A [2⁺ + 4] Polar Cycloaddition of α-Thiocarbocations with 1,3-Dienes: Synthesis and Thermal Reaction of 1-Acyl-1-methylthio-2-vinylcyclopropanes

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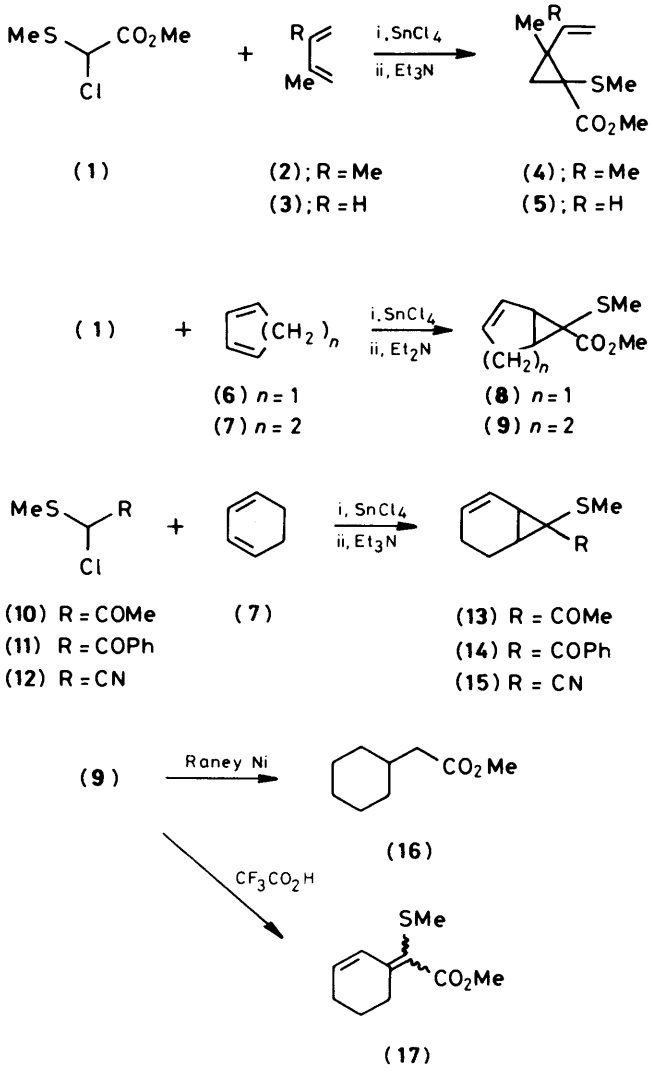
Treatment of methyl 2-chloro-2-(methylthio)acetate, 1-chloro-1-(methylthio)propan-2-one, chloro(methylthio)methyl phenyl ketone, or 2-chloro-2-(methylthio)acetonitrile with 1,3-dienes in the presence of stannic chloride followed by addition of triethylamine gave 1-acyl- or 1-cyano-1-(methylthio)-2-vinylcyclopropanes. A mechanistic interpretation of this reaction is presented. Thermal behaviour of the vinylcyclopropanes is also described.

In our previous publications[1] we reported the reaction of chloromethyl phenyl sulphides with styrene in the presence of stannic chloride which gave the thiochroman ring system. The products of this reaction were believed to arise *via* [4⁺ + 2] polar cycloaddition of an α-(phenylthio)carbocation intermediate resulting from the action of stannic chloride on α-chloro sulphides. We have been led to examine the reaction of chloromethyl methyl sulphides with 1,3-dienes in the presence of stannic chloride, in the hope that a [2⁺ + 4] cycloaddition might result.[2] In this paper, we wish to present our findings in this relatively unexplored area of the polar cycloaddition.[3]



Scheme 1.

Results and Discussion

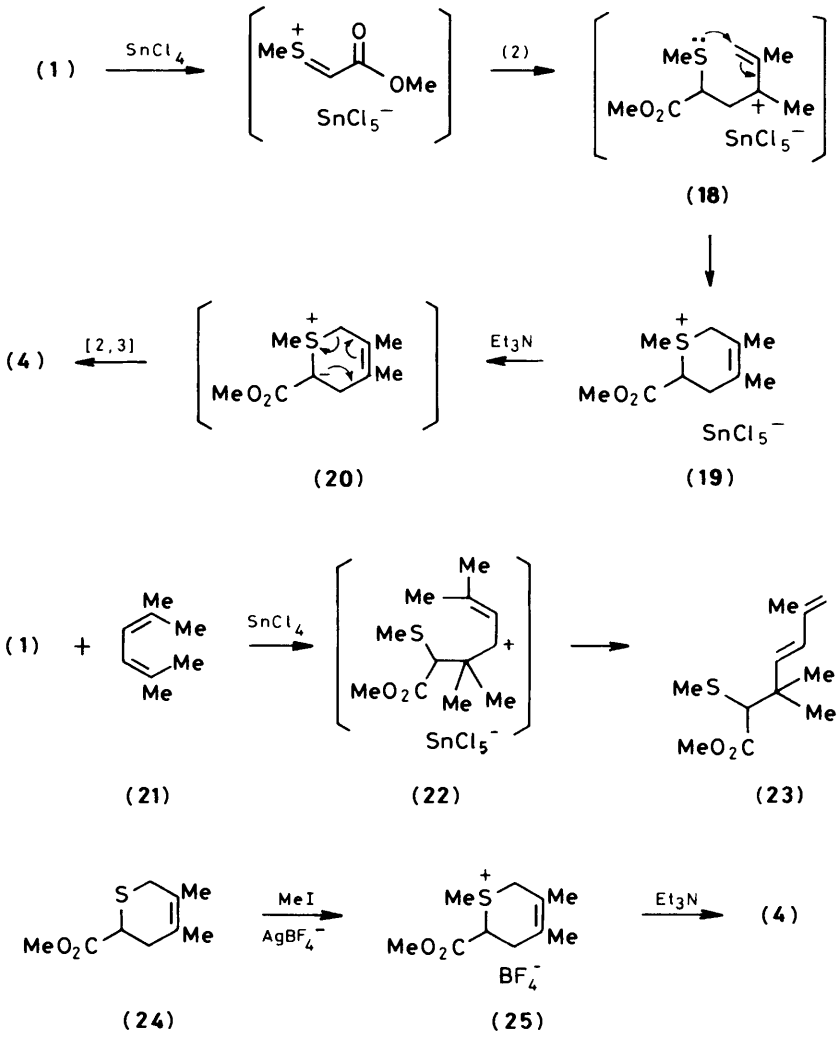
A solution of equimolar amounts of methyl 2-chloro-2-(methylthio)acetate (**1**) and 2,3-dimethylbuta-1,3-diene (**2**) in dry methylene chloride was treated with one mole equivalent of stannic chloride at −20 °C for 10 min, and then triethylamine was added to the reaction mixture and work-up gave the vinylcyclopropane (**4**) in 71% yield. Similarly, the reaction of compound (**1**) with isoprene (**3**), cyclopentadiene (**6**), or cyclohexa-1,3-diene (**7**) gave the corresponding vinylcyclopropanes (**5**) (75%), (**8**) (39%), and (**9**) (65%).

An analogous transformation was also achieved by using 1-chloro-1-(methylthio)propan-2-one (**10**), chloro(methylthio)-methyl phenyl ketone (**11**), and 2-chloro-2-(methylthio)acetonitrile (**12**). Thus, the reaction of the chlorides (**10**)—(**12**) with cyclohexa-1,3-diene (**7**) under the same conditions afforded the vinylcyclopropanes (**13**) (43%), (**14**) (53%), and (**15**) (58%), respectively. All the vinylcyclopropanes were obtained as a single stereoisomer.

The structural assignment of the vinylcyclopropanes was based on spectroscopic evidence and chemical transformations. For example, the i.r. spectrum of the vinylcyclopropane (**4**) showed an ester carbonyl band at 1 720 cm^{-1}, and the n.m.r. spectrum revealed a *C*-methyl singlet (3 H) at δ 1.24, a vinylic methyl singlet (3 H) at δ 1.83, an *S*-methyl singlet (3 H) at δ 2.11, and an *O*-methyl singlet (3 H) at δ 3.78, two doublets due to ring protons at δ 1.34 (*J* 5.6 Hz) and 1.70 (*J* 5.6 Hz), and two broad singlets due to vinylic protons at δ 4.86 and 4.95. The vinylcyclopropane structure was further confirmed by reduction of (**9**) with Raney nickel to give methyl cyclohexylacetate (**16**).[4] In addition, treatment of (**9**) with trifluoroacetic acid gave compound (**17**) as a mixture of geometric isomers. The stereochemistry of the vinylcyclopropanes has not been determined yet, but the following mechanistic consideration implies the methylthio group to be *cis* to the olefinic moiety.†

A mechanistic rationalization of the formation of the

† At present, we have no way of confirming this stereochemistry: for example, irradiation of the signal at δ 2.11 (SMe) in compound (**4**) failed to show enhancement of either signal at δ 4.86 or 4.95 (=CH_2).



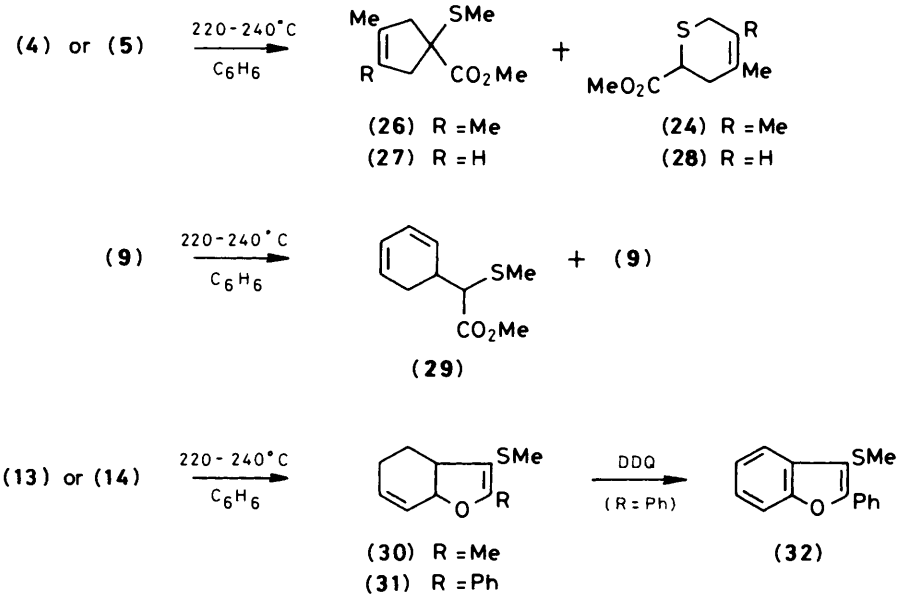
Scheme 2.

vinylcyclopropanes (Scheme 2) is based on the assumption that the chloro sulphide [*e.g.* (**1**)] with the aid of stannic chloride attacks one of the double bonds in the 1,3-diene [*e.g.* (**2**)] to form a new resonance-stabilized carbenium ion (**18**). This step is then followed by ring-closure to lead to the [$2^+ + 4$] cycloadduct (**19**). This stepwise mechanism was supported by the isolation of the non-cyclized product (**23**) from the reaction of compound (**1**) with 2,5-dimethylhexa-2,4-diene (**21**); treatment of (**1**) with (**21**) in the presence of stannic chloride gave a complex mixture of several products, from which the diene (**23**) was isolated and characterized (see the Experimental section). In this case the ring-closure becomes unfavourable probably because of the presence of two methyl groups at the terminus of the double bond of the carbenium intermediate (**22**). Subsequent deprotonation of the adduct (**19**) with triethylamine forms the sulphonium ylide (**20**), which undergoes a [2,3] sigmatropic rearrangement to give compound (**4**). If this mechanism is correct, the vinyl and methylthio groups should be *cis* to each other. The exclusive formation of the 2-methyl-2-vinylcyclopropane (**5**) rather than an alternative isopropenylcyclopropane derivative from the reaction of compounds (**1**) and (**3**) may reflect the difference in the stability of the intermediary carbenium ions [corresponding to (**18**)] (tertiary *versus* secondary carbenium ions).

Strong support for the proposed mechanistic scheme was derived from the isolation of the intermediate (**19**). When the reaction was carried out in chloroform instead of methylene chloride, a dark brown oil of compound (**19**) precipitated. Evidence for the structure of this oil was obtained by an examination of the n.m.r. spectrum (in CD_3CN), which showed a broad singlet (6 H) due to two vinylic methyl groups at δ 1.80, two multiplets (2 H each, 3-H and 6-H) at δ 2.7—3.0 and 3.7—4.0, an S^+-methyl singlet (3 H) at δ 2.90, an *O*-methyl singlet at δ 3.82, and a triplet (1 H, 2-H, *J* 6 Hz) at δ 4.59.

The structure (**19**) was further confirmed by a comparison of the n.m.r. spectrum with that of the tetrafluoroborate (**25**) which was obtained by methylation of methyl 5,6-dihydro-3,4-dimethyl-2H-thiin-6-carboxylate (**24**)[5] with methyl iodide in the presence of silver tetrafluoroborate. Base-promoted rearrangement of both (**19**) and (**25**) gave rise to (**4**) in high yield.

The thermal rearrangement of vinylcyclopropanes to cyclopentenes has been well documented.[6] Consequently our attention was directed to the thermal behaviour of the vinylcyclopropanes thus obtained. On heating at 220—240 °C in benzene for 10 h, compound (**4**) was converted into the cyclopentene (**26**) (34%) along with the dihydrothiin (**24**)[5] (14%). The structure of (**26**) was assigned on the basis of the spectroscopic evidence (see the Experimental section). Similarly, the vinylcyclopropane (**5**) was transformed in this temperature



Scheme 3.

range to compounds (**27**) (39%) and (**28**) (23%). However, the cyclic vinylcyclopropane (**9**) was rather stable under these conditions but prolonged heating (16 h) gave a ring-opened product (**29**) (18%) together with unchanged starting material (23%).

In sharp contrast, the ketones (**13**) and (**14**) afforded the dihydrofuran derivatives (**30**) (30%) and (**31**) (36%) respectively, as the major products. The structures of (**30**) and (**31**) were assigned on the basis of the spectroscopic evidence (see the Experimental section) and the following transformation. Oxidation of (**31**) with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) gave 3-methylthio-2-phenylbenzo[*b*]furan (**32**).

Experimental

I.r. spectra were recorded with a JASCO A-100 spectrophotometer. N.m.r. spectra were determined with a Varian XL-300 (300 MHz) or JEOL JNM-PMX 60 (60 MHz) spectrometer, and δ values are quoted relative to tetramethylsilane. Mass spectra were obtained on a Hitachi M-80 instrument operating at 20 eV. Chromatographic separation was performed with silica gel 60 (63—200 μm) (Merck).

Methyl 2-chloro-2-(methylthio)acetates (**1**), 1-chloro-1-methylthiopropan-2-one (**10**), phenyl chloro(methylthio)methyl ketone (**11**), and 2-chloro-2-(methylthio)acetonitrile (**12**) were prepared as described in the literature.[7]

Methyl 2-Isopropenyl-2-methyl-1-(methylthio)cyclopropane-1-carboxylate (**4**).—To a stirred solution of the chloride (**1**) (2.0 g, 13 mmol) and 2,3-dimethylbuta-1,3-diene (**2**) (1.2 g, 15 mmol) in methylene chloride (40 ml) was added stannic chloride (1.7 ml, 15 mmol) at −20 °C under a nitrogen atmosphere. After the reaction mixture had been stirred at the same temperature for 10 min, triethylamine (9.2 ml, 66 mmol) was added. The mixture was stirred at room temperature for 10 min and ether was added and the precipitated salt was filtered off. The filtrate was concentrated and the residual oil was distilled at 65—66 °C (1 mmHg) to give the *methyl ester* (**4**) (1.9 g, 71%) (Found: M^+, 200.0852. $C_{10}H_{16}O_2S$ requires *M*, 200.0870); $\nu_{max.}$($CHCl_3$) 1 720 cm^{-1}; δ ($CDCl_3$; 300 MHz) 1.24 (3 H, s, CMe), 1.34 (1 H, d, *J* 5.6 Hz, ring-H), 1.70 (1 H, d, *J* 5.6 Hz, ring-H), 1.83 (3 H, br s, vinylic Me), 2.11 (3 H, s, SMe), 3.78 (3 H, s, OMe), and 4.86, 4.95 (1 H each, both br s, $=CH_2$). This compound decomposed during silica gel chromatography.

Methyl 2-methyl-1-(methylthio)-2-vinylcyclopropane-1-carboxylate (**5**).—Using a procedure similar to that described above, the *methyl ester* (**5**) (2.0 g, 75%) was obtained from the chloride (**1**) (2.2 g, 14 mmol) and isoprene (**3**) (1.1 g, 16 mmol) as an oil; b.p. 108—110 °C (20 mmHg) (Found: M^+, 186.0725. $C_9H_{14}O_2S$ requires *M*, 186.0714); $\nu_{max.}$($CHCl_3$) 1 720 cm^{-1}; δ ($CDCl_3$; 300 MHz) 1.26 (3 H, s, CMe), 1.74 (1 H, d, *J* 5.1 Hz, ring-H), 2.16 (1 H, d, *J* 5.1 Hz, ring-H), 2.21 (3 H, s, SMe), 3.76 (3 H, s, OMe), 5.05—5.30 (2 H, m, $=CH_2$), and 6.09 (1 H, dd, *J* 17.6 and 10.7 Hz, =CH). This compound decomposed during silica gel chromatography.

Methyl 6-(Methylthio)bicyclo[3.1.0]*hex-2-ene-6-carboxylate* (**8**).—Using a procedure similar to that described for compound (**4**), the *methyl ester* (**8**) (0.70 g, 39%) was obtained from the chloride (**1**) (1.5 g, 9.8 mmol) and cyclopentadiene (**6**) (0.71 g, 11 mmol) as an oil after purification by column chromatography [silica gel–hexane–ethyl acetate (5:1)] (Found: C, 58.4; H, 6.6. $C_9H_{12}O_2S$ requires C, 58.7; H, 6.6%); $\nu_{max.}$($CHCl_3$) 1 710 cm^{-1}; δ ($CDCl_3$; 300 MHz) 2.01 (3 H, s, SMe), 2.27—2.37 (1 H, m, 4-H), 2.53 (1 H, t, *J* 6.8 Hz, 1-H), 2.66 (1 H, ddt, *J* 19.4, 6.9, and 2.7 Hz, 4-H), 2.82 (1 H, dt, *J* 6.8 and 2.7 Hz, 5-H), 3.76 (3 H, s, OMe), 5.74—5.79 (1 H, m, olefinic-H), and 5.84—5.90 (1 H, m, olefinic-H).

Methyl 7-(Methylthio)bicyclo[4.1.0]*hept-2-ene-7-carboxylate* (**9**).—Using a procedure similar to that described for (**4**), the *methyl ester* (**9**) (1.09 g, 65%) was obtained from the chloride (**1**) (1.3 g, 8.5 mmol) and cyclohexa-1,3-diene (**7**) (0.75 g, 9.3 mmol) as an oil after purification by column chromatography (silica gel—benzene) (Found: M^+, 198.0727. $C_{10}H_{14}O_2S$ requires *M*, 198.0714); $\nu_{max.}$($CHCl_3$) 1 715 cm^{-1}; δ ($CDCl_3$; 300 MHz) 1.91—2.28 (6 H, m, 1-, 4-, 5-, and 6-H), 2.12 (3 H, s, SMe), 3.75 (3 H, s, OMe), 5.80—5.88 (1 H, m, 3-H), and 5.92 (1 H, dt, *J* 10.2 and 3.8 Hz, 2-H).

Methyl 7-(Methylthio)bicyclo[4.1.0]*hept-2-en-7-yl Ketone* (**13**).—Using a procedure similar to that described for compound (**4**), the *ketone* (**13**) (0.87 g, 43%) was obtained from

the chloride (**10**) (1.5 g, 11 mmol) and cyclohexa-1,3-diene (**7**) (0.98 g, 12 mmol) as an oil after purification by column chromatography (silica gel–benzene) (Found: M^+, 182.0762. $C_{10}H_{14}OS$ requires M, 182.0764); $\nu_{max.}$($CHCl_3$) 1 680 cm^{-1}; δ ($CDCl_3$; 60 MHz) 1.5—2.3 (6 H, m, 1-, 4-, 5-, and 6-H), 2.06 (3 H, s, SMe), 2.48 (3 H, s, COMe), and 5.8—5.9 (2 H, m, olefinic-H).

7-(*Methylthio*)*bicyclo*[4.1.0]*hept*-2-*en*-7-*yl Phenyl Ketone* (**14**).—Using a similar procedure to that described for compound (**4**), the *ketone* (**14**) (0.93 g, 53%) was obtained from the chloride (**11**) (1.4 g, 7.2 mmol) and cyclohexa-1,3-diene (**7**) (0.63 g, 7.9 mmol) as an oil after purification by column chromatography [silica gel–benzene–hexane (2:1)] (Found: C, 73.6; H, 6.6. $C_{15}H_{16}SO$ requires C, 73.7; H, 6.6%); $\nu_{max.}$($CHCl_3$) 1 650 cm^{-1}; δ ($CDCl_3$; 60 MHz) 1.3—2.5 (6 H, m, 1-, 4-, 5-, and 6-H), 1.76 (3 H, s, SMe), 5.5—6.0 (2 H, m, olefinic-H), 7.1—7.5 (3 H, m, ArH), and 7.7—8.0 (2 H, m, ArH).

7-(*Methylthio*)*bicyclo*[4.1.0]*hept*-2-*ene*-7-*carbonitrile* (**15**).—Using a similar procedure to that described for compound (**4**), the *nitrile* (**15**) (0.89 g, 58%) was obtained from the chloride (**12**) (1.1 g, 9.3 mmol) and cyclohexa-1,3-diene (**7**) (0.83 g, 10 mmol) as an oil after purification by column chromatography (silica gel–benzene) (Found: M^+, 165.0593. $C_9H_{11}NS$ requires M, 165.0611); $\nu_{max.}$($CHCl_3$) 2 320 cm^{-1}; δ ($CDCl_3$; 300 MHz) 1.91—2.00 (2 H, m, 5-H), 2.05—2.27 (4 H, m, 1-, 4-, and 6-H), 2.23 (3 H, s, SMe), 5.77—5.85 (1 H, m, 3-H), and 5.96 (1 H, dt, J 10.5 and 3.6 Hz, 2-H).

Methyl Cyclohexylacetate (**16**).—A mixture of compound (**9**) (0.17 g, 0.85 mmol) and W-2 Raney nickel (*ca.* 1 g) in ethanol (5 ml) was refluxed for 1.5 h. After the Raney nickel had been filtered off, the filtrate was concentrated. An oily residue was purified by chromatography (silica gel–hexane) to give the *methyl ester* (**16**)[4] (0.53 g, 58%) as an oil, which was identified by comparison of the i.r. and n.m.r. spectra with those of an authentic sample.

Methyl 2-(*Methylthio*)-2-(*cyclohex*-2-*enylidene*)*acetate* (**17**).—To a solution of compound (**9**) (0.80 g, 4.0 mmol) in methylene chloride (4 ml) was added trifluoroacetic acid (1.4 g, 12 mmol) at 0 °C, and the reaction mixture was stirred at room temperature for 2 h and concentrated. The residue was chromatographed (silica gel–benzene) to give the *methyl ester* (**17**) (0.59 g, 74%) as a 1 : 1 mixture of the geometrical isomers (Found: M^+, 198.0722. $C_{10}H_{14}O_2S$ requires M, 198.0714); $\nu_{max.}$($CHCl_3$) 1 715 cm^{-1}; δ ($CDCl_3$; 60 MHz) 1.4—2.4 (4 H, m, 2 × CH_2), 2.19, 2.21, (1.5 H each, both s, SMe), 2.4—2.8 (2 H, m, CH_2), 3.83 (3 H, s, OMe), 6.00 (0.5 H, dt, J 10 and 4 Hz, olefinic-H), 6.17 (0.5 H, dt, J 10 and 4 Hz, olefinic-H), 6.48 (0.5 H, dt, J 10 and 2 Hz, olefinic-H), and 6.93 (0.5 H, dt, J 10 and 4 Hz, olefinic-H).

6-*Methoxycarbonyl*-1,3,4-*trimethyl*-5,6-*dihydro*-2H-*thiinium Pentachlorostannate* (**19**).—To a solution of (**1**) (0.31 g, 2 mmol) and (**2**) (0.18 g, 2.2 mmol) in chloroform (5 ml) was added stannic chloride (0.57 g, 2.2 mmol) at −20 °C. The mixture was stirred at the same temperature for 10 min and a brown oil was carefully separated and transferred to an n.m.r. tube. This oil was dissolved in trideuterioacetonitrile and the n.m.r. spectrum was measured, δ (CD_3CN; 60 MHz) 1.80 (6 H, br s, vinylic Me), 2.7—3.0 (2 H, m, 5-H), 2.90 (3 H, s, SMe), 3.7—4.0 (2 H, m, 2-H), 3.82 (3 H, s, OMe), and 4.59 (1 H, t, J 6 Hz, 6-H).

Methyl 3,3,6-*Trimethyl*-2-(*methylthio*)*hepta*-4,6-*dienoate* (**23**).—Using a procedure similar to that described for compound (**4**), the chloride (**1**) (2.34 g, 15 mmol) was allowed to react with 2,5-dimethylhexa-2,4-diene (**21**) (1.83 g, 16.6 mmol) and work-up gave a mixture of several products, from which the *methyl ester* (**23**) (0.51 g, 15%) was isolated by column chromatography (silica gel–benzene) (Found: M^+, 228.1195. $C_{12}H_{20}O_2S$ requires M, 228.1183); $\nu_{max.}$($CHCl_3$) 1 740 cm^{-1}; δ ($CDCl_3$; 60 MHz) 1.16 (6 H, s, CMe_2), 1.76 (3 H, br s, 6-Me), 2.03 (3 H, s, SMe), 3.07 (1 H, s, 2-H), 3.61 (3 H, s, OMe), 4.86 (2 H, br s, =CH_2), 5.67 (1 H, d, J 17 Hz, 4- or 5-H), and 6.10 (1 H, d, J 17 Hz, 5- or 4-H).

5,6-*Dihydro*-6-*methoxycarbonyl*-1,3,4-*trimethyl*-2H-*thiinium Tetrafluoroborate* (**25**).—A mixture of the dihydrothiin (**24**)[5] (0.10 g, 0.54 mmol), methyl iodide (0.15 g, 1.1 mmol), and silver tetrafluoroborate (0.11 g, 0.54 mmol) was stirred at room temperature for 3 h. The oil which separated was washed with dry ether and dried *in vacuo* to give the *sulphonium salt* (**25**) (155 mg, 100%). Its n.m.r. spectrum in trideuterioacetonitrile was essentially the same as that of the sulphonium salt (**19**).

Conversion of the Sulphonium Salts (**19**) *and* (**25**) *to the Methyl Ester* (**4**).—To a solution of the sulphonium salt (**25**) (155 mg, 0.54 mmol) in methylene chloride (5 ml) was added triethylamine (0.1 ml). The mixture was stirred for 30 min and concentrated to give compound (**4**) (90 mg, 89%). Similar treatment of compound (**19**) gave the methyl ester (**4**) which was identified by ^1H n.m.r. spectroscopy.

Thermolysis of Methyl Ester (**4**).—A solution of the methyl ester (**4**) (630 mg, 3.1 mmol) in benzene (30 ml) was heated in a sealed tube at 220—240 °C for 10 h. The solvent was evaporated off and the residue was chromatographed [silica gel–hexane–ethyl acetate (19:1)] to give *methyl* 3,4-*dimethyl*-1-(*methylthio*)*cyclopent*-3-*ene*-1-*carboxylate* (**26**) (217 mg, 34%) and the dihydrothiin (**24**)[5] (82 mg, 14%).

Compound (**26**) was an oil (Found: M^+, 200.0846. $C_{10}H_{16}O_2S$ requires M, 200.0870); $\nu_{max.}$($CHCl_3$) 1 720 cm^{-1}; δ ($CDCl_3$; 60 MHz) 1.60 (6 H, br s, 2 × CMe), 2.11 (3 H, s, SMe), 2.48, 3.04 (2 H each, br AB system, J 16 Hz, 2 × CH_2), and 3.73 (3 H, s, OMe).

Thermolysis of Methyl Ester (**5**).—A solution of the methyl ester (**5**) (537 mg, 2.9 mmol) in benzene (30 ml) was heated in a sealed tube at 220—240 °C for 13 h and work-up gave *methyl* 3-*methyl*-1-(*methylthio*)*cyclopent*-3-*ene*-1-*carboxylate* (**27**) (209 mg, 39%) and *methyl* 5,6-*dihydro*-4-*methyl*-2H-*thiin*-6-*carboxylate* (**28**) (113 mg, 23%).

Compound (**27**) was an oil (Found: M^+, 186.0733. $C_9H_{14}O_2S$ requires M, 186.0714); $\nu_{max.}$ (liquid film) 1 730 cm^{-1}; δ ($CDCl_3$; 60 MHz) 1.73 (3 H, br s, CMe), 2.10 (3 H, s, SMe), 2.1—3.4 (4 H, m, 2 × CH_2), 3.73 (3 H, s, OMe), and 4.9—5.3 (1 H, m, =CH).

Compound (**28**) was an oil (Found: M^+, 172.0541. $C_8H_{12}O_2S$ requires M, 172.0556); $\nu_{max.}$ (liquid film) 1 735 cm^{-1}; δ ($CDCl_3$; 60 MHz) 1.75 (3 H, br s, CMe), 2.0—2.6 (2 H, m, CH_2), 2.8—3.3 (2 H, m, CH_2), 3.72 (3 H, s, OMe), 3.67 (1 H, t, J 6.5 Hz, 6-H), and 5.3—5.7 (1 H, m, olefinic-H).

Thermolysis of Methyl Ester (**9**).—A solution of the methyl ester (**9**) (519 mg, 2.6 mmol) in benzene (30 ml) was heated in a sealed tube at 220—240 °C for 16 h and work-up gave *methyl* 2-(*cyclohexa*-2,4-*dienyl*)-2-(*methylthio*)*acetate* (**29**) (94 mg, 18%) as a mixture of diastereoisomers and unchanged (**9**) (117 mg, 23%).

Compound (**29**) was an oil (Found: M^+, 198.0716. $C_{10}H_{14}O_2S$ requires M, 198.0714); $\lambda_{max.}$ (hexane) 259 nm (ε 3 200); $\nu_{max.}$ (liquid film) 1 730 cm^{-1}; δ ($CDCl_3$; 60 MHz) 1.6—2.9 (3 H, m), 2.08, 2.12 (1.5 H each, both s, SMe), 3.26 (1 H, d, J 10 Hz, CH), 3.74 (3 H, s, OMe), and 5.5—6.1 (4 H, m, olefinic-H).

Thermolysis of the Ketone (**13**).—A solution of the ketone (**13**) (503 mg, 2.8 mmol) in benzene (30 ml) was heated in a sealed tube at 220—240 °C for 16 h and work-up gave 3a,4,5,7a-*tetrahydro*-2-*methyl*-3-(*methylthio*)*benzo*[b]*furan* (**30**) (153 mg, 30%) as an oil (Found: M^+, 182.0745. $C_{10}H_{14}OS$ requires M, 182.0764); δ ($CDCl_3$; 60 MHz) 1.1—2.3 (4 H, m, 4- and 5-H), 1.88, 1.91 (1.5 H each, both s, SMe), 2.12 (3 H, s, Me), 2.6—3.1 (1 H, m, 3a-H), 4.5—4.8 (1 H, m, 7a-H), and 5.7—6.3 (2 H, m, olefinic-H).

Thermolysis of Ketone (**14**).—A solution of the ketone (**14**) (621 mg, 2.5 mmol) in benzene (30 ml) was heated in a sealed tube at 220—240 °C for 16 h. Work-up gave 3a,4,5,7a-*tetrahydro*-3-(*methylthio*)-2-*phenylbenzo*[b]*furan* (**31**) (222 mg, 36%) as an oil (Found: M^+, 244.0916. $C_{15}H_{16}OS$ requires M, 244.0920); δ ($CDCl_3$; 60 MHz) 1.0—2.3 (4 H, m, 4- and 5-H), 2.24 (3 H, s, SMe), 2.9—3.4 (1 H, m, 3a-H), 4.87 (1 H, br dd, *J* 9 and 3 Hz, 7a-H), 5.9—6.4 (2 H, m, olefinic-H), 7.2—7.7 (3 H, m, ArH), and 7.9—8.2 (2 H, m, ArH).

3-(*Methylthio*)-2-*phenylbenzo*[b]*furan* (**32**).—A solution of the tetrahydrobenzo[*b*]furan (**31**) (75 mg, 0.3 mmol) and DDQ (141 mg, 0.6 mmol) in benzene (5 ml) was refluxed for 1 h. The mixture was filtered and the filtrate was concentrated. The residual oil was chromatographed [silica gel–hexane–benzene (2:1)] to give the *benzo*[b]*furan* (**32**) (18 mg, 25%) as an oil (Found: M^+, 240.0602. $C_{15}H_{12}OS$ requires M, 240.0608); δ ($CDCl_3$; 60 MHz) 2.39 (3 H, s, SMe), and 7.1—8.4 (9 H, m, ArH).

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