

## Synthesis of some Thiophenium Bis(*t*-butoxycarbonyl)methylides

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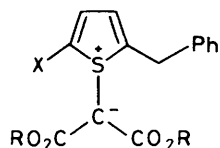
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Thiophene derivatives react with di-*t*-butyl diazomalonate in the presence of rhodium(II) carboxylates to yield thiophenium bis(*t*-butoxycarbonyl)methylides. Rhodium(II) hexanoate is a more efficient catalyst than rhodium(II) acetate, shortening reaction times and increasing yields of the ylides. Series of 2-halogeno-, 2-alkyl-, 2-benzyl-5-halogeno-, and 2-benzyl-5-alkyl-thiophenium ylides are described. Whilst 2-methyl-, 2-ethyl-, and 2-isopropyl-thiophenes readily form the ylides in good yield, 2-*t*-butylthiophene appears to undergo further reaction to yield 1,3-bis-*t*-butoxycarbonyl-2-(3-*t*-butyl-6,6-bis-*t*-butoxycarbonyl-2-thioniabicyclo[3.1.0]hex-3-en-2-yl)methanide (**2**) whose structure has been confirmed by X-ray crystallography.

During the course of a study of the dynamic <sup>1</sup>H n.m.r. properties of thiophenium bis(alkoxycarbonyl)methylides<sup>1</sup> we required a number of substituted ylides and herein we report the synthesis and characterisation of these compounds.

In the first instance, we were seeking to measure the barrier to inversion at sulphur and we considered that the best approach to this problem was in an investigation of the variable-temperature <sup>1</sup>H n.m.r. spectra of the ylide (**1**) in which the benzylic proton are diastereotopic when the sulphur atom is pyramidal, but when inversion is rapid on the n.m.r. time scale the benzylic methylene protons become equivalent.<sup>2</sup> Although it proved possible to prepare (**1**; R = Me, X = H) in good yield, it was difficult to obtain accurate values for the inversion barrier at sulphur owing to the similarity in chemical-shift values of the benzylic methylene and the methyl ester resonances. For this reason, we chose to investigate the synthesis of the bis(*t*-butoxycarbonyl)methylides since the *t*-butyl signal is expected to resonate at a lower chemical-shift value, leaving the benzylic protons amenable to complete lineshape analysis.

Reaction of 2-benzylthiophene<sup>3</sup> with di-*t*-butyldiazomalonate resulted in the formation of the ylide (**1**; R = Bu<sup>t</sup>, X = H) as a crystalline solid in excellent yield. Although detailed examination of the appearance of the benzylic methylene protons in the variable-temperature <sup>1</sup>H n.m.r. spectrum of (**1**; R = Bu<sup>t</sup>, X = H) permitted the evaluation of the barrier to



inversion at sulphur in this system, the results were complicated by the observation that lineshape analysis of the *t*-butyl signal under similar conditions, whilst giving a similar value for the free energy of activation for this process, gave entropies of activation which were markedly different. It was felt that further light might be shed on this system by the analysis of a series of derivatives (**1**; R = Bu<sup>t</sup>, X), where X could be varied in size and electronegativity to probe both steric and electronic effects.

A series of 2-benzyl-5-alkylthiophenes were prepared under standard conditions by benzylation of the corresponding 2-alkylthiophenes followed by Wolff-Kishner reduction. 2-Methylthiophene was commercially available but it was necessary to synthesize 2-ethylthiophene by reduction of 2-acetylthiophene.<sup>4</sup> 2-Isopropylthiophene was prepared by a

Table 1.

Thiophene	Yield (%)	Method* (reaction time)
Thiophene	80	B (8 h)
2-Methylthiophene	37	A (3 d)
	92	B (16 h)
2-Ethylthiophene	38	A (6 h)
	80	B (6 h)
2-Isopropylthiophene	26	A (3 d)
	78	B (6 h)

\* For details of methods see Experimental section.

sequence involving Grignard addition of methylmagnesium iodide to 2-acetylthiophene followed by dehydration and catalytic reduction. Although 2-*t*-butylthiophene proved difficult to prepare, it was obtained in low yield by spinning-band distillation of a mixture of *t*-butylthiophenes formed by Friedel-Crafts alkylation of thiophene using *t*-butyl chloride.<sup>3</sup> All attempts to prepare 2-benzoyl-5-*t*-butylthiophene by benzylation of 2-*t*-butylthiophene failed in our hands.

Since initial attempts to produce the 2-benzyl-5-halogeno-thiophenes by benzylation of the corresponding halogeno-thiophenes resulted in substitution of the halogen by the benzoyl group, the 2-benzyl-5-halogenothiophenes were prepared by halogenation of 2-benzylthiophene under conditions analogous to those used for the halogenation of thiophene itself.

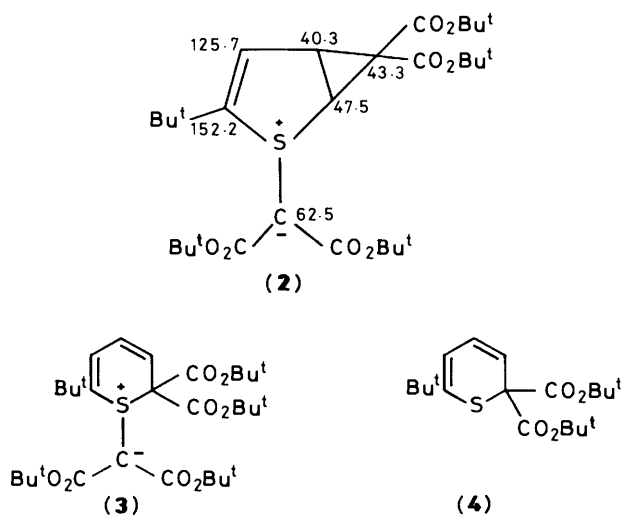
In our earlier studies<sup>5</sup> we have carried out the ylide-forming reactions using the rhodium(II) acetate-catalysed addition of the diazo compound to a given thiophene, where an excess of the thiophene was used as a solvent, relying on the low boiling points of the thiophenes used to facilitate isolation of the ylides when they failed to crystallise from solution under the normal reaction conditions. However in the case of the benzylthiophenes, the lack of volatility of these compounds precluded the use of such experimental conditions. In these circumstances we sought methods of effecting the ylide-forming reactions of the thiophene and the diazo ester in a suitable solvent.

Initially we examined the reaction of 2-alkylthiophenes with 1 equiv. of di-*t*-butyl diazomalonate<sup>6</sup> in methylcyclohexane as a solvent, using rhodium(II) acetate as the catalyst. Under these conditions, however, the reactions were very slow, sometimes only giving modest yields of the ylides after several days. Since it was evident that the rhodium(II) acetate only had a very low solubility in methylcyclohexane, the hydrocarbon-soluble rhodium(II) hexanoate was prepared and used as the catalyst. The effect was dramatic; reaction times were reduced from days to hours, and yields doubled (Table 1).

Somewhat surprisingly, the catalyst also proved to be more resistant to poisoning. Occasionally when using rhodium(II) acetate as the catalyst, the characteristic green colour of the catalyst would give way to a dark red or brown colouration and associated with this colour change was a slowing or halting of the reaction. However, when rhodium(II) hexanoate was used, although this colour change was sometimes observed, it usually gives way to the blue-green colouration on addition of the diazo ester and the reactions proceed rapidly.

With this modified procedure it proved possible to synthesize the 2-alkylthiophenium bis(t-butoxycarbonyl)methylides derived from methyl-, ethyl-, and isopropyl-thiophene. However, the reaction of 2-t-butylthiophene with di-t-butyl diazomalonate was anomalous in that no ylide was formed. T.l.c. examination of the reaction mixture revealed one major product which was considerably less polar than was expected for the ylide. This was isolated by column chromatography as a colourless crystalline compound with a mass spectrum and elemental analysis consistent with a 2:1 adduct of bis(t-butoxycarbonyl)carbene with the 2-t-butylthiophene.

The 250 MHz  $^1\text{H}$  n.m.r. spectrum of this compound showed five non-equivalent t-butyl resonances and an ABX spin system with a one-proton multiplet at  $\delta$  6.1 and a two-proton multiplet at  $\delta$  3.45 with coupling constants of  $J = 7, 3,$  and  $0.7$  Hz. These data were consistent with two possible structures (2) or (3), with



(2) resulting from cyclopropanation of the ylide or (3) being formed from the 2*H*-thiopyran (4). The  $^{13}\text{C}$  n.m.r. spectrum however pointed clearly to (2) as the most probable structure with only two signals at 125.7 and 152.2 corresponding to  $\text{sp}^2$  hybridised carbon atoms in carbon-carbon double bonds; the thiopyran structure (3) would formally require four such signals.  $^{13}\text{C}$  Chemical shifts of the atoms in the bicyclic ring and the ylidic carbon atom are shown in structure (2). Final confirmation of structure (2) came from an X-ray crystal structure determination (see Figure).

The X-ray crystal structure of (2) (see Figure) shows that it contains the thioniabicyclo[3.1.0]hex-3-ene ring system which has not previously been characterised crystallographically. The closest analogue of this system in the literature is of an azoniabicyclo[3.1.0]hex-3-ene<sup>8</sup> system. The principal difference between the two ring systems is that in (2) the five-membered ring is planar (maximum deviation is for C-5 which is displaced 0.02 Å from the mean plane of S-1, C-2, C-4, C-5, C-6) whereas in the nitrogen substituted case, whilst the four carbon atoms in the ring are planar, the nitrogen atom is displaced 0.23 Å from the plane in the 'anti' sense to the cyclopropane ring. It is not

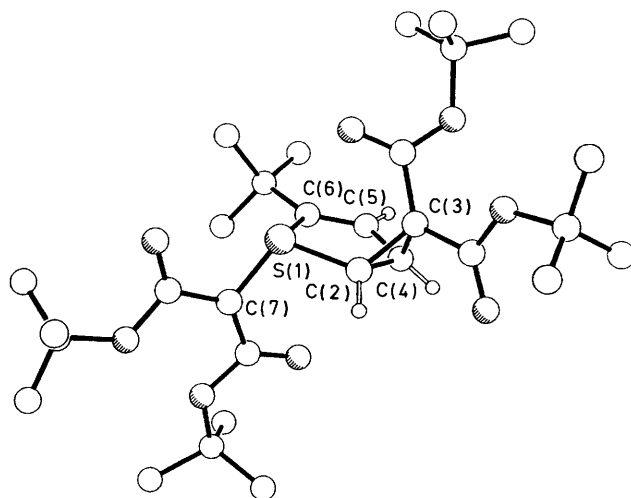


Figure. Molecular structure of compound (2), protons [except H(2), H(4), and H(5)] omitted for clarity

possible to be certain whether the other minor differences in bond lengths and angles in the two analogous systems are due to steric/electronic effects of substituting sulphur for nitrogen, or due to the ylidic nature of the sulphur atom.

Having established the reaction conditions for ylide formation with the simple alkyl- and halogeno-thiophene models, the 2-benzyl-5-alkyl- and 2-benzyl-5-halogeno-thiophenes were found to react under similar experimental conditions to produce the required ylides for dynamic  $^1\text{H}$  n.m.r. studies, the details of which will be reported elsewhere.

## Experimental

N.m.r. spectra were recorded on a Perkin-Elmer R32 (90 MHz) and a Bruker WM 250 (250 MHz). Infrared spectra were recorded on a Perkin-Elmer 577 and mass spectra, including accurate mass measurements on a Jeol JMS D100 spectrometer. M.p.s were recorded on a Kofler block and are uncorrected.

*Preparation of 2-Benzyl-5-alkylthiophenes.*—Stannic chloride (65 g, 0.25 mol) was added to a mixture of the 2-alkylthiophene and benzoyl chloride (35 g, 0.25 mol) in dry benzene (250 ml) at 0 °C over 1 h. The mixture was stirred for a further hour at room temperature after which hydrochloric acid (1*M*; 100 ml) was added dropwise and stirring continued for 5 min. The organic phase was separated, washed with water, dried ( $\text{MgSO}_4$ ), and evaporated under reduced pressure to leave the crude 2-benzoyl-5-alkylthiophene which was used directly in the next step.

The crude 2-benzoyl-5-alkylthiophene was dissolved in digol (300 ml) containing potassium hydroxide (45 g, 0.8 mol) and 64% hydrazine (45 g, 0.9 mol). The mixture was heated under reflux with distillation of water and excess hydrazine for 2 h, when the internal temperature of the distillation flask had reached 150 °C. The residue was then heated under reflux for a further 30 min, after which it was cooled and poured into water (1.5 dm<sup>3</sup>). The resultant mixture was extracted with ether (3 × 100 ml) and the ether extracts were combined, washed with water (2 × 100 ml), dried ( $\text{MgSO}_4$ ), and evaporated. The crude product was dried over calcium hydride overnight and distilled from calcium hydride.

*2-Benzyl-5-methylthiophene.* Yield 15.7 g (33%), b.p. 74–76 °C at 0.1 Torr, m.p. 5 °C;  $v_{\text{max}}$  (film) 3 060, 3 020, 1 495, and 1 450  $\text{cm}^{-1}$ ;  $\delta$ ( $\text{CDCl}_3$ ) 7.0 (5 H, s), 6.4 (2 H, s), 3.9 (2 H, s), and

2.2 (3 H, s) (Found:  $M^+$ , 188.0655.  $C_{12}H_{12}S$  requires  $M^+$ , 188.0659).

**2-Benzyl-5-ethylthiophene.** Yield 9.3 g (19%), b.p. 87–88 °C at 0.1 Torr;  $v_{\max.}$ (film) 3 060, 3 020, 1 600, 1 500, and 1 450  $cm^{-1}$ ;  $\delta(CDCl_3)$  7.5 (5 H, s), 6.4 (2 H, s), 3.9 (2 H, s), 2.6 (2 H, q), and 1.1 (3 H, t) (Found:  $M^+$ , 202.0818.  $C_{13}H_{14}S$  requires  $M^+$ , 202.0817).

**2-Benzyl-5-isopropylthiophene.** Yield 13.4 g (25%), b.p. 90–91 °C at 0.1 Torr;  $v_{\max.}$ (film) 3 060, 3 020, 2 960, 1 600, 1 495, and 1 450  $cm^{-1}$ ;  $\delta(CDCl_3)$  7.2 (5 H, s), 6.5 (2 H, s), 4.0 (2 H, s), 3.0 (1 H, heptet), and 1.2 (6 H, d) (Found:  $M^+$ , 216.0968.  $C_{14}H_{16}S$  requires  $M^+$ , 216.0972).

**2-Benzyl-5-chlorothiophene.**—2-Benzylthiophene (10 g) was stirred at room temperature during the addition of sulphuryl chloride (7.8 g) over 30 min. A vigorous evolution of gas was evident and the resultant mixture was stirred at room temperature until gas evolution ceased. The resultant mixture was dissolved in dichloromethane (50 ml) and washed with water (2 × 25 ml) and saturated aqueous sodium hydrogen carbonate (25 ml). The organic phase was dried ( $MgSO_4$ ), filtered, and evaporated and the residue dried over calcium hydride. Distillation yielded the title compound (8.5 g, 71%), b.p. 94–96 °C at 0.2 Torr;  $v_{\max.}$ (film) 3 060, 3 010, 2 900, 1 600, 1 540, 1 490, and 1 430  $cm^{-1}$ ;  $\delta(CDCl_3)$  7.2 (5 H, s), 6.6 (1 H, d), 6.45 (1 H, d), and 4.0 (2 H, s) (Found:  $M^+$ , 208.0101.  $C_{11}H_9^{35}ClS$  requires  $M^+$ , 208.0113).

**2-Benzyl-5-bromothiophene.**—2-Benzylthiophene (10 g) was dissolved in dry dimethylformamide (25 ml) and a solution of *N*-bromosuccinimide (10.2 g) in dry dimethylformamide (25 ml) was added. The mixture was stirred at room temperature for 24 h after which it was poured into water (500 ml) and extracted with diethyl ether (3 × 100 ml). The combined ether extracts were washed with water (4 × 100 ml), dried ( $MgSO_4$ ), filtered, and evaporated under reduced pressure. The crude product was dried over, and distilled from, calcium hydride to give the title compound (12.6 g, 86%), b.p. 98–102 °C at 0.2 Torr;  $v_{\max.}$ (film) 3 010, 2 900, 1 600, 1 500, and 1 440  $cm^{-1}$ ;  $\delta(CDCl_3)$  7.1 (5 H, s), 6.7 (1 H, d), 6.4 (1 H, d), and 3.9 (2 H, s) (Found:  $M^+$ , 251.9602.  $C_{11}H_9^{79}BrS$  requires  $M^+$ , 251.9609).

**2-Benzyl-5-iodothiophene.**—A mixture of 2-benzylthiophene (10 g) and iodine (4.32 g) was stirred at room temperature. Nitric acid (8M; 1.5 ml) was added to initiate the reaction and a further quantity of nitric acid (8M; 5 ml) was added over 30 min. The mixture was then heated at reflux for 30 min after which the organic phase was separated from the residual nitric acid. Aqueous sodium hydroxide (40%, w/v; 20 ml) was added and the mixture heated under reflux for 30 min; the organic layer was then separated, washed with water, and dried ( $CaCl_2$ ). Column chromatography (silica; light petroleum–ethyl acetate gradient) yielded the title compound (4.6 g, 43%) as an oil;  $v_{\max.}$ (film) 3 010, 2 900, 1 600, 1 490, 1 450, and 1 430  $cm^{-1}$ ;  $\delta(CDCl_3)$  7.1 (5 H, s), 6.9 (1 H, d), 6.35 (1 H, d), and 4.0 (2 H, s) (Found:  $M^+$ , 299.9473.  $C_{11}H_9I S$  requires  $M^+$ , 299.9472).

**General Method for the Preparation of Thiophenium Bis-(*t*-butoxycarbonyl)methylides.**—The thiophene (10 mmol) was dissolved in methylcyclohexane (10 ml) containing rhodium(II) acetate dimer (10 mg) (Method A), or rhodium(II) hexanoate dimer (10 mg) (Method B). Di-*t*-butyl diazomalonate (10 mmol) was added and the mixture stirred at room temperature until diazo absorption was absent in its i.r. spectrum. If a solid was precipitated, it was filtered off and recrystallised. If the product failed to crystallise from the reaction mixture the solvent was removed under reduced pressure and the residue purified by column chromatography.

**Thiophenium bis(*t*-butoxycarbonyl)methylide: Method B.** After 8 h, filtration yielded the title compound (2.4 g, 80%), m.p. 140–142 °C (MeCN);  $v_{\max.}$ (KBr) 3 080, 2 960, 1 650, 1 475, and 1 440  $cm^{-1}$ ;  $\delta(CDCl_3)$  7.05 (4 H, m) and 1.4 (18 H, s) (Found: C, 60.65; H, 7.5.  $C_{15}H_{22}O_4S$  requires C, 60.40; H, 7.38%).

**2-Methylthiophenium bis(*t*-butoxycarbonyl)methylide: Method A.** After 3 d, filtration yielded the title compound (0.58 g, 37%), m.p. 133–135 °C (methylcyclohexane);  $v_{\max.}$ (KBr) 2 980, 1 710, 1 480, and 1 450  $cm^{-1}$ ;  $\delta(CDCl_3)$  7.0 (3 H, m), 2.5 (3 H, s), and 1.7 (18 H, s) (Found: C, 61.2; H, 8.0.  $C_{16}H_{24}O_4S$  requires C, 61.37; H, 7.69%).

**Method B.** After 16 h, filtration yielded the product (2.9 g, 92%) with physical and spectroscopic properties identical with those described above.

**2-Ethylthiophenium bis(*t*-butoxycarbonyl)methylide: Method A.** After 6 h, filtration yielded the title compound (1.24 g, 38%), m.p. 108–109 °C (methylcyclohexane);  $v_{\max.}$ (KBr) 3 060, 2 960, 1 675, 1 650, 1 460, and 1 450  $cm^{-1}$ ;  $\delta(CDCl_3)$  6.8 (3 H, m), 2.6 (2 H, q), and 1.4 (21 H, 18 H singlet and 3 H singlet superimposed) (Found: C, 62.7; H, 8.33.  $C_{17}H_{26}O_4S$  requires C, 62.64; H, 7.98%).

**Method B.** After 6 h, filtration yielded the title compound (2.62 g, 80%) with physical and spectroscopic properties identical with those described above.

**2-Isopropylthiophenium bis(*t*-butoxycarbonyl)methylide: Method A.** After 3 d, the reaction was complete as evidenced by the lack of a diazo absorption in the i.r. spectrum, but no product had crystallised from solution. The solvent was removed under reduced pressure and the crude product purified by column chromatography (silica; dichloromethane) to yield the title compound (0.86 g, 26%), m.p. 118–119 °C (light petroleum);  $v_{\max.}$ (KBr) 3 020, 2 980, 1 700, 1 680, 1 470, and 1 450  $cm^{-1}$ ;  $\delta(CDCl_3)$  6.7 (3 H, m), 2.9 (1 H, heptet), and 1.3 (24 H, overlapping 18 H singlet and 6 H doublet) (Found: C, 63.6; H, 8.55.  $C_{18}H_{28}O_4S$  requires C, 63.53; H, 8.24%).

**Method B.** After 6 h, work-up conditions similar to those described above yielded a product (2.58 g, 78%) with physical and spectroscopic properties identical with those described above.

**Reaction of Di-*t*-butyl Diazomalonate with 2-*t*-Butylthiophene.**—Di-*t*-butyl diazomalonate (1.21 g) was added to a solution of 2-*t*-butylthiophene (0.7 g) in methylcyclohexane (5 ml) containing rhodium(II) hexanoate (5 mg). The solution was stirred at room temperature for 24 h after which time the reaction was complete (i.r.). The solvent was removed and the residue chromatographed (silica; light petroleum–ethyl acetate, 4:1). The fractions containing the major product were combined, the solvent evaporated, and the residue crystallised from methylcyclohexane to yield 1,3-bis-*t*-butoxycarbonyl-2-(3-*t*-butyl-6,6-bis-*t*-butoxycarbonyl-2-thioniabicyclo[3.1.0]hex-3-en-2-yl)methanide (**2**)<sup>8</sup> (0.44 g, 28%), m.p. 175–178 °C;  $v_{\max.}$ ( $CCl_4$ ) 2 970, 2 920, 1 730, 1 690, 1 630, 1 480, and 1 450  $cm^{-1}$ ;  $\delta(CDCl_3)$  6.1 (1 H, dd,  $J$  0.7 and 3 Hz), 3.45 (2 H, m,  $J$  0.7, 3, and 7 Hz), 1.4–1.55 (36 H, four singlets), and 1.1 (9 H, s); <sup>13</sup>C ( $CDCl_3$ ) 27.9, 28.0, 28.8 (× 2), 30.5, 35.0, 40.3, 43.3, 47.5, 62.5, 78.5, 78.6, 82.7, 83.7, 125.7, 152.2, 162.1, 164.9, 165.0, and 165.1 (Found: C, 63.25; H, 8.7.  $C_{30}H_{48}O_8S$  requires C, 63.35; H, 8.52%).

**2-Chlorothiophenium bis(*t*-butoxycarbonyl)methylide: Method A.** After 3 d, filtration yielded the title compound (1.5 g, 42%) (benzene);  $v_{\max.}$ (KBr) 3 060, 2 980, 1 690, 1 650, 1 540, 1 480, and 1 450  $cm^{-1}$ ;  $\delta(CDCl_3)$  6.9 (3 H, m) and 1.4 (18 H, s) (Found: C, 54.2; H, 6.35.  $C_{15}H_{21}ClO_4S$  requires C, 54.20; H, 6.32%).

**2-Bromothiophenium bis(*t*-butoxycarbonyl)methylide: Method B.** After 30 min, filtration yielded the title compound (2.5 g, 66%), m.p. 140–143 °C (decomp.) (benzene);  $v_{\max.}$ (KBr)

**Table 2.** Atomic co-ordinates ( $\times 10^4$ ) and temperature factors ( $\text{\AA}^2 \times 10^3$ ) for compound (2)

Atom	x	y	z
S(1)	6 035(1)	4 205(1)	2 733(1)
C(2)	4 691(2)	4 579(1)	2 863(2)
C(3)	4 490(3)	5 203(1)	2 394(2)
C(4)	4 847(3)	5 118(1)	3 527(2)
C(5)	6 057(3)	5 183(1)	3 844(2)
C(6)	6 764(3)	4 760(2)	3 556(2)
C(7)	5 961(3)	3 503(1)	3 281(2)
C(8)	6 386(3)	3 034(1)	2 625(3)
O(9)	6 739(3)	3 135(1)	1 808(2)
O(10)	6 312(2)	2 472(1)	2 994(2)
C(11)	6 733(4)	1 939(2)	2 470(3)
C(12)	7 967(5)	2 014(3)	2 311(5)
C(13)	6 598(6)	1 431(2)	3 228(4)
C(14)	6 055(6)	1 846(3)	1 492(5)
C(15)	5 574(3)	3 457(1)	4 290(2)
O(16)	5 203(2)	3 887(1)	4 745(2)
O(17)	5 658(2)	2 889(1)	4 679(2)
C(18)	5 343(3)	2 756(2)	5 706(3)
C(19)	4 081(4)	2 883(2)	5 800(4)
C(20)	5 591(5)	2 074(2)	5 799(4)
C(21)	6 088(4)	3 110(2)	6 459(3)
C(22)	3 247(3)	5 341(2)	2 199(3)
O(23)	2 544(3)	5 169(2)	2 747(3)
O(24)	3 040(2)	5 653(1)	1 373(2)
C(25)	1 870(4)	5 830(2)	1 001(3)
C(26)	1 201(6)	5 277(3)	786(7)
C(27)	1 321(5)	6 214(3)	1 748(4)
C(28)	2 076(6)	6 187(5)	80(5)
C(29)	5 329(3)	5 463(2)	1 693(2)
O(30)	5 966(3)	5 153(1)	1 249(2)
O(31)	5 290(2)	6 058(1)	1 651(2)
C(32)	5 932(4)	6 396(2)	894(3)
C(33)	5 619(5)	6 161(2)	-149(3)
C(34)	5 499(7)	7 040(2)	984(5)
C(35)	7 167(5)	6 370(3)	1 208(5)
C(36)	8 037(3)	4 711(2)	3 741(3)
C(37)	8 328(4)	4 199(2)	4 482(4)
C(38)	8 588(4)	4 574(3)	2 749(4)
C(39)	8 510(5)	5 311(2)	4 157(5)

3 060, 2 900, 1 690, 1 640, 1 570, and 1 490  $\text{cm}^{-1}$ ;  $\delta(\text{CDCl}_3)$  7.0 (3 H, m) and 1.4 (18 H, s) (Found: C, 48.05; H, 5.8.  $\text{C}_{15}\text{H}_{21}\text{BrO}_4\text{S}$  requires C, 47.80; H, 5.72%).

**2-Iodothiophenium bis(*t*-butoxycarbonyl)methylide: Method B.** After 30 min, filtration yielded the title compound (3.2 g, 75%), m.p. 134–134.5 °C (benzene);  $\nu_{\text{max.}}$ (KBr) 3 060, 2 970, 1 670, 1 650, and 1 460  $\text{cm}^{-1}$ ;  $\delta(\text{CDCl}_3)$  7.1 (3 H, m) and 1.4 (18 H, s) (Found: C, 42.25; H, 4.5.  $\text{C}_{15}\text{H}_{21}\text{IO}_4\text{S}$  requires C, 42.45; H, 4.95%).

**2-Benzyl-5-methylthiophenium bis(*t*-butoxycarbonyl)methylide: Method B.** After 16 h, removal of the solvent followed by column chromatography (silica;  $\text{CHCl}_2$ ) yielded the title compound (1.8 g, 44%), m.p. 78–79 °C;  $\nu_{\text{max.}}$ (KBr) 3 050, 2 960, 2 920, 1 700, 1 630, and 1 450  $\text{cm}^{-1}$ ;  $\delta(\text{CDCl}_3)$  7.35 (5 H, s), 6.6 (2 H, s), 3.85 (2 H, s), 2.2 (3 H, s), and 1.4 (18 H, s) (Found: C, 68.5; H, 7.45.  $\text{C}_{23}\text{H}_{30}\text{SO}_4$  requires C, 68.62; H, 7.51%).

**2-Benzyl-5-ethylthiophenium bis(*t*-butoxycarbonyl)methylide: Method B.** After 24 h, removal of the solvent followed by column chromatography (silica; light petroleum–ethyl acetate, 4:1) yielded the title compound (2.4 g, 75%) as a viscous oil;  $\nu_{\text{max.}}$ (film) 2 600, 1 705, 1 640, and 1 455  $\text{cm}^{-1}$ ;  $\delta(\text{CDCl}_3)$  7.4 (5 H, s), 6.65 (2 H, s), 3.9 (2 H, s), 2.6 (2 H, q), 1.4 (18 H, s), and 1.2 (3 H, t) (Found: C, 69.2; H, 7.85.  $\text{C}_{24}\text{H}_{32}\text{SO}_4$  requires C, 69.20; H, 7.74%).

**2-Benzyl-5-isopropylthiophenium bis(*t*-butoxycarbonyl)-**

**Table 3.** Bond lengths ( $\text{\AA}$ )

S(1)–C(2)	1.794(3)	S(1)–C(6)	1.809(3)
S(1)–C(7)	1.702(3)	C(2)–C(3)	1.511(4)
C(2)–C(4)	1.473(4)	C(3)–C(4)	1.543(4)
C(3)–C(22)	1.496(5)	C(3)–C(29)	1.503(5)
C(4)–C(5)	1.462(5)	C(5)–C(6)	1.315(5)
C(6)–C(36)	1.502(5)	C(7)–C(8)	1.451(5)
C(7)–C(15)	1.438(5)	C(8)–O(9)	1.201(4)
C(8)–O(10)	1.326(4)	O(10)–C(11)	1.456(4)
C(11)–C(12)	1.485(7)	C(11)–C(13)	1.511(6)
C(11)–C(14)	1.491(8)	C(15)–O(16)	1.211(4)
C(15)–O(17)	1.346(4)	O(17)–C(18)	1.458(4)
C(18)–C(19)	1.519(6)	C(18)–C(20)	1.522(5)
C(18)–C(21)	1.499(6)	O(22)–O(23)	1.191(5)
C(22)–O(24)	1.298(5)	O(24)–C(25)	1.481(5)
C(25)–C(26)	1.459(9)	C(25)–C(27)	1.474(8)
C(25)–C(28)	1.479(10)	C(29)–O(30)	1.190(5)
C(29)–O(31)	1.302(4)	O(31)–C(32)	1.485(5)
C(32)–C(33)	1.497(6)	C(32)–C(34)	1.504(7)
C(32)–C(35)	1.484(7)	C(36)–C(37)	1.512(6)
C(36)–C(28)	1.527(7)	C(36)–C(39)	1.516(7)

**Table 4.** Bond angles ( $^\circ$ )

C(2)–S(1)–C(6)	91.3(1)	C(2)–S(1)–C(7)	107.6(2)
C(6)–S(1)–C(7)	112.4(2)	S(1)–C(2)–C(3)	119.2(2)
S(1)–C(2)–C(4)	110.1(2)	C(3)–C(2)–C(4)	62.3(2)
C(2)–C(3)–C(4)	57.6(2)	C(2)–C(3)–C(22)	112.3(3)
C(4)–C(3)–C(22)	113.4(3)	C(2)–C(3)–C(29)	120.2(3)
C(4)–C(3)–C(29)	119.7(3)	C(22)–C(3)–C(29)	119.0(3)
C(2)–C(4)–C(3)	60.1(2)	C(2)–C(4)–C(5)	109.5(3)
C(3)–C(4)–C(5)	118.0(3)	C(4)–C(5)–C(6)	117.7(3)
S(1)–C(6)–C(5)	111.3(2)	S(1)–C(6)–C(36)	118.6(2)
C(5)–C(6)–C(36)	129.9(3)	S(1)–C(7)–C(8)	110.7(2)
S(1)–C(7)–C(15)	119.0(2)	C(8)–C(7)–C(15)	130.1(3)
C(7)–C(8)–O(9)	123.8(3)	C(7)–C(8)–O(10)	113.7(3)
O(9)–C(8)–O(10)	122.4(3)	C(8)–O(10)–C(11)	122.3(3)
O(10)–C(11)–C(12)	110.0(3)	O(10)–C(11)–C(13)	102.7(3)
C(12)–C(11)–C(13)	108.4(4)	O(10)–C(11)–C(14)	110.1(4)
C(12)–C(11)–C(14)	111.4(5)	C(13)–C(11)–C(14)	113.8(4)
C(7)–C(15)–O(16)	123.4(3)	C(7)–C(15)–O(17)	113.5(3)
O(16)–C(15)–O(17)	123.1(3)	C(15)–O(17)–C(18)	121.6(2)
O(17)–C(18)–C(19)	110.0(3)	O(17)–C(18)–C(20)	102.3(3)
C(19)–C(18)–C(20)	110.8(4)	O(17)–C(18)–C(21)	113.7(3)
C(19)–C(18)–C(21)	112.5(3)	C(20)–C(18)–C(21)	110.5(3)
C(3)–C(22)–O(23)	122.3(4)	C(3)–C(22)–O(24)	112.4(3)
O(23)–C(22)–O(24)	125.3(4)	C(22)–O(24)–C(25)	122.6(3)
O(24)–C(25)–C(26)	109.0(4)	O(24)–C(25)–C(27)	111.0(4)
C(26)–C(25)–C(27)	110.5(5)	O(24)–C(25)–C(28)	102.5(4)
C(26)–C(25)–C(28)	112.8(6)	C(27)–C(25)–C(28)	110.6(5)
C(3)–C(29)–O(30)	122.9(3)	C(3)–C(29)–O(31)	112.4(3)
O(30)–C(29)–O(31)	124.7(3)	C(29)–O(31)–C(32)	120.5(3)
O(31)–C(32)–C(33)	110.1(4)	O(31)–C(32)–C(34)	103.0(4)
C(33)–C(32)–C(34)	109.2(4)	O(31)–C(32)–C(35)	108.5(4)
C(33)–C(32)–C(35)	115.2(5)	C(34)–C(32)–C(35)	110.0(5)
C(6)–C(36)–C(37)	110.0(3)	C(6)–C(36)–C(38)	110.0(3)
C(37)–C(36)–C(38)	108.8(4)	C(6)–C(36)–C(39)	109.6(3)
C(37)–C(36)–C(39)	110.0(4)	C(38)–C(36)–C(39)	108.5(4)

**methylide: Method B.** After 24 h, evaporation of the solvent followed by column chromatography (silica; light petroleum–ethyl acetate, 4:1) yielded the title compound (2.4 g, 56%) as a viscous oil,  $\nu_{\text{max.}}$ (film) 2 970, 2 930, 1 705, 1 640, and 1 455  $\text{cm}^{-1}$ ;  $\delta(\text{CDCl}_3)$  7.35 (5 H, s), 6.6 (2 H, s), 3.85 (2 H, s), 2.9 (1 H, heptet), 1.4 (18 H, s), and 1.3 (6 H, d) (Found: C, 69.6; H, 8.05.  $\text{C}_{25}\text{H}_{34}\text{SO}_4$  requires C, 69.73; H, 7.96%).

**2-Benzyl-5-chlorothiophenium bis(*t*-butoxycarbonyl)methylide: Method B.** After 24 h, filtration yielded the title compound (2.2 g, 51%), m.p. 125–127 °C (benzene–hexane);  $\nu_{\text{max.}}$ (KBr) 2 900, 1 710, 1 650, 1 530, 1 500, 1 480, 1 460, and 1 420  $\text{cm}^{-1}$ ;

$\delta(\text{CDCl}_3)$  7.3 (5 H, m), 6.7 (1 H, d), 6.5 (1 H, m), 3.8 (2 H, s), and 1.4 (18 H, s) (Found: C, 62.5; H, 6.75.  $\text{C}_{22}\text{H}_{27}\text{ClO}_4\text{S}$  requires C, 62.53; H, 6.39%).

*2-Benzyl-5-bromothiophenium bis(t-butoxycarbonyl)methylide: Method B.* After 24 h, filtration yielded the title compound (2.3 g, 49%), m.p. 123–125 °C (benzene–hexane);  $\nu_{\text{max.}}(\text{KBr})$  2 900, 1 690, 1 650, 1 515, 1 500, 1 470, 1 450, and 1 425  $\text{cm}^{-1}$ ;  $\delta(\text{CDCl}_3)$  7.4 (5 H, m), 7.0 (1 H, d), 6.55 (1 H, m), 3.9 (2 H, s), and 1.4 (18 H, s) (Found: C, 56.45; H, 5.95.  $\text{C}_{22}\text{H}_{27}\text{BrO}_4\text{S}$  requires C, 56.57; H, 5.78%).

*2-Benzyl-5-iodothiophenium bis(t-butoxycarbonyl)methylide: Method B.* After 24 h, filtration yielded the title compound (3.4 g, 67%), m.p. 159–162 °C (benzene);  $\nu_{\text{max.}}(\text{KBr})$  2 980, 1 670, 1 650, 1 500, 1 470, 1 450, and 1 420  $\text{cm}^{-1}$ ;  $\delta(\text{CDCl}_3)$  7.4 (5 H, m), 7.2 (1 H, d), 6.5 (1 H, m), 3.9 (2 H, s), and 1.4 (18 H, s) (Found: C, 51.15; H, 5.25.  $\text{C}_{22}\text{H}_{27}\text{IO}_4\text{S}$  requires C, 51.40; H, 5.25%).

*Crystal Data.*— $\text{C}_{30}\text{H}_{48}\text{O}_8\text{S}$ ,  $M = 578.7$ , monoclinic,  $a = 11.728(7)$ ,  $b = 21.858(12)$ ,  $c = 13.23(7)$  Å,  $\beta = 93.45(4)^\circ$ ,  $U = 3\,386$  Å<sup>3</sup>,  $\mu(\text{Cu-K}\alpha) = 11.6$   $\text{cm}^{-1}$ ,  $\lambda = 1.541\,78$  Å, space group  $P2_1/a$ ,  $Z = 4$ ,  $D_c = 1.12$   $\text{g cm}^{-3}$ ,  $F(000) = 1\,232$ . Approximate crystal dimensions  $0.5 \times 0.3 \times 0.7$  mm.

*Data Collection and Processing.*—3 347 Independent reflections, 2 871 considered observed [ $|F_o| > 3\sigma(|F_o|)$ ,  $\theta \leq 50^\circ$ ], were measured on a Nicolet R3m diffractometer with Cu-K $\alpha$  radiation (graphite monochromator) using  $\omega$  scans. Data corrected for Lorentz and polarisation factors, no absorption correction applied.

*Structure Analysis and Refinement.*—The structure was solved by direct methods and the non-hydrogen atoms refined anisotropically. The hydrogen atoms on C(2), C(4), and C(5) were located from  $\Delta F$  maps and refined isotropically. All methyl groups were idealised and refined as rigid bodies. Refinement was by block-cascade full-matrix least-squares and converged to give  $R = 0.057$ ,  $R_w = 0.062$  [ $w^{-1} = \sigma^2(F) + 0.000\,94F^2$ ]. Computations were carried out with an Eclipse S140 computer using the SHELXTL<sup>9</sup> program system. Fractional atomic coordinates for the non-hydrogen atoms are given in Table 2. Tables 3 and 4 list bond lengths and bond angles respectively.

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