Thermally Induced Rearrangement of Thiopheniobis(alkoxycarbonyl)methanides

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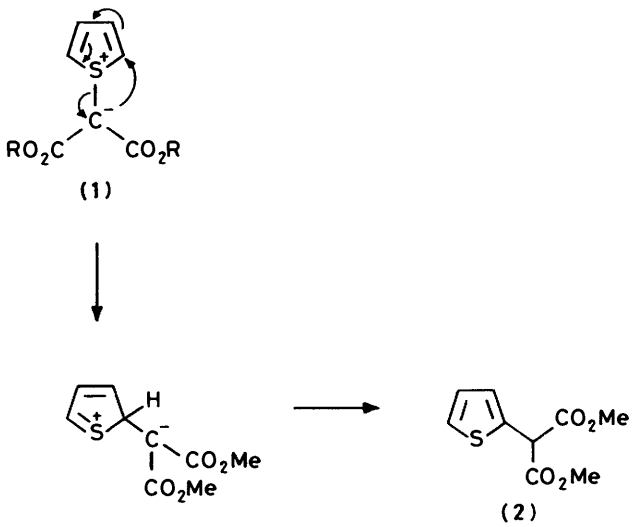
Thiopheniobis(alkoxycarbonyl)methanides undergo intramolecular rearrangement when heated, to give 2*H*-thiopyrans as thermally unstable kinetic products. When the methanides are subjected to prolonged heating thiophene-2-malonates are produced as the major rearrangement products. A mechanism for these transformations is advanced in an attempt to rationalise the known reactivity of thiophene and its derivatives towards diazoalkanes.

In our initial studies of the reactions of thiophenes with diazoalkanes [1] we have shown that copper-catalysed addition of dimethyl diazomalonate to thiophene gives rise to dimethyl 2-(2-thienyl)malonate as the major product.[2] When rhodium(II) acetate was used as a catalyst, the product, formed in high yield was thiopheniobis(methoxycarbonyl)methanide.[3] In view of the differences in reaction conditions *viz.* the necessity of carrying out the reaction at reflux under conditions of copper catalysis, as opposed to the room temperature reaction for the rhodium(II) acetate-catalysed reaction, it seemed probable that in both instances the initial product was the ylide (**1**; R = Me), but that at higher temperatures the ylide underwent rearrangement to the malonate (**2**). When the melting point of the ylide (**1**) was determined it was observed that decomposition to a yellow–brown oil took place and t.l.c. of this oil indicated that (**2**) had been formed. The simple expedient of fusion of the ylide followed by preparative t.l.c. purification of the crude product gave (**2**) in 33% yield, however an improved yield (60%) was obtained by refluxing (**1**; R = Me) in thiophene. The temperature at which the rearrangement was carried out played an important role in determining the yield of (**2**) and this observation is possibly of some importance, *vide infra*.

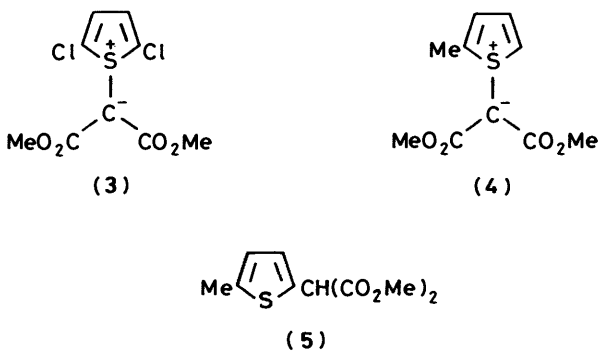
It occurred to us that two possible mechanisms could be in operation; first, the initial fragmentation of the ylide to the free thiophene and bis(methoxycarbonyl)carbene could occur, and the resultant carbene could then function as an electrophile at position two of the thiophene ring. Precedent for this possibility exists in our own work in that 2,5-dichlorothiopheniobis-(methoxycarbonyl)methanide (**3**) may be successfully employed as a carbene transfer agent under the influence of metal catalysts.[4,5] However, all attempts at trapping bis(methoxycarbonyl)carbene under the rearrangement conditions failed to yield the anticipated addition or insertion products.

At this stage the alternative mechanism, an intramolecular walk of the ylidic carbon from sulphur to C-1 of the thiophene ring, seemed more attractive (Scheme 1) and cross-over experiments supported this view. Thus when (**1**; R = Me) was heated in 2-methylthiophene at reflux, the only observable product, formed in 82% yield, was (**2**). Similarly when 2-methylthiopheniobis(methoxycarbonyl)methanide (**4**) was heated at reflux in thiophene the only observable product was dimethyl 2-(5-methyl-2-thienyl)malonate (**5**), formed in 88% yield.

Inductive activation of an arene by an alkyl group is well established and 2-methylthiophene would be expected to display a partial rate factor for reaction with an electrophilic carbene, at position five of the thiophene ring, substantially greater than for reaction of thiophene at position two under similar conditions (*cf.* partial rate factors for benzene and toluene during analogous electrophilic substitution reactions).

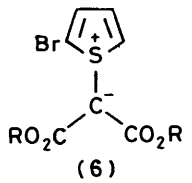


Scheme 1.



In these circumstances if a free carbene was involved in the rearrangement (**1**) ⟶ (**2**) and the reaction was carried out in 2-methylthiophene as a solvent, then (**5**) would be the expected product. Thus, failure to observe the formation of (**5**) provides convincing evidence for an intramolecular rearrangement.

During our attempts to investigate the generality of this reaction we have extended our study to a number of thiophene analogues. 2-Bromothiopheniobis(methoxycarbonyl)-methanide (**6**; R = Me), on being heated for 2 h at reflux in toluene, resulted in the formation of a deep red solution. Removal of the toluene and flash column chromatography of the residue, gave, in 90% yield, a red oil which was confirmed to



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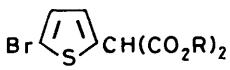

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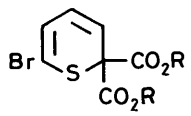

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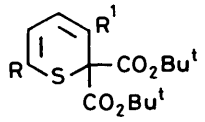


(9)

be isomeric with the ylide (**6**; R = Me) by accurate mass measurement, however the ^{1}H n.m.r. spectrum did not display the characteristic malonate methine proton, ruling out (**7**; R = Me) as the structure of this product. The ester protons appeared as a six-proton singlet at δ4.25, with the remaining three protons appearing as an ABX spin system with coupling constants of 6, 10, and 1.5 Hz, between 5.8 and 6.5. These data were most consistent with the 2*H*-thiopyran structure (**8**; R = Me).

Rearrangement of 2*H*-thiopyrans to thiophene derivatives is well documented,[6–8] however thiophenium ylides have only recently become the subject of detailed study and this would appear to be the first example of the rearrangement of a thiopheniobis(alkoxycarbonyl)methanide to a 2*H*-thiopyran. It therefore seemed prudent to confirm the 2*H*-thiopyran structure by preparing a crystalline derivative for full *X*-ray crystallographic analysis. Attempts to hydrolyse (**8**; R = Me) under acidic or basic conditions resulted in extensive decomposition. Treatment of (**8**; R = Me) with iodotrimethylsilane[9] at ambient temperature failed to affect ester cleavage and at elevated temperatures extensive rearrangement of the 2*H*-thiopyran to the malonate (**7**; R = Me) was observed. Tertiary butyl esters are known[10] to be more susceptible to cleavage by iodotrimethylsilane and hence derivatives such as (**8**; R = Bu^t) should prove more amenable to derivatisation.

Reaction of di-t-butyl diazomalonate with 2-bromothiophene resulted in the formation of the ylide (**6**; R = Bu^t) in 87% yield which was smoothly converted to the 2*H*-thiopyran (**8**; R = Bu^t) in 75% yield. Since (**8**; R = Bu^t) was a crystalline solid, no further derivatisation was necessary and the structure was confirmed by a full *X*-ray crystallographic analysis.[11] In view of the crystalline nature of the 2*H*-thiopyran (**8**; R = Bu^t) and the ease of isolation and purification of the bis(t-butoxycarbonyl)-methanides, we have examined the synthesis of a number of analogues (Table 1).

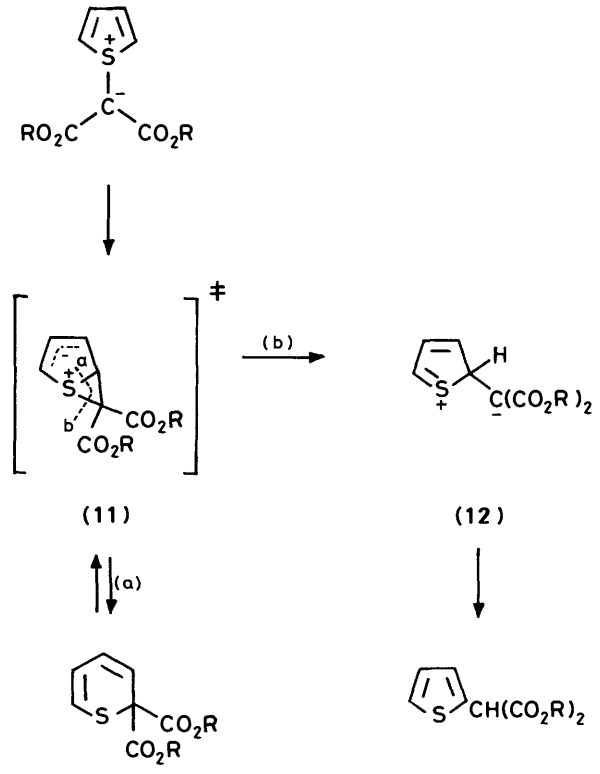
From these results a number of observations are of interest. In the case of the reaction of 3-bromothiophene with di-t-butyl diazomalonate no ylide was isolated and the only isolable product was the 2*H*-thiopyran (**9**; R = H, R′ = Br) whose structure was confirmed[11] by *X*-ray crystallography. 2-Phenoxymethylthiophene reacted with di-t-butyl diazomalonate to yield the corresponding ylide, but this ylide was exceptionally labile, rearranging to the 2*H*-thiopyran (**9**; R = CH_2OPh, R′ = H) during recrystallisation from methylcyclohexane.

It was also of interest to note that the 2*H*-thiopyran derived from the bis(t-butoxycarbonyl)methanide of thiophene itself (**9**; R = R′ = H) was a crystalline solid and since the ^{1}H n.m.r. of this compound was available for comparison purposes, we redirected our attention towards the thermal rearrangement of (**1**; R = Bu^t). After a solution of (**1**; R = Bu^t) in toluene had been heated at reflux for 10 min approximately 25% of the ylide had been converted to a less polar product. The reaction time was kept short to prevent further rearrangement to the malonate (**2**). Chromatographic separation of the product and analysis of the 250 MHz ^{1}H n.m.r. spectrum (Table 2) confirmed the 2*H*-thiopyran structure (**10**).

Table 1

Thiophene	Yield of ylide	Yield of 2H-Thiopyran
Thiophene	80	84
3-Methylthiophene	72	98
2-Bromothiophene	87	75
2-Iodothiophene	75	60
2-Phenoxymethylthiophene	64	97
3-Bromothiophene		22

Analysis of the results above may be carried out at two levels. The intramolecular nature of the rearrangement of the



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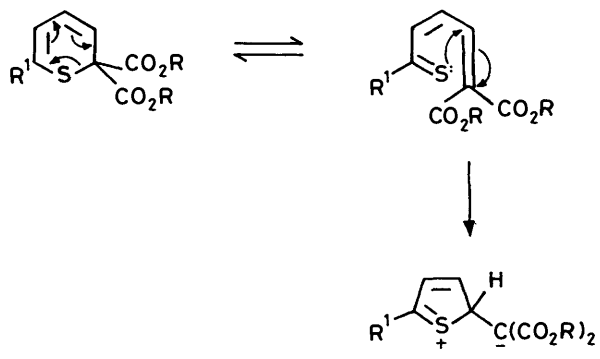
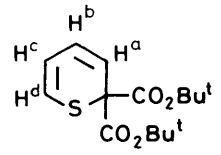
Scheme 2.



Scheme 3.

Table 2.



(10)

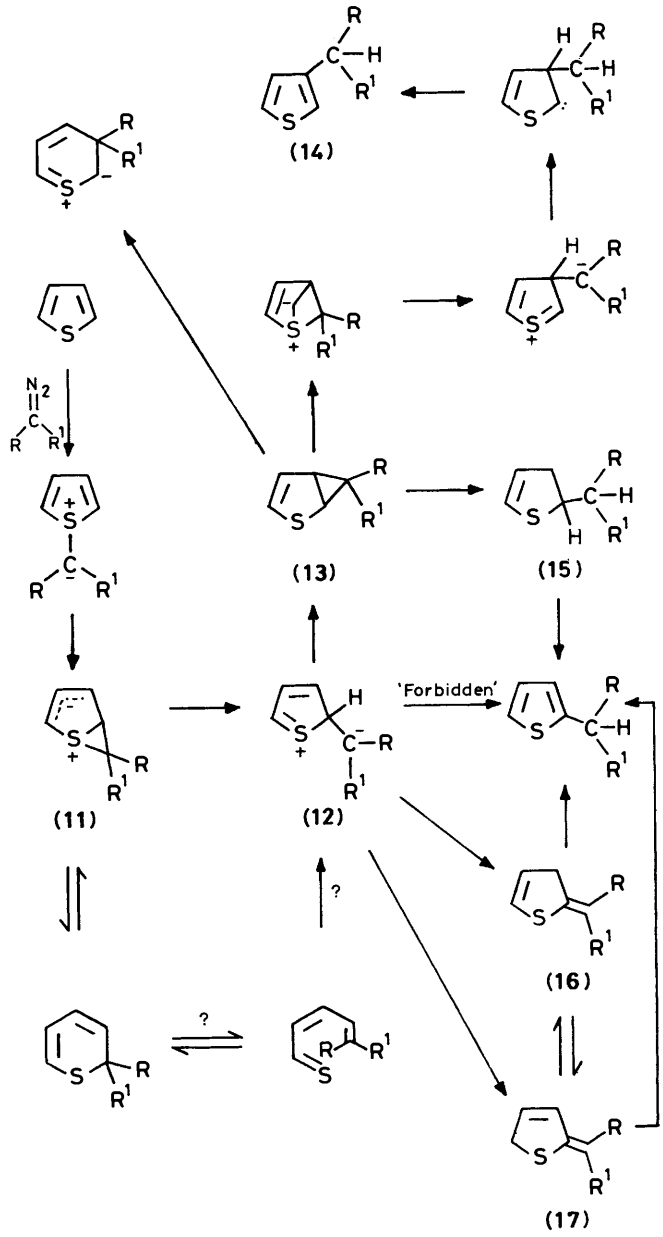
δ_H(p.p.m.)	J(Hz)
H^a 5.81	J_{ab} 9.94
H^b 6.82	J_{ac} 0.53
H^c 6.23	J_{ad} 1.20
H^d 6.26	J_{bc} 7.04
	J_{bd} −0.37
	J_{cd} 9.86

thiophenium ylide, through the 2*H*-thiopyran to the thiophene has been confirmed as being intramolecular. However the mechanics of the processes whereby the ylide undergoes ring expansion to the 2*H*-thiopyran and subsequent ring contraction and rearrangement of the 2*H*-thiopyran to the 2-malonate requires elaboration. We have proposed a mechanism involving attack of the ylidic carbon atom at C-2 of the thiophene ring to generate the bicyclic ylide (**11**) (either as a formal intermediate or as a transition state, Scheme 2).[12] Cleavage at (*a*) would then lead to the intermediate (**12**), which on proton transfer would lead to the thiophene-2-malonate, whereas cleavage at (*b*) would result in 2*H*-thiopyran formation. A similar mechanism to this was proposed by Walker and co-workers[13] for the rearrangement of 1-fluoren-9-ylidene-1,2,5-triphenyl-λ^5-phosphole.

Rearrangement of the 2*H*-thiopyran to the malonate might be envisaged as occurring by an alternative mechanism involving the electrocyclic ring opening of the thiopyran to the thiocarbonyl derivative (Scheme 3), followed by Michael addition of the sulphur atom at the alkylidene malonate to generate (**12**), however this mechanism can be ruled out since in the case of (**8**) such a ring opening would result in the formation of a thioacyl bromide and all attempts to trap such an intermediate by carrying out the rearrangement in alcoholic media have failed.

So far five product types have been observed to result following addition of diazoalkanes to thiophene derivatives; thiophenium ylides, 2*H*-thiopyrans, 2-substituted thiophenes, 2,3-cyclopropanated thiophenes, and 3-substituted thiophenes, and there can be little doubt that these products occur as distinct intermediates along a branching reaction pathway. Evidence has already been presented to suggest that the relative stability of individual products is sensitive to electronic and steric effects. Some of the possible reaction pathways and intermediates are indicated in (Scheme 4).

The available evidence suggests that the first reaction to occur in all reactions of diazoalkanes with thiophene derivatives is ylide formation. In those circumstances where R and R′ are able to aid in delocalisation of the negative charge on the ylidic carbon atom as in the bis(alkoxycarbonyl)methanides or the cyclopentadienides,[14] then the resulting ylides are sufficiently stable to be isolated. 2*H*-Thiopyran formation and migration of the substituent from sulphur to C-2 of the thiophene ring both occur by way of the bicyclic ylide (**11**), with 2*H*-thiopyrans representing kinetic products. The betaine (**12**) seems to be the lynch-pin in further rearrangements on this complex potential energy surface with the energies of the various pathways being governed by the groups R and R′. Thus when R = R′ = H[15] or when R = H, R′ = CO_2Et,[1] formation of the 2,3-cyclopropanated thiophene (**13**) occurs. This presumably reflects the



Scheme 4.

inherent instability of the earlier intermediates on the reaction pathway. A number of possible rearrangement products of (**13**) are shown (Scheme 4) although as yet only the 3-acetic ester (**14**; R = H, R′ = CO_2Et) has been observed.[16]

Direct rearrangement of (**12**) to 2-substituted thiophene derivatives is a thermally forbidden reaction and rearrangement may occur by way of a high energy pathway involving carbenic intermediates *e.g.* (**15**) or by way of derivatives such as (**16**) or (**17**). Although little is known about such systems in the thiophene series, the corresponding furan analogues are well known.[17] Some light on the activation energies of formation and the relative stabilities of the intermediates in Scheme 4 appear in the following paper.

Experimental

N.m.r. spectra were recorded on Perkin-Elmer R32 (90 MHz) and Bruker WM250 (250 MHz) instruments. Infra-red spectra

were recorded on a Perkin-Elmer 577 spectrophotometer and mass spectra including accurate mass measurements were obtained on a JEOL JMS D100 spectrometer. Melting points were recorded on a Kofler block and are uncorrected.

2-Methylthiopheniobis(methoxycarbonyl)methanide.—Dimethyl diazomalonate (1.58 g, 10 mmol) was added dropwise over a period of 1 h to a solution of rhodium(II) acetate (5 mg) in 2-methylthiophene (10 ml). Stirring was continued at room temperature until the diazo-stretch (2 100 cm^{-1}) was no longer present, and the precipitated solid was isolated by filtration to yield (**8**) (2.1 g, 92%), m.p. 146—146.5 °C (ethyl acetate), $\nu_{max.}$ ($CHCl_3$) 1 680, 1 650, 1 435, 1 330, 1 240—1 210br, and 1 090 cm^{-1}; δ($CDCl_3$) 7.1 (1 H, m), 6.85 (2 H, m), 3.67 (6 H, s), and 2.25 (3 H, s) (Found: C, 52.3; H, 5.3; S, 14.4. $C_{10}H_{12}O_4S$ requires C, 52.65; H, 5.3; S, 14.05%).

Thermolysis of Thiopheniobis(methoxycarbonyl)—methanide (**1**).—(*a*) *Solid.* Thiopheniobis(methoxycarbonyl)methanide [1] (0.227 g) was placed in a glass tube and heated in an oil bath at 140—150 °C. The solid melted to form a yellow–brown oil which was purified by preparative t.l.c. [SiO_2; light petroleum (b.p. 60—80 °C)–ethyl acetate (85:15)] to give dimethyl 2-thienylmalonate (**2**) (0.071 g, 33%) as a pale yellow oil, $\nu_{max.}$(film) 2 955, 1 735, 1 432, and 1 240 cm^{-1}; δ($CDCl_3$) 7.1 (3 H, m), 5.0 (1 H, s), and 4.7 (6 H, s) (Found: C, 50.2; H, 4.7; S 15.05%; M^+, 214.0281. $C_9H_{10}O_4S$ requires C, 50.45; H, 4.7; S, 14.95%; *M*, 214.0300).

(*b*) *In thiophene.* Thiopheniobis(methoxycarbonyl)methanide (0.209 g) in thiophene (5 ml) was heated under reflux overnight until t.l.c. (SiO_2–$CHCl_3$) indicated that the reaction was complete. The thiophene was evaporated under reduced pressure and the crude product was purified by p.l.c. to give dimethyl 2-thienylmalonate (**2**) (0.121 g, 60%) as a yellow oil, with identical physical and spectral properties to those described above.

(*c*) *In 2-methylthiophene.* Thiopheniobis(methoxycarbonyl)-methanide (0.5 g) in 2-methylthiophene (10 ml) was heated under reflux for 3 h until no starting material remained (t.l.c.). The excess of 2-methylthiophene was removed under reduced pressure and the resultant oil was purified by flash column chromatography (SiO_2–$CHCl_3$) to give dimethyl 2-thienylmalonate (**2**) (0.41 g, 82%) as a pale yellow oil with physical and spectral properties identical to those described above.

Thermolysis of 2-Methylthiopheniobis(methoxycarbonyl)-methanide.—(*a*) *In 2-methylthiophene.* 2-Methylthiopheniobis-(methoxycarbonyl)methanide (**4**) (1.0 g) in 2-methylthiophene (10 ml) was heated under reflux for 2.5 h after which time t.l.c. [SiO_2; $CHCl_3$–MeOH (96:4)] indicated that no starting ylide remained. The excess of 2-methylthiophene was removed under reduced pressure and the crude residue was distilled in a Kugelrohr to yield dimethyl 2-(5′-methyl-2′-thienyl)malonate (**5**) (0.94 g, 94%) as a pale yellow oil, b.p. 100—115 °C at 0.1 Torr; $\nu_{max.}$(film) 3 000, 2 955, 1 740, 1 435, 1 360, 1 305, 1 235, 1 150, 1 050, 1 020, 930, 910, 805, 750, and 665 cm^{-1}; δ($CDCl_3$) 6.80 (1 H, d), 6.55 (1 H, m), 4.80 (1 H, s), 3.68 (6 H, s), and 2.40 (3 H, s) (Found: C, 52.55; H, 5.3; S, 13.9. $C_{10}H_{12}OS$ requires C, 52.61; H, 5.30; S, 14.05%).

(*b*) *In thiophene.* The above reaction was repeated using the ylide (**4**) (0.5 g) in thiophene (10 ml) at reflux for 36 h until no starting ylide remained on t.l.c. (as above). The excess of thiophene was removed under reduced pressure and the crude product purified by flash column chromatography over silica ($CHCl_3$) to give (**5**) (0.44 g, 88%) as a pale yellow oil which had physical and spectroscopic properties identical to those reported above.

Thermolysis of Thiopheniobis(methoxycarbonyl)methanide in the Presence of Alkenes.—In general a solution of the ylide (**1**) (0.2 g) in dry acetonitrile (10 ml) was added to a solution of the alkene substrate in acetonitrile (1.0 mmol in 5 ml) and the mixture stirred at 60 °C. The disappearance of (**1**) was monitored by t.l.c. (SiO_2–$CHCl_3$) until no starting material remained. The solvent was removed under reduced pressure and the crude product chromatographed on silica. In all cases (**2**) was the only product. Alkenes used in this way were vinyl acetate, cyclohexene, and ethyl cinnamate. In addition, similar results were obtained with dimethyl acetylenedicarboxylate.

Dimethyl 6-Bromo-2H-thiopyran-2,2-dicarboxylate.—2-Bromothiopheniobis(methoxycarbonyl)methanide [1] (0.488 g) in dry toluene (10 ml) was heated at reflux until no more ylide remained [t.l.c: SiO_2; light petroleum (b.p. 40—60 °C)–ethyl acetate (2:1); 2 h]. The toluene was evaporated and the residue was chromatographed to yield a red oil (0.44 g, 90%), $\nu_{max.}$(film) 2 950, 1 740, 1 540, and 1 430 cm^{-1}; δ($CDCl_3$) 6.5—5.8 (3 H, m, ABX, *J* 10, 6 and 1.5 Hz) and 5.75 (6 H, s) (Found: M^+ 291.9413. $C_9H_9BrO_4S$ requires *M*, 291.9406).

2-Phenoxymethylthiophene.—A mixture of *N*-bromosuccinimide (49 g, 0.27 mol) and AIBN * (0.5 g) was added in portions to 2-methylthiophene (29.4 g, 0.3 mol) and AIBN (0.5 g) in refluxing benzene. The addition was conducted as rapidly as foaming would permit (30 min). The mixture was cooled and filtered, the solvent removed under reduced pressure, and the residue distilled to yield 2-bromomethylthiophene (15 g, 28%), b.p. 59 °C (0.2 Torr).[17] δ($CDCl_3$), 2.9 (3 H, m) and 4.7 (2 H, s).

The 2-bromomethylthiophene (15 g) was added to an ethanolic solution of sodium phenoxide (9.86 g, 85 mmol). An immediate precipitation of sodium bromide resulted during an exothermic reaction. After stirring overnight and refluxing for a further 30 min, the ethanol was evaporated and the residue partitioned between diethyl ether (100 ml) and water (100 ml). The ethereal layer was separated and washed with water (2 × 50 ml), dried ($MgSO_4$) and evaporated. After two distillations *2-phenoxymethylthiophene* was obtained as a low melting solid, (10.1 g, 63%), b.p. 102—104 °C (0.2 Torr), m.p. 23 °C, $\nu_{max.}$(film) 3 010, 2 920, 1 580, and 1480 cm^{-1}; δ($CDCl_3$) 7.1 (8 H, m) and 5.0 (2 H, s) (Found: M^+, 190.0439. $C_{11}H_{10}OS$ requires *M*, 190.0452).

General Method of Preparation of Thiopheniobis(t-butoxycarbonyl)methanides.—The thiophene (10 mmol) was dissolved in dry methylcyclohexane containing rhodium(II) hexanoate (10 mg). Di-t-butyl diazomalonate (2.42 g, 10 mmol) was added and the mixture was stirred until no diazo band remained in the i.r. spectrum of the reaction mixture. If a solid precipitated it was isolated by filtration, washed with methylcyclohexane, and dried. If the ylide remained in solution the solvent was removed under reduced pressure and the residue was chromatographed.

Thiopheniobis(t-butoxycarbonyl)methanide. After 8 h, filtration yielded the *title compound* (2.4 g, 80%), m.p. 140—142 °C (acetonitrile); $\nu_{max.}$(KBr) 3 080, 2 960, 1 650, 1 475, and 1 440 cm^{-1}; δ($CDCl_3$) 7.05 (4 H, m) and 1.4 (18 H, s) (Found: C, 60.66; H, 7.50. $C_{15}H_{22}O_4S$ requires C, 60.40; H, 7.38%).

3-Methylthiopheniobis(t-butoxycarbonyl)methanide. After 3 h, filtration yielded the *title compound* (2.3 g, 72%), m.p. 117—118 °C (ethyl acetate), $\nu_{max.}$(KBr) 3 100, 2 980, 1 640, 1 470, and 1 450 cm^{-1}; δ($CDCl_3$) 7.0 (2 H, m), 6.5 (1 H, m), 2.2 (2 H, d), and 1.3 (18 H, s) (Found: C, 61.45; H, 8.05. $C_{16}H_{24}O_4S$ requires C, 61.54; H, 7.69%).

2-Bromothiopheniobis(t-butoxycarbonyl)methanide. After 30 min, filtration of the reaction mixture yielded the *title compound* (3.28 g, 87%), m.p. 140—143 °C (decomp.) (benzene), $\nu_{max.}$(KBr) 3 060, 2 900, 1 690, 1 570, 1 490, and 1 450 cm^{-1}; δ($CDCl_3$) 7.0 (3

* Azoisobutyronitrile

H, m) and 1.4 (18 H, s) (Found: C, 48.0; H, 5.8. $C_{15}H_{21}BrO_4S$ requires C, 47.80; H, 5.57%).

2-Iodothiopheniobis(t-butoxycarbonyl)methanide. After 30 min, filtration of the reaction mixture yielded the *title compound* (3.2 g, 75%), m.p. 134—134.5 °C (benzene), $\nu_{max.}$(KBr) 3 060, 2 970, 1 670, 1 650, and 1 460 cm^{-1}; $\delta(CDCl_3)$ 7.1 (3 H, m) and 1.4 (18 H, s) (Found: C, 42.25; H, 4.75. $C_{15}H_{21}IO_4S$ requires C, 42.45; H, 4.95%).

2-(Phenoxymethyl)thiopheniobis(t-butoxycarbonyl)methanide. After 5 h, filtration of the reaction mixture yielded the *title compound* (2.5 g, 64%), m.p. 102—104 °C (cold crystallisation from toluene), $\nu_{max.}$(KBr) 3 000, 2 900, 1 730, 1 470, and 1 400 cm^{-1}; $\delta(CDCl_3)$ 7.1 (8 H, m), 5.0 (2 H, s), and 1.45 (18 H, s). Found: C, 65.23; H, 6.95. $C_{22}H_{28}O_5S$ requires C, 65.35; H, 6.93%.

Dimethyl 2H-Thiopyran-2,2-dicarboxylate.—Thiopheniobis(methoxycarbonyl)methanide (0.5 g) in dry toluene (5 ml) was heated at reflux for 10 min. The cooled solution was filtered and the solvent was evaporated under reduced pressure. Chromatography of the residue on silica, eluting with dichloromethane, yielded the *title compound* (0.15 g, 30%) as a yellow oil, $\nu_{max.}$(film) 3 000, 2 940, 1 730, and 1 430 cm^{-1}; $\delta(CDCl_3)$ 6.4—5.6 (4 H, m) and 3.8 (6 H, m) (Found: M^+, 214.0292. $C_9H_{10}O_4S$ requires M, 214.0300).

Dimethyl 6-Bromo-2H-thiopyran-2,2-dicarboxylate.—2-Bromothiopheniobis(methoxycarbonyl)methanide (0.488 g) in toluene (10 ml) was heated at reflux until no starting ylide remained [t.l.c: SiO_2; light petroleum (b.p. 40—60 °C)–ethyl acetate (2:1); 2 h]. The toluene was evaporated under reduced pressure and the residue was chromatographed on silica, to yield the *title compound* (0.44 g) as a red oil, $\nu_{max.}$(film) 2 950, 1 740, 1 540, and 1 430 cm^{-1}; $\delta(CDCl_3)$ 6.5—5.8 (3 H, m, ABX, J 10, 6, and 1.5 Hz) and 5.75 (6 H, s) (Found: M^+ 291.9413. $C_9H_9BrO_4S$ requires M 291.9406).

Di-t-butyl 2H-Thiopyran-2,2-dicarboxylate.—Thiopheniobis(t-butoxycarbonyl)methanide (0.5 g) in xylene (10 ml) was heated under reflux for 5 min. After the solvent had been evaporated, the residue was chromatographed on silica gel, eluting with light petroleum (b.p. 40—60 °C)–ethyl acetate (4:1) to yield the *title compound* (0.42 g, 84%), m.p. 93—94 °C (MeOH), $\nu_{max.}$(KBr) 2 980, 1 725, 1 550, 1 450, and 1 390 cm^{-1}; $\delta(CDCl_3)$ 6.4—5.6 (4 H, m) and 1.4 (18 H, s) (Found: C, 60.15; H, 7.45. $C_{15}H_{22}O_4S$ requires C, 60.40; H, 7.38%).

Di-t-butyl 4-Methyl-2H-thiopyran-2,2-dicarboxylate.—3-Methylthiopheniobis(t-butoxycarbonyl)methanide (0.5 g) in toluene (10 ml) was heated under reflux for 20 min. Evaporation of the reaction mixture and chromatography of the residue on silica gel, eluting with light petroleum (b.p. 40—60 °C)–ethyl acetate (9:1) gave the *title compound* (0.49 g, 98%) as a yellow oil, $\nu_{max.}$(film) 2 980, 2 910, 1 710, and 1 450 cm^{-1}; $\delta(CDCl_3)$ 6.3—5.6 (3 H, m), 1.85 (3 H, s), and 1.5 (18 H, s) (Found: M^+ 312.1420. $C_{16}H_{24}O_4S$ requires M, 312.1396).

Di-t-butyl 6-Iodo-2H-thiopyran-2,2-dicarboxylate.—2-Iodothiopheniobis(methoxycarbonyl)methanide (0.1 g) in dry toluene was heated at reflux for 20 min. After the solvent had been evaporated, the residue was chromatographed on silica gel eluting with light petroleum (b.p. 40—60 °C)–ethyl acetate (9:1), to yield the *title compound* (0.06 g, 60%) as a yellow oil, $\nu_{max.}$(film) 2 800, 2 100, 1 720, 1 520, and 1 450 cm^{-1}; $\delta(CDCl_3)$ 6.7 (1 H, m). 5.9 (2 H, d), and 1.45 (18 H, s) (Found: M^+, 424.0235. $C_{15}H_{21}IO_4S$ requires M, 424.0208).

Di-t-butyl 6-(Phenoxymethyl)-2H-thiopyran-2,2-dicarboxylate.—2-(Phenoxymethyl)thiopheniobis(t-butoxycarbonyl)-methide (0.5 g) in methylcyclohexane (10 ml) was heated at reflux for 1 min. After the solvent had been evaporated, the residue was chromatographed (as above) to yield the *title compound* (0.47 g, 97%) as a yellow oil, $\nu_{max.}$ (film) 2 960, 2 920, 1 730, 1 590, 1 490, and 1 450 cm^{-1}; $\delta(CDCl_3)$ 7.4—6.7 (5 H, m), 6.3—5.5 (3 H, m), 4.5 (2 H, s), and 1.4 (18 H, s) (Found: M^+, 404.1617. $C_{22}H_{28}O_5S$ requires M, 404.1658).

Di-t-butyl 6-Bromo-2H-thiopyran-2,2-dicarboxylate.—2-Bromothiopheniobis(t-butoxycarbonyl)methanide (0.5 g) in xylene (10 ml) was heated at reflux for 5 min and then rapidly cooled to 0 °C. The xylene was removed under reduced pressure and the residual oil was chromatographed on silica to yield the *title compound* (0.38 g, 75%), m.p. 75 °C, $\nu_{max.}$(KBr) 2 975, 1 735, 1 550, 1 370, 1 250, and 1 150 cm^{-1}; $\delta(CDCl_3)$ 5.854 (1 H, d, J 10.07 Hz), 6.088 (1 H, dd, J 10.07 and 6.53 Hz), 6.476 (1 H, d, J 6.53 Hz), and 1.442 (18 H, s) (Found M^+, 376.0345. $C_{15}H_{21}BrO_4S$ requires M, 376.0345).

Di-t-butyl 5-Bromo-2H-thiopyran-2,2-dicarboxylate.—3-Bromothiophene (3.03 g) in methylcyclohexane (50 ml) was stirred at room temperature and rhodium(II) hexanoate (10 mg) was added. Di-t-butyl diazomalonate (4.5 g) was added dropwise over 30 min and the mixture was stirred until no diazoester remained (overnight). The solvent was removed under reduced pressure to leave a brown oil which was chromatographed over silica to yield the *title thiopyran* (0.52 g, 22%), m.p. 92—94 °C (ethanol), $\nu_{max.}$(KBr) 2 970, 1 720, 1 540, 1 450, 1 280—1 230, and 1 145 cm^{-1}; $\delta(CDCl_3)$ 5.775 (1 H, dd, J 10.42. and 0.90 Hz), 6.168 (1 H, dd, J 10.42 and 1.09 Hz), and 6.399 (1 H, dd, J 1.09 and 0.90 Hz) (Found: C, 44.64, H, 5.77%; M^+, 376.0401. $C_{15}H_{21}BrO_4S$ requires C, 47.75; H, 5.61%; M, 376.0345.

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