H, m) and 7.74 (1 H, d, *J* 7.6);  $\delta_C$  24.8 (q), 26.0 (q), 26.3 (q), 26.6 (q), 30.3 (q), 47.0 (d), 49.1 (s), 56.2 (s), 74.3 (s), 123.7 (d), 126.1 (d), 127.5 (d), 128.2 (d), 141.8 (s) and 146.2 (s).

3',3',4',4'-Tetramethyl-3-phenylspiro[1,3-dihydro-2-benzothiophene-1,2'-thietane] **21c**. (Isomer-1), mp 95–96 °C (Found: C, 73.6; H, 6.9.  $C_{20}H_{22}S_2$  requires C, 73.55; H, 6.8%);  $\nu_{max}(\text{KBr})/\text{cm}^{-1}$  1590, 1485, 1465, 1445, 1365, 815, 780, 745, 710 and 700;  $\delta_H$  1.15 (3 H, s), 1.33 (3 H, s), 1.38 (3 H, s), 1.80 (3 H, s), 5.53 (1 H, s), 6.74 (1 H, d, *J* 7.6), 7.01–7.37 (7 H, m) and 7.69 (1 H, d, *J* 7.6);  $\delta_C$  24.1 (q), 25.1 (q), 26.2 (q), 30.3 (q), 49.7 (s), 56.5 (d), 56.9 (s), 72.5 (s), 125.0 (d), 126.0 (d), 127.2 (d), 127.4 (d), 127.7 (d), 128.5 (d), 129.3 (d), 140.8 (s), 143.3 (s) and 145.4 (s). (Isomer-2), oil;  $\nu_{max}(\text{film})/\text{cm}^{-1}$  1600, 1475, 1445, 805, 780, 750, 715 and 700;  $\delta_H$  0.83 (3 H, s), 1.17 (3 H, s), 1.39 (3 H, s), 1.64 (3 H, s), 5.62 (1 H, s), 7.05–7.38 (8 H, m) and 7.84 (1 H, d, *J* 7.9);  $\delta_C$  24.8 (q), 25.8 (q), 26.6 (q), 30.4 (q), 48.8 (s), 55.5 (d), 56.7 (s), 74.7 (s), 125.8 (d), 126.6 (d), 126.9 (d), 127.6 (d), 127.9 (d), 128.3 (s), 144.1 (s) and 144.3 (s).

## References

- A. Ohno, *Int. J. Sulfur Chem., Part B*, 1971, **6**, 183; A. Ohno, in *Organic Chemistry of Sulfur*, ed. S. Oae, Plenum Press, New York, 1977, p. 189.
- J. D. Coyle, *Chem. Soc. Rev.*, 1975, **4**, 523; *Tetrahedron*, 1985, **41**, 5395.
- P. de Mayo, *Acc. Chem. Res.*, 1976, **9**, 52.
- N. J. Turro, V. Ramamurthy, W. Cherry and W. Farneth, *Chem. Rev.*, 1978, **78**, 125.
- V. Ramamurthy, in *Organic Photochemistry*, ed. A. Padwa, Marcel Dekker, New York, 1985, vol. 7, p. 231.
- M. Sakamoto, S. Watanabe, T. Fujita and T. Nishio, *J. Synth. Org. Chem. Jpn.*, 1994, **52**, 658.
- (a) K. H. Grellman and E. Tauer, *Tetrahedron Lett.*, 1967, 1909; (b) J. L. Fourrey, P. Jouin and J. Moron, *Tetrahedron Lett.*, 1974, 3005; (c) P. Jouin and J. L. Fourrey, *Tetrahedron Lett.*, 1975, 1329; (d) C. Marazano, J. L. Fourrey and B. C. Das, *Chem. Commun.*, 1977, 742; (e) B. C. Das, J. L. Fourrey, C. Marazano, A. Merriën and J. Polonsky, *J. Chem. Res., Synop.*, 1978, 370; (f) R. Paramasivam, R. Polaniappan and V. T. Pamakrishnan, *J. Chem. Soc., Chem. Commun.*, 1979, 260; (g) P. de Mayo, L. K. Sydness and G. Wenska, *J. Org. Chem.*, 1980, **45**, 1549; (h) A. Couture, R. Dubiez and A. Lablanche-Combiér, *J. Chem. Soc., Chem. Commun.*, 1982, 842; *J. Org. Chem.*, 1984, **49**, 714; (i) M. Machida, K. Oda and Y. Kanaoka, *Tetrahedron Lett.*, 1984, **25**, 409; (j) E. Sato, Y. Ikeda and Y. Kanaoka, *Chem. Lett.*, 1987, 273; (k) E. Sato, Y. Ikeda and Y. Kanaoka, *Chem. Pharm. Bull.*, 1990, **38**, 1205; (l) T. Nishio, *J. Chem. Soc., Perkin Trans. 1*, 1987, 1225; (m) T. Nishio,

- M. Fujisawa and Y. Omote, *J. Chem. Soc., Perkin Trans. 1*, 1987, 2523; (n) E. Sato, M. Hasebe, T. Nishio, Y. Ikeda and Y. Kanaoka, *Liebigs Ann. Chem.*, 1988, 733; (o) T. Nishio, N. Okuda and Y. Omote, *J. Chem. Soc., Perkin Trans. 1*, 1988, 1663; (p) T. Nishio, *J. Chem. Res., Synop.*, 1989, 204; (q) T. Nishio, N. Okuda and C. Kashima, *J. Chem. Soc., Perkin Trans. 1*, 1991, 141; (r) T. Nishio and N. Okuda, *J. Org. Chem.*, 1992, **57**, 4000; (s) T. Nishio, Y. Mori and A. Hosomi, *J. Chem. Soc., Perkin Trans. 1*, 1993, 2197; (t) K. Oda and M. Machida, *J. Chem. Soc., Chem. Commun.*, 1993, 437; *Chem. Pharm. Bull.*, 1993, **41**, 1299; (u) T. Nishio, Y. Mori, I. Iida and A. Hosomi, *Helv. Chim. Acta*, 1994, **77**, 981.
- 8 (a) H. Gotthardt and M. Listl, *Chem. Ber.*, 1974, **107**, 2552; (b) P. Ooms and W. Hartmann, *Tetrahedron Lett.*, 1987, **28**, 2701; (c) P. Wipf and H. Heimgartner, *Helv. Chim. Acta*, 1987, **70**, 992; (d) S. Devanathan and V. Ramamurthy, *J. Org. Chem.*, 1988, **53**, 741.
- 9 T. H. Lowry and S. Richardson, in *Mechanism and Theory in Organic Chemistry*, Harper & Row, New York, 1976, p. 57.
- 10 U. Prey, B. Kerres and H. Berbalk, *Monatsh Chem.*, 1960, **91**, 319.
- 11 G. Bendz and A. Thalen, *Arkiv. Kemi*, 1959, **14**, 519 (*Chem. Abstr.*, 1961, **55**, 4446d).

Paper 4/05859C

Received 26th September 1994

Accepted 18th November 1994