

## Ylide Formation and Rearrangement in the Thermal Reaction of 6*H*-Dibenzo[*b,d*]thiopyran and its 6-Phenyl Derivative with Diazoalkanes

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Reaction of 6-phenyl-6*H*-dibenzo[*b,d*]thiopyran (1b) with diphenyldiazomethane (2a) in refluxing benzene affords 6,6,7-triphenyl-6,7-dihydrodibenzo[*b,d*]thiepin (3b) as major product, together with minor amounts of 6-diphenylmethyl-6-phenyl-6*H*-dibenzo[*b,d*]thiopyran (4b). Analogous results are obtained from the reaction of 6*H*-dibenzo[*b,d*]thiopyran (1a); however, in this case the yields of the corresponding ring-expansion and insertion products (3a) and (4a) are similar. Copper(II) sulphate-catalysed thermal decomposition of ethyl diazoacetate (2b) in the presence of (1b) yields mainly ethyl 6-phenyl-6*H*-dibenzo[*b,d*]thiopyran-6-ylacetate (4d), together with minor amounts of (probably) 6-ethoxycarbonyl-7-phenyl-6,7-dihydrodibenzo[*b,d*]thiepin (3d), but only the product of insertion of ethoxycarbonylcarbene into the C(6)–H bond, *i.e.* (4c), is observed from the reaction of (2b) with (1a). Formation of the products (3) and (4) is rationalized in terms of a thermal ylide exchange reaction of the unstable sulphonium ylides (7a–d), initially produced in competition with a Stevens-type rearrangement.

In support of the above mechanism, pyrolysis of the stable 6*H*-dibenzo[*b,d*]thiopyran-5-*io*-(bismethoxycarbonyl)methanide (7e) gave only the product of insertion of bismethoxycarbonylcarbene into the C(6)–H bond, *i.e.* the malonate (4e), whereas almost exclusive formation of the ring-expansion product (3f) occurred on pyrolysis of the 6-phenyl derivative of the ylide (7e).

IN recent years considerable attention has been devoted to reactions of carbenes with sulphur compounds, leading to sulphonium ylides by electrophilic attack of singlet carbenes on the nonbonding electron pair of the sulphur atom.<sup>1</sup> Stable sulphonium ylides can be obtained with strongly electrophilic carbenes carrying electron-withdrawing substituents, whereas with less electrophilic carbenes products have been accounted for by assuming the intermediacy of unstable sulphonium ylides.<sup>1</sup> A great variety of sulphur compounds, including cyclic and acyclic alkyl and aryl sulphides, have been shown to be able to trap carbenes.<sup>1,2</sup> Even sulphur compounds such as vinyl sulphides, thiophen, and dibenzothiophen, in which the sulphur lone pair is highly delocalized, have been shown to react with appropriate carbenes to give stable sulphonium ylides.<sup>1</sup> Thus reactions of carbenes with sulphur compounds appear to provide a useful approach to the generation of sulphonium ylides and to the study of their rearrangement, which has attracted much interest from both a theoretical and a synthetic standpoint.<sup>3</sup> Most recently, in a study<sup>4</sup> of the reactivity of 1,2,3-benzothiadiazole with diphenylcarbene, we stated that 6-phenyl-6*H*-dibenzo[*b,d*]thiopyran (1b), arising as major product from attack of triplet diphenylcarbene on the sulphur atom of benzothiadiazole, is capable of reacting with diphenyldiazomethane (2a) to give 6,6,7-triphenyl-6,7-dihydrodibenzo[*b,d*]thiepin (3b) and 6-diphenylmethyl-6-phenyl-6*H*-dibenzo[*b,d*]thiopyran (4b); however no experimental details of the reaction nor any mechanistic rationalisation were reported.<sup>4</sup> In this paper we give a full account of the reaction of thiopyran (1b) with diphenyldiazomethane (2a), together with related results obtained from a study of the reactivity of (1b) with ethyl diazoacetate (2b) and dimethyl diazomalonalate (2c), and of the parent dibenzothiopyran (1a) with the diazoalkanes (2a–c); these results provide the first examples of ylide forma-

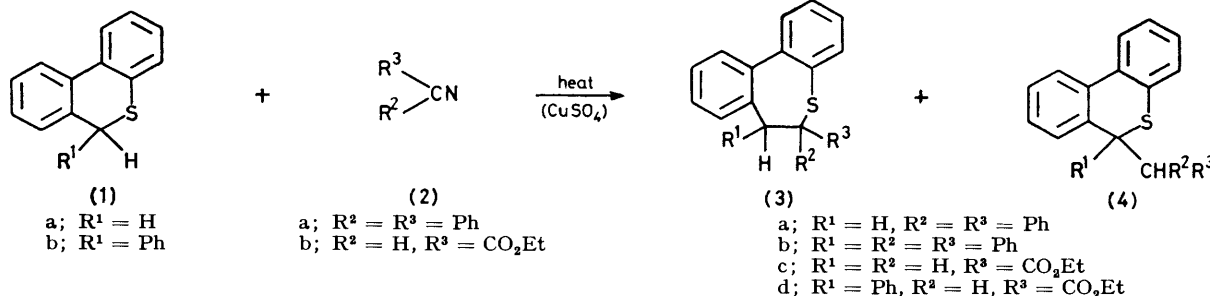
tion and rearrangement in the dibenzo[*b,d*]thiopyran series.

### RESULTS AND DISCUSSION

Reaction of 6-phenyl-6*H*-dibenzo[*b,d*]thiopyran (1b) with equimolar amounts of diphenyldiazomethane (2a) in refluxing benzene for *ca.* 10 h (until disappearance of the diazo-band at 2100 cm<sup>-1</sup> was observed in the i.r. spectrum) gave, after column chromatography of the reaction mixture, 6,6,7-triphenyl-6,7-dihydrodibenzo[*b,d*]thiepin (3b) and 6-diphenylmethyl-6-phenyl-6*H*-dibenzo[*b,d*]thiopyran (4b) in 58 and 29% yields, respectively [based on (1b) consumed; 55% was recovered unchanged]. Benzophenone azine and benzophenone, the common products of thermal decomposition of diphenyldiazomethane (2a), were also isolated. When the same reaction was carried out using a four-fold excess of the diazoalkane (2a), almost complete consumption of (1b) could be achieved, the conversion yields of products (3b) and (4b) remaining substantially unchanged. Compound (4b) has been reported previously.<sup>4</sup> The dihydrothiepin (3b) was identified on the basis of elemental analysis as well as spectral and chemical evidence. The n.m.r. spectrum showed a one-proton singlet at  $\delta$  5.01 and a complex pattern due to *ca.* 23 protons in the aromatic region. The mass spectrum exhibited the molecular ion at  $m/z$  440 (44%) and predominant fragment ions at  $m/z$  273 (54%), 242 (100), 167 (37), 166 (35), and 165 (90). The base peak at  $m/z$  242 (C<sub>19</sub>H<sub>14</sub><sup>+</sup>) might be attributed to loss of Ph<sub>2</sub>CS from the molecular ion, whereas loss of Ph<sub>2</sub>CH from the molecular ion would give the ion at  $m/z$  273 (C<sub>19</sub>H<sub>13</sub>S<sup>+</sup>). Chemical support for the assigned structure was provided by desulphurisation with Raney nickel in boiling benzene, which led to 1,1,2-triphenyl-2-(biphenyl-2-yl)ethane (5a) in 50% yield.

Analogous results were obtained by treating 6*H*-

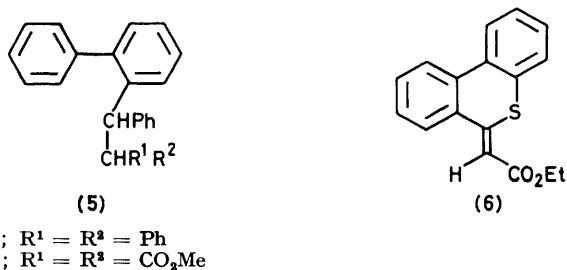
dibenzo[*b,d*]thiopyran (1a) with equimolar amounts of diphenyldiazomethane (2a). In this case chromatography of the reaction mixture afforded unchanged (1a) (60%), and similar amounts of 6,6-diphenyl-6,7-dihydrodibenzo[*b,d*]thiopin (3a) and 6-diphenylmethyl-6*H*-dibenzo[*b,d*]thiopyran (4a) in an overall yield of 75%. Minor amounts of tetraphenylethane contaminated with an unidentified product which could not be separated were also isolated. The mass spectrum of the mixture appeared to indicate that the unknown had a molecular ion at *m/z* 394 and a base peak at 197, thus possibly pointing to a dimeric product of 6*H*-dibenzo[*b,d*]thiopyran-6-yl radical.



SCHEME 1

Spectroscopic data and elemental analysis were consistent with the proposed structures (3a) and (4a). In particular the n.m.r. spectrum of (3a) showed a two-proton singlet at  $\delta$  3.23, whereas a two-proton AB quartet at  $\delta$  3.83 and 4.3 with *J* 11.5 Hz was observed in the spectrum of (4a).

The mass spectra of (3a) and (4a) showed fragmentation patterns analogous to those exhibited by compounds (3b) and (4b), respectively.



Copper(II) sulphate-catalysed thermal decomposition of ethyl diazoacetate (2b) in refluxing benzene containing equivalent amounts of (1a) gave ethyl 6*H*-dibenzo[*b,d*]thiopyran-6-ylacetate (4c) (44%) and ethyl 6*H*-dibenzo[*b,d*]thiopyran-6-ylideneacetate (6) (7%) as the only identifiable products, together with starting thiopyran (1a) (45%). Structure (4c) was readily assigned on the basis of spectral evidence and elemental analysis (see Experimental section). As for the acetate (6), the i.r. spectrum showed, as expected, a low frequency carbonyl band at 1 695 cm<sup>-1</sup> and the n.m.r. spectrum featured one kind of ethoxy-group and a one-proton singlet at  $\delta$  6.33,

thus indicating the presence of only one geometrical isomer of (6).

The observed chemical shift value of the one-proton singlet ascribable to the  $\alpha$ -H leads us to assign the acetate (6) the *Z*-configuration; such a proton would be expected to absorb at higher field in the *E*-configuration.<sup>5</sup> The formation of the product (6) appears to be due to further reaction of the initially formed acetate (4c), as evidenced by control experiments which showed that treatment of (4c) with ethyl diazoacetate (2b) under the same conditions could induce some conversion of (4c) into (6).

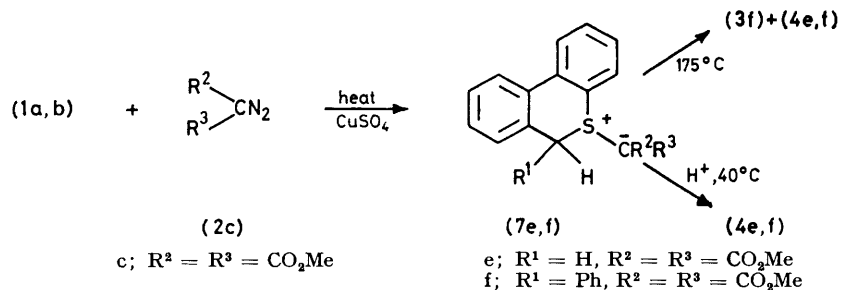
Treatment of 6-phenyl-6*H*-dibenzo[*b,d*]thiopyran (1b) with ethyl diazoacetate (2b) under the same conditions as

reported for (1a) furnished a complex mixture of products (t.l.c.). Column chromatography afforded the major product (38%) which was found to be ethyl 6-phenyl-6*H*-dibenzo[*b,d*]thiopyran-6-ylacetate (4d), contaminated probably by some isomeric 6-ethoxycarbonyl-7-phenyl-6,7-dihydrodibenzo[*b,d*]thiopin (3d) as evidenced by spectroscopic data in addition to elemental analysis. The i.r. spectrum showed a carbonyl stretching band at 1 735 cm<sup>-1</sup> with shoulder at 1 745 cm<sup>-1</sup>, and the mass spectrum exhibited one molecular ion at *m/z* 360. The n.m.r. spectrum, in addition to two kinds of ethoxy-group, showed a two-proton singlet due to the  $\alpha$ -protons of the acetate (4d), and a two-proton AB quartet with *J* 5 Hz, apparently due to 6-H and 7-H of the thiopin (3d), present in the ratio *ca.* 20 : 1. Other, minor products, which could not be identified, and some polymeric material were also obtained.

Repeated chromatography of the isolated mixture of (4d) and (3d) allowed separation of the pure acetate (4d); attempts to obtain the thiopin (3d) free of (4d) were unsuccessful and thus full confirmation of its structure could not be achieved.

Reaction of the dibenzothiopyrans (1a and b) with dimethyl diazomalonate (2c) in refluxing benzene in the presence of copper(II) sulphate furnished dibenzothiopyran-5-*io*(bismethoxycarbonyl)methanides (7e and f), which could be isolated in good yields. The ylides (7e and f) are fairly stable compounds which undergo thermal rearrangement at temperatures above 150 °C or acid-catalysed rearrangement in mild conditions. Pyrolysis of the ylide (7e) at 175 °C in a sealed tube gave dimethyl 6*H*-dibenzo[*b,d*]thiopyran-6-ylmalonate (4e) in

70% yield. Under the same conditions the ylide (7f) furnished 6,6-bis(methoxycarbonyl)-7-phenyl-6,7-dihydrodibenzo[*b,d*]thiepin (3f) and dimethyl 6-phenyl-6*H*-dibenzo[*b,d*]thiopyran-6-ylmalonate (4f) in yields of 75 and 2%, respectively. On the other hand the sulphonium ylides (7e) and (7f) on refluxing in methylene chloride in the presence of acetic acid were converted into the rearranged products (4e) and (4f) in 90 and 60% yields respectively; in these cases no evidence of the formation of any ring-expansion product (3e) or (3f) was obtained. Moreover the ylides (7e and f) were stable in boiling methylene chloride in the absence of acid (Scheme 2).



SCHEME 2

The structures of the malonates (4e and f) were fully supported by spectroscopic data and elemental analysis. The i.r. spectra showed two carbonyl stretching bands in the range 1 765—1 745 cm<sup>-1</sup> and the mass spectra showed a molecular ion peak of low abundance and a base peak due to [M - CH(CO<sub>2</sub>Me)<sub>2</sub>]<sup>+</sup>. Further confirmation of these structures was obtained from the n.m.r. spectra (see Experimental section).

The dihydrothiepin (3f) exhibited two i.r. absorptions in the carbonyl region at 1 750 and 1 735 cm<sup>-1</sup>; the n.m.r. spectrum showed two diastereotopic methoxy-groups, a one-proton singlet at δ 4.58, and a multiplet due to 13 protons in the aromatic region. The mass spectrum showed, in addition to the molecular ion, important fragment ions due to [M - S]<sup>+</sup>, [M - CO<sub>2</sub>Me]<sup>+</sup>, [M - CH(CO<sub>2</sub>Me)<sub>2</sub>]<sup>+</sup>, and [M - PhCH=C(CO<sub>2</sub>Me)<sub>2</sub>]<sup>+</sup>.

Chemical confirmation of the structure (3f) was obtained from desulphurisation, which gave 1,1-bis(methoxycarbonyl)-2-phenyl-2-(biphenyl-2-yl)ethane (5b) as the only isolated product, in 62% yield.

The relative yields of 6,7-dihydrodibenzo[*b,d*]thiepins (3) and dibenzo[*b,d*]thiopyrans (4) obtained by thermal reaction of the thiopyrans (1a and b) with diazoalkanes (2a and b) and from pyrolysis of the ylides (7e and f) are collected in the Table.

Products arising from reaction of the dibenzothiopyrans (1a and b) with diphenyldiazomethane (2a) and ethyl diazoacetate (2b) can be reasonably rationalized by assuming that the sulphur site of (1a) and (1b) is capable of trapping the intermediate carbene (or carbenoid complex), leading initially to the unstable sulphonium ylides (7a—d). The intermediacy of un-

stable sulphonium ylides in thermal or photochemical decomposition of diphenyldiazomethane (2a)<sup>6</sup> and of ethyl diazoacetate (2b)<sup>1,2a,b,7</sup> in the presence of sulphur compounds has been suggested previously to account for the products observed. Stevens-type rearrangement of the ylides (7) would afford the ring-expansion products (3), whereas thermal ylide exchange would lead to the endocyclic ylides (8) and then to dibenzothiopyrans (4) by subsequent Stevens rearrangement. This hypothesis appears to be supported by the formation of analogous Stevens rearrangement products from pyrolysis of dibenzothiopyranio(bismethoxycarbonyl)methanides (7e and f) (Scheme 3).

The relative yields of products (3) and (4) (Table) are markedly influenced both by the presence of the 6-phenyl substituent and by the nature of the groups R<sup>2</sup> and R<sup>3</sup> linked to the methanide carbon atom in the sulphonium ylides (7). This observation is explicable

TABLE

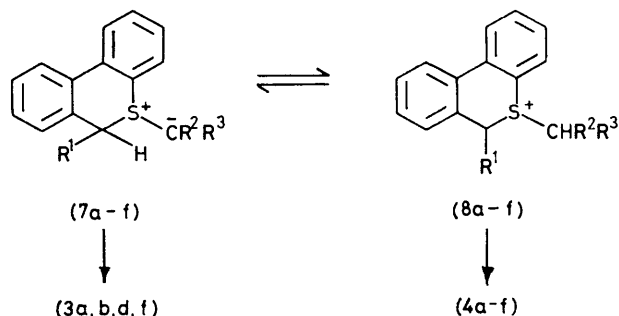
Product ratios of 6,7-dihydrodibenzo[*b,d*]thiepins (3) and dibenzo[*b,d*]thiopyrans (4) from thermal reaction of the dibenzo[*b,d*]thiopyrans (1a and b) with the diazoalkanes (2a and b) in refluxing benzene and from pyrolysis at 175 °C of the sulphonium ylides (7e and f)

Dibenzo[ <i>b,d</i> ]-thiopyran	Diazoalkane	Sulphonium ylide	Product ratios (%)	
			(3)	(4)
(1a)	(2a)	c	55 (3a)	45 (4a)
(1a)	(2b) <sup>a</sup>	c		100 (4c)
(1a)	(2c)	(7e) <sup>b</sup>		100 (4e)
(1b)	(2a) <sup>a</sup>	c	67 (3b)	33 (4b)
(1b)	(2b)	c	5 (3d)	95 (4d)
(1b)	(2c)	(7f) <sup>b</sup>	97 (3f)	3 (4f)

<sup>a</sup> Carried out in the presence of anhydrous copper(II) sulphate. <sup>b</sup> Isolated from copper(II) sulphate-catalysed thermal decomposition of dimethyl diazomalonnate (2c) in the presence of (1a) and (1b), respectively. <sup>c</sup> Sulphonium ylide not observed.

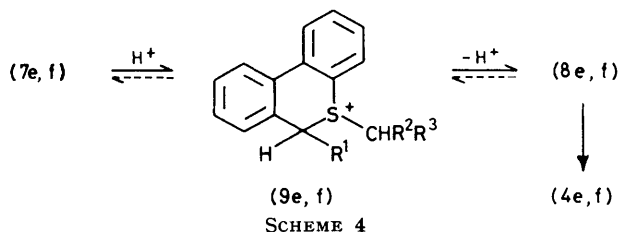
in terms of the relative stabilities of the first-formed ylides (7), which depend on the electron-withdrawing power of R<sup>2</sup> and R<sup>3</sup>, and of the enhanced migratory aptitude of C-6, arising from the 6-phenyl substituent. With the strongly resonance-stabilized ylides (7e and f), proton transfer leading to the much less stabilized ylides (8e and f) and/or Stevens rearrangement affording the ring-expansion products (3e and f) require high-energy conditions, under which the ylides (8e and f) would be expected to be destroyed rapidly by reversion

to the ylides (7e and f) and/or Stevens rearrangement to the dibenzothiopyrans (4e and f). The great reactivity (and poor stability) of the ylides (8) is apparent from our observations that acid-catalysed decomposition of (7e



SCHEME 3

and f) in refluxing dichloromethane yields rearranged products (4e and f), no intermediate ylides (8) being detectable by t.l.c. during the reaction. Under such conditions the added acid would reasonably induce proton transfer from (7e and f) to (8e and f) through intermediate sulphonium ions (9e and f), followed by Stevens rearrangement of the resulting sulphonium ylides (8e and f) (Scheme 4).



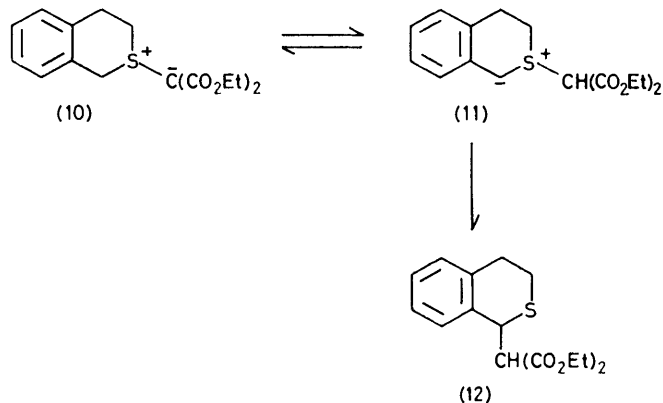
SCHEME 4

Pyrolysis of the ylide (7e) gives the dibenzothiopyran (4e) as the only rearranged product, thus indicating that proton transfer affording the endocyclic ylide (8e), followed by rearrangement to (4e) takes place exclusively at the expense of the Stevens rearrangement which could give the ring expansion product (3e). This trend is analogous to that previously observed with isothiochroman-2-yl(bisethoxycarbonyl)methanide (10) which on pyrolysis at 150 °C gave diethyl isothiochroman-1-ylmalonate (12) as the only isolated product through intermediate formation of the endocyclic ylide (11).<sup>2a</sup>

The results obtained from the ylides (7e) and (10) contrast with those reported by Ando and his co-workers<sup>8</sup> for pyrolysis of the acyclic benzylmethylsulphonium ylide (13) which furnished benzylmalonate (14) as the only product in 90% yield.

As previously suggested,<sup>2a</sup> a more favourable stereochemistry for proton transfer in the cyclic ylides (7e) and (10) with respect to the acyclic ylide (13) might explain the different behaviour observed. In the case of pyrolysis of the ylide (7f), the almost exclusive formation of the ring-expansion product (3f) at the expense of the dibenzothiopyran (4f) indicates that in this case the thermal ylide exchange process is almost completely

suppressed by the competing Stevens rearrangement leading to (3f), which is facilitated by the enhanced migratory aptitude of C-6 due to the 6-phenyl substituent.



With the less resonance-stabilized ylides (7c, and d), proton transfer leading to the endocyclic ylides (8c and d) and the following Stevens rearrangement to the dibenzothiopyrans (4c and d) appears to be largely preferred over Stevens rearrangement to the ring-expansion products (3c and d). In fact the dibenzothiopyran (4c) would be the only product arising from the ylide (7c) initially formed, whereas the ylide (7d) would give mainly the dibenzothiopyran (4d), together with small amounts of the possible ring expansion product (3d). It



would be reasonable to assume that the strongly reduced stability of the ylides (7c and d) with respect to the sulphonium ylides (7e and f) would cause proton transfer to be much more favoured; thus in such cases thermal ylide exchange (7)  $\rightleftharpoons$  (8) would readily occur, reaction products essentially (or exclusively) arising from Stevens rearrangement of the less stable endocyclic ylides (8c and d).

Finally, the thermal reaction of the dibenzothiopyrans (1a and b) with diphenyldiazomethane (2a) affords similar yields of the dihydrothiepins (3a and b) and the thiopyrans (4a and b), arising from Stevens rearrangement of the ylides (7a and b) and (8a and b), respectively. These findings suggest that the ylides (7a and b) and (8a and b) undergo a rapid exchange in competition with a ready Stevens rearrangement as a consequence of comparable stability and high reactivity arising from poor resonance stabilization.

#### EXPERIMENTAL

I.r. and n.m.r. spectra are for solutions in carbon disulphide unless otherwise stated. 6*H*-Dibenzo[*b,d*]thiopyran (1a),<sup>9</sup> 6-phenyl-6*H*-dibenzo[*b,d*]thiopyran (1b),<sup>4</sup> diphenyldiazomethane (2a),<sup>10</sup> and dimethyldiazomalonnate (2c)<sup>8</sup> were

prepared according to the literature. Ethyl diazoacetate (2b) was a commercial product. Column chromatography was carried out on Merck silica gel (0.040–0.063 mm particle size).

**Reactions of 6H-Dibenzo[b,d]thiopyran (1a) and 6-Phenyl-6H-dibenzo[b,d]thiopyran (1b) with Diazoalkanes (2a–c).**—**General procedure.** To solutions of the thiopyrans (1a and b) (5 mmol) in dry benzene (10 ml) the appropriate diazoalkane (2a–c) (5 mmol) was added, followed in some cases by anhydrous copper(II) sulphate (15 mg). The mixtures were refluxed under nitrogen for 8–15 h (until the diazo band at *ca.* 2 040 cm<sup>-1</sup> in the i.r. spectrum had disappeared). The excess of benzene was distilled off, and the residue was chromatographed on silica gel.

**Dibenzothiopyran (1b) with diphenyldiazomethane (2a).** Chromatography with n-pentane gave (i) unchanged (1b) (55%); (ii) 6,6,7-triphenyl-6,7-dihydrodibenzo[b,d]thiopyran (3b) (58%), m.p. 214–216 °C;  $\nu_{\max}$  3 050, 3 020, 1 030, 760, 745, 730, 720, 700, and 690 cm<sup>-1</sup>;  $\delta$ (CDCl<sub>3</sub>) 5.01 (1 H, s), 6.57–6.72 (2 H, m), and 6.8–7.7 (21 H, m); *m/z* 440 (*M*<sup>+</sup>, 44%), 408 (2), 273 (54), 242 (100), 241 (39), 198 (18), 197 (20), 167 (37), 166 (35), and 165 (90) (Found: C, 87.25; H, 5.4; S, 7.25. C<sub>32</sub>H<sub>24</sub>S requires C, 87.25; H, 5.5; S, 7.3%); (iii) 6-diphenylmethyl-6-phenyl-6H-dibenzo[b,d]thiopyran (4b) (29%), identical with a specimen independently prepared.<sup>4</sup> Further elution with 20% ether-pentane gave a mixture of benzophenone azine<sup>11</sup> and benzophenone (0.35 g).

When dibenzothiopyran (1b) was reacted with a four-fold excess of diphenyldiazomethane (2a) under the same conditions, unchanged (1b) was recovered in 7% yield, the conversion yields of products (3b) and (4b) remaining substantially unaltered.

**Dibenzothiopyran (1a) with diphenyldiazomethane (2a).** Chromatography with n-pentane afforded (i) unchanged (1a) (60%); (ii) 6,6-biphenyl-6,7-dihydrodibenzo[b,d]thiopyran (3a) (41%), m.p. 160–161 °C (from benzene-pentane);  $\nu_{\max}$  3 050, 3 020, 1 030, 768, 758, 745, 735, 720, and 690 cm<sup>-1</sup>;  $\delta$  3.23 (2 H, s), 6.2–6.43 (1 H, m), and 6.73–7.5 (17 H, m); *m/z* 364 (*M*<sup>+</sup>, 93%), 331 (35), 197 (100), 184 (93), 167 (46), 166 (43), and 165 (75) (Found: C, 85.75; H, 5.55; S, 8.65. C<sub>28</sub>H<sub>20</sub>S requires C, 85.7; H, 5.55; S, 8.8%); (iii) 6-diphenylmethyl-6H-dibenzo[b,d]thiopyran (4a) (34%), m.p. 138–140 °C (from petroleum, b.p. 60–80 °C);  $\nu_{\max}$  745, 740, 728, and 692 cm<sup>-1</sup>;  $\delta$  3.83 (1 H, d, *J* 11.5 Hz), 4.3 (1 H, d, *J* 11.5 Hz), and 6.3–7.93 (18 H, m); *m/z* 364 (*M*<sup>+</sup>, 0.5%), 197 (100), and 165 (17) (Found: C, 85.75; H, 5.55; S, 8.75%); (iv) 70 mg of a mixture containing mainly tetraphenylethane with minor amounts of an inseparable, unidentified product, as evidenced by the i.r. spectrum (which was almost identical with that of an authentic specimen of tetraphenylethane<sup>12</sup>); the mass spectrum of the mixture showed, in addition to peaks at *m/z* 334 (*M*<sup>+</sup>) and 167 (100%) due to tetraphenylethane, peaks at *m/z* 394 (*M*<sup>+</sup>), 197 (100%), and 165 attributable to the contaminating product. Elution with 20% ether-pentane gave a mixture of benzophenone azine<sup>11</sup> and benzophenone (0.37 g).

**Dibenzothiopyran (1a) with ethyl diazoacetate (2b).** Chromatography with n-pentane furnished unchanged (1a) (45%). Elution with 5% ether-pentane gave (i) ethyl 6H-dibenzo[b,d]thiopyran-6-ylacetate (4c) (44%), a light yellow oil;  $\nu_{\max}$  1 735 cm<sup>-1</sup> (C=O);  $\delta$  0.95 (3 H, t, *J* 7.5 Hz), 2.56 (2 H, d, *J* 8 Hz), 3.88 (2 H, q, *J* 7.5 Hz), 4.3 (1 H, t, *J* 8 Hz), and 6.72–7.68 (8 H, m); *m/z* 284 (*M*<sup>+</sup>, 22%), 255

(5), 210 (7), and 197 (100) (Found: C, 71.95; H, 5.65; S, 11.2. C<sub>17</sub>H<sub>16</sub>O<sub>2</sub>S requires C, 71.8; H, 5.65; S, 11.3%); (ii) ethyl (Z)-6H-dibenzo[b,d]thiopyran-6-ylideneacetate (6) (7%) as yellow needles, m.p. 88–90 °C (from ethanol);  $\nu_{\max}$  1 695 cm<sup>-1</sup> (C=O);  $\delta$  1.27 (3 H, t, *J* 7.5 Hz), 4.16 (2 H, q, *J* 7.5 Hz), 6.33 (1 H, s), and 7–7.95 (8 H, m); *m/z* 282 (*M*<sup>+</sup>, 70%), 253 (8), 237 (30), 210 (100), 209 (20), 208 (32), and 165 (51) (Found: C, 72.45; H, 4.95; S, 11.45. C<sub>17</sub>H<sub>14</sub>O<sub>2</sub>S requires C, 72.3; H, 5.0; S, 11.35%).

Further elution with ether afforded intractable material.

**Dibenzothiopyran (1b) with ethyl diazoacetate (2b).** Chromatography with n-pentane gave unchanged (1b) (50%). Elution with 5% ether-pentane afforded (i) a mixture of inseparable unidentified products (20 mg); (ii) an isomeric mixture of ethyl 6-phenyl-6H-dibenzo[b,d]thiopyran-6-ylacetate (4d) and, probably, 6-ethoxycarbonyl-7-phenyl-6,7-dihydrodibenzo[b,d]thiopyran (3d) (38%) (Found: C, 76.25; H, 5.65; S, 9.05. C<sub>23</sub>H<sub>20</sub>O<sub>2</sub>S requires C, 76.65; H, 5.6; S, 8.9%). The i.r. spectrum showed a carbonyl band at 1 735 with shoulder at 1 745 cm<sup>-1</sup>; the mass spectrum exhibited only one molecular ion at *m/z* 360 in addition to peaks at *m/z* 287, 273, 254, and 184; the n.m.r. spectrum showed peaks due to (4d) at  $\delta$  0.9 (3 H, t, *J* 7.5 Hz), 3.07 (2 H, s), 3.7 (2 H, q, *J* 7.5 Hz), and 6.85–7.7 (13 H, m), whereas peaks due to (3d) appeared at  $\delta$  1.13 (3 H, t, *J* 7.5 Hz), 3.99 (2 H, q, *J* 7.5 Hz), 4.27 (1 H, d, *J* 5 Hz), 4.82 (1 H, d, *J* 5 Hz), and 6.85–7.7 (13 H, m). Relative intensities of peaks due to (4d) and (3d) indicated the two components to be present in the ratio *ca.* 20:1. Full confirmation of n.m.r. spectral assignments to (4d) and (3d) came from inspection of the n.m.r. spectrum of dibenzothiopyran (4d), which could be obtained pure from repeated chromatography of the isolated mixture. In fact chromatography of the mixture (200 mg) with 3% ether-pentane yielded a few fractions containing pure thiopyran (4d) (50 mg) together with fractions always containing (4d) as the main component. Pure (4d) was a light yellow oil,  $\nu_{\max}$  1 735 cm<sup>-1</sup> (C=O); *m/z* 360 (*M*<sup>+</sup>, 19%) and 273 (100).

**Dibenzothiopyran (1a) with dimethyl diazomalonate (2c).** Elution with n-pentane afforded unchanged (1a) (10%); elution with ether yielded 6H-dibenzo[b,d]thiopyran-5-*io*(bismethoxycarbonyl)methanide (7e) (85%), m.p. 186–188 °C (from benzene);  $\nu_{\max}$  (CHCl<sub>3</sub>) 1 680 and 1 645 cm<sup>-1</sup> (C=O) (Found: C, 65.9; H, 4.85; S, 9.8. C<sub>18</sub>H<sub>16</sub>O<sub>4</sub>S requires C, 65.85; H, 4.9; S, 9.75%).

**Dibenzothiopyran (1b) with dimethyl diazomalonate (2c).** Elution with n-pentane gave unchanged (1b) (12%); elution with ether afforded 6-phenyl-6H-dibenzo[b,d]thiopyran-5-*io*(bismethoxycarbonyl)methanide (7f) (90%), m.p. 189–190 °C (from benzene);  $\nu_{\max}$  (CHCl<sub>3</sub>) 1 685 and 1 650 cm<sup>-1</sup> (C=O) (Found: C, 71.2; H, 5.05; S, 7.8. C<sub>24</sub>H<sub>20</sub>O<sub>4</sub>S requires C, 71.25; H, 5.0; S, 7.95%).

**Pyrolysis of 6H-Dibenzo[b,d]thiopyran-5-*io*(bismethoxycarbonyl)methanide (7e).**—The ylide (7e) (1g) was sealed in a Pyrex tube without degassing and heated at 175 °C for 2 h, after which t.l.c. showed that complete decomposition of (7e) had occurred. Chromatography of the mixture on silica gel, using petroleum (b.p. 60–80 °C) as eluant, afforded fractions containing a complex mixture of unidentified products (50 mg). Elution with 10% ether-pentane furnished dimethyl 6H-dibenzo[b,d]thiopyran-6-ylmalonate (4e) (0.7 g, 70%) as a thick oil;  $\nu_{\max}$  1 765 and 1 750 cm<sup>-1</sup> (C=O);  $\delta$  3.23 (1 H, d, *J* 11 Hz), 3.28 (3 H, s), 3.57 (3 H, s), 4.4 (1 H, d, *J* 11 Hz), and 7–7.73 (8 H, m); *m/z* 328 (*M*<sup>+</sup>, 17%), 197 (100), and 165 (10) (Found: C,

65.8; H, 4.9; S, 9.7.  $C_{18}H_{16}O_4S$  requires C, 65.85; H, 4.9; S, 9.75%.

**Pyrolysis of 6-Phenyl-6H-dibenzo[b,d]thiopyran-5-*io*(bis-methoxycarbonyl)methanide (7f).**—The ylide (7f) (2 g) was heated at 175 °C for 1 h as described for the ylide (7e). Chromatography of the mixture on silica gel gave, on elution with 5% ether-petroleum (b.p. 60–80 °C), a mixture of unidentified products (30 mg). Elution with 10% ether-petroleum furnished (i) 6,6-bis(methoxycarbonyl)-7-phenyl-6,7-dihydrodibenzo[b,d]thiepin (3f) (1.5 g, 75%), m.p. 136–137 °C;  $\nu_{\max}$  1750 and 1735  $cm^{-1}$  (C=O); 3.4 (3 H, s), 3.57 (3 H, s), 4.58 (1 H, s), and 6.9–7.5 (13 H, m);  $m/z$  404 ( $M^+$ , 57%), 372 (20), 345 (25), 312 (31), 313 (18), 285 (31), 273 (27), 242 (38), 241 (42), and 184 (100) (Found: C, 71.5; H, 5.05; S, 8.0.  $C_{24}H_{20}O_4S$  requires C, 71.25; H, 5.0; S, 7.95%); (ii) dimethyl 6-phenyl-6H-dibenzo[b,d]-thiopyran-6-ylmalonate (4f) (40 mg, 2%), as a thick oil;  $\nu_{\max}$  1760 and 1745  $cm^{-1}$  (C=O);  $\delta$  3.27 (3 H, s), 3.43 (3 H, s), 4.18 (1 H, s), and 6.9–7.6 (13 H, m);  $m/z$  404 ( $M^+$ , 13%), 345 (5), and 273 (100) (Found: C, 71.4; H, 4.95; S, 7.85%).

**Acid-catalysed Rearrangement of Ylides (7e) and (7f).**—Solutions of the ylides (7e and f) (100 mg) in methylene chloride (3 ml) containing a few drops of acetic acid were refluxed for 5–8 h until t.l.c. showed disappearance of starting material. The solvent was distilled off and the oily residue was chromatographed on silica gel using 5% ether-petroleum (b.p. 60–80 °C) as eluant. The ylide (7e) gave traces of 6H-dibenzo[b,d]thiopyran (1a) and dimethyl 6H-dibenzo[b,d]thiopyran-6-ylmalonate (4e) (90 mg, 90%).

The ylide (7f) afforded (i) traces of 6-phenyl-6H-dibenzo[b,d]thiopyran (1b); (ii) a mixture of unidentified products (20 mg); and (iii) dimethyl 6-phenyl-6H-dibenzo[b,d]thiopyran-6-ylmalonate (4f) (60 mg, 60%).

**Desulphurisation of 6,6,7-Triphenyl-6,7-dihydrodibenzo[b,d]thiepin (3b).**—Compound (3b) (1.3 g) and freshly prepared Raney nickel<sup>13</sup> (ca. 13 g) were refluxed in dry benzene (130 ml) for 8 h. The nickel was filtered off and washed with ether and the organic phase evaporated. The residue was purified by elution with n-pentane through a silica gel column to give 1,1,2-triphenyl-2-(biphenyl-2-yl)ethane (5a) (0.6 g, 50%), m.p. 138–140 °C (from benzene-pentane);  $\delta$ (CDCl<sub>3</sub>) 4.73 (2 H, s) and 6.7–7.75 (24 H, m);  $m/z$  410 ( $M^+$ , 2%), 243 (70), 167 (63), and 165 (100) (Found: C, 93.95; H, 6.3.  $C_{25}H_{26}$  requires C, 93.6; H, 6.4%).

**Desulphurisation of 6,6-Bis(methoxycarbonyl)-7-phenyl-6,7-dihydrodibenzo[b,d]thiepin (3f).**—Compound (3f) (350 mg) was treated with Raney nickel (ca. 3.5 g) in refluxing benzene (30 ml) for 2 h. The nickel was filtered off and the excess of solvent removed, and the residue was chromatographed on silica gel. Elution with 5% ether-pentane afforded 1,1-bis(methoxycarbonyl)-2-phenyl-2-(biphenyl-2-yl)ethane (5b) (200 mg, 62%), m.p. 132–133 °C;  $\nu_{\max}$  1760 and 1740  $cm^{-1}$  (C=O);  $\delta$ (CDCl<sub>3</sub>) 3.32 (3 H, s), 3.52 (3 H, s), 4.3 (1 H, d, J 12 Hz), 4.93 (1 H, d, J 12 Hz), and 6.67–7.53 (14 H, m);  $m/z$  374 ( $M^+$ , 49%), 314 (15), 283 (7), 282 (9), 255 (55), 243 (12), 241 (15), and 165 (100) (Found: C, 77.2; H, 5.85.  $C_{24}H_{22}O_4$  requires C, 77.0; H, 5.9%).

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