Addition of Methyl But-2-enedithioate to Cyclopentadiene. Cyclopentadiene as a Dienophile

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Methyl but-2-enedithioate (**1**) acts as a heterodiene in undergoing cycloaddition to cyclopentadiene as dienophile, giving the bicyclic thiopyran (**4**). A possible alternative mode of cycloaddition to give the norbornenedithioester (**6**) followed by rearrangement to (**4**) is ruled out by a control experiment using (**6**) prepared by a different route.

In the preceding paper[1] we described the cycloaddition reactions of methyl but-2-enedithioate (**1**) with some dienophiles and dienes. As part of this work we investigated the reaction between compound (**1**) and cyclopentadiene. The present paper is concerned with the structure of the adduct formed and the mode of its formation.

Treatment of the thioester (**1**), formed separately or generated *in situ*[1] with cyclopentadiene, gave a single 1:1 adduct isolated in good yield together with some of the dimer of (**1**).[1,2] Four possible structures for the adduct, without stereochemical implications, are shown in which cyclopentadiene acts formally either as the diene, (**2**) and (**3**), or as the dienophile, (**4**) and (**5**). Only structures (**4**) and (**5**) are compatible with the ^{13}C n.m.r. spectrum of the adduct, which shows four olefinic carbon signals, three appearing as doublets and one as a singlet in the off-resonance decoupled spectrum.

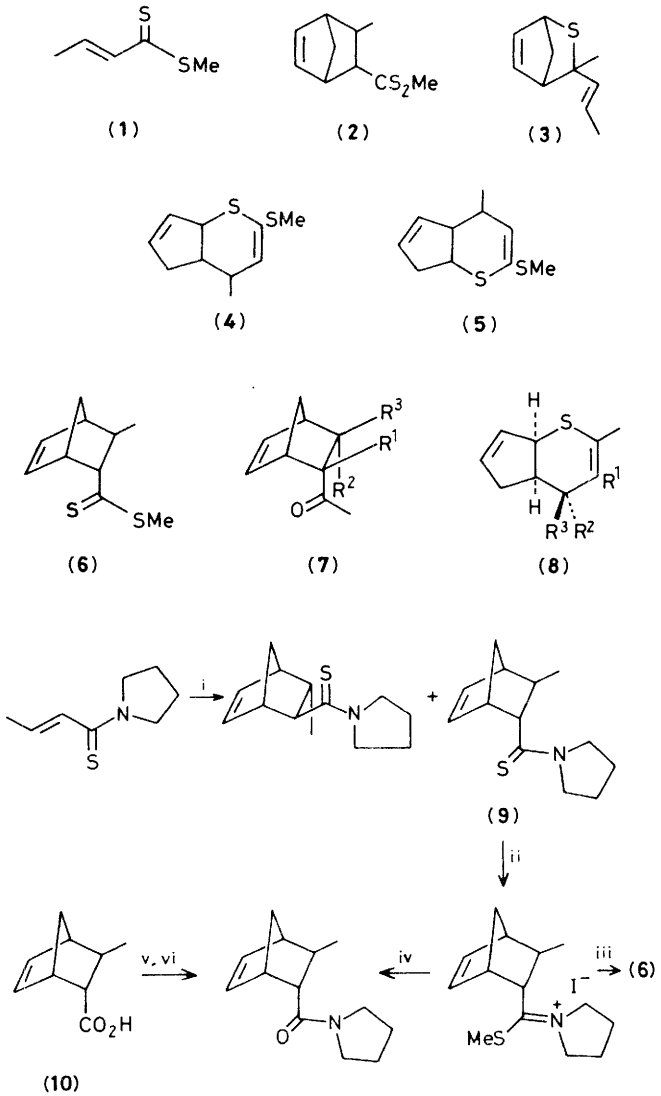
The full n.m.r. data for the adduct (see Experimental section) are better interpreted in terms of the structure (**4**) than (**5**), and this assignment is confirmed by an alternative preparation of the adduct, described below.

There are two potential mechanisms whereby compound (**4**) could have been formed, the one involving [4 + 2]-cycloaddition with the dithioester (**1**) acting as the diene and cyclopentadiene as the dienophile, and the other occurring *via* cycloaddition with cyclopentadiene as the diene to give (**2**)≡(**6**) followed by a [3,3]-sigmatropic rearrangement to (**4**). Precedent for the latter mechanism is provided by the work of Vialle *et al.*[3] who showed that attempts to prepare thioketones from the norbornenes (**7**) gave directly the substituted thiopyrans (**8**), analogous to (**4**). In one case, with the dimethylnorbornene (**7**; $R^1 = H$, $R^2 = R^3 = Me$), the intermediate thioketone was isolated and shown to rearrange to (**8**; $R^1 = H, R^2 = R^3 = Me$) on warming.

To distinguish between the two possibilities, the bicyclic dithioester (**6**) was prepared by the route summarised in the Scheme. The constitution of (**6**) obtained was corroborated as shown in the Scheme by correlation with the known crotonic acid–cyclopentadiene adduct (**10**).[4] The neat dithioester (**6**) was unstable at room temperature and became gummy after a few hours. However, in carbon tetrachloride solution it was more stable, and after 41 h at 20 °C it showed no observable rearrangement to the thiopyran (**4**).

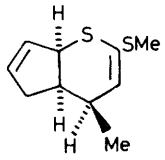
The reaction between methyl but-2-enedithioate (**1**) and an excess of cyclopentadiene in carbon tetrachloride to give the thiopyran (**4**) was monitored by n.m.r. at 18 °C. There was *ca.* 75% reaction after 3 h and after 20 h the reaction was complete. From the observed stability of the dithioester (**6**) at this temperature it is clear that it cannot be an intermediate in the formation of compound (**4**) from cyclopentadiene and the dithioester (**1**).

However, on heating (**6**) in carbon tetrachloride for 16 h under reflux, rearrangement to the thiopyran (**4**), spectroscopically identical with that obtained by cycloaddition, did occur.† That the rearrangement was concerted, rather than a retro Diels–Alder reaction followed by readdition, was



Scheme. *Reagents:* i, cyclopentadiene–$ZnCl_2$–CH_2Cl_2; ii, MeI–CH_2Cl_2; iii, H_2S–THF–pyridine at −20 °C; iv, H_2O–THF–Et_3N; v, $(COCl)_2$–C_6H_6; vi, pyrrolidine–benzene

† The thioamide (**9**) (see Scheme) showed no sign of rearrangement to the corresponding thiopyran after being reluxed in toluene for 8 h.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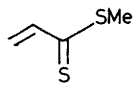
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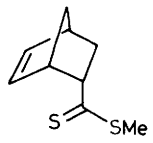
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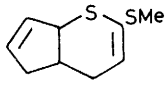
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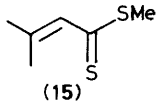
(15)

indicated by the absence of any dithioester (**1**) dimer in the product. A control experiment showed that a 1:1 mixture of compound (**1**) and cyclopentadiene gave a mixture of the product (**4**) and the dimer in about equal proportions.

If the rearrangement of the dithioester (**6**) to compound (**4**) is concerted, the stereochemistry of (**4**) must be as shown in structure (**11**). Thus, the cycloaddition of the dithioester (**1**) to cyclopentadiene is highly stereoselective, leading to the isomer (**11**) which is expected from *endo*-addition with cyclopentadiene acting as the dienophile.

It might be expected that methyl dithioacrylate (**12**) would be more reactive than compound (**1**) on both steric and electronic grounds.[5] We attempted to study the reaction of (**12**) with cyclopentadiene by generating it *in situ*[1] in the presence of excess of cyclopentadiene. Two unstable products were obtained, considered to be the norbornene dithioester (**13**) and the thiopyran (**14**) on the basis of the spectroscopic data (see Experimental section). A control experiment showed that compound (**13**) did not isomerise to (**14**) under the reaction conditions, and thus (**13**) and (**14**) were primary products of the cycloaddition. Apparently the dithioester (**12**) can act as both diene and dienophile towards cyclopentadiene.

The β,β-disubstituted dithioester (**15**) proved to be unreactive towards cyclopentadiene and it was recovered unchanged after being heated with a six-fold excess of cyclopentadiene at 70 °C until all the cyclopentadiene had dimerised (7 h).

Experimental

For details of the n.m.r. instruments used see the preceding paper.[1] Ether refers to diethyl ether.

4-*Methyl*-2-*methylthio*-4,5,8,9-*tetrahydrocyclopenta*[b]*thiopyran*.—(*a*) Methyl 3-hydroxybutanedithioate[1] (9 g, 60 mmol), cyclopentadiene (21 g, 320 mmol), and acetic anhydride (13 g, 130 mmol) in pyridine (90 ml) were heated at 60 °C. After 2.5 h, t.l.c. indicated that no dithioester remained. Water (5 ml) was added, and, after 10 min, the product was partitioned between ether (100 ml) and water (100 ml) and isolated with ether. Distillation gave the *thiopyran* (7.4 g, 62%), b.p. 104 °C at 0.04 mmHg (Found: C, 60.55; H, 7.05. $C_{10}H_{14}S_2$ requires C, 60.55; H, 7.1%); δ (300 MHz; $CDCl_3$) 1.20 (3 H, d, *J* 6.9 Hz, Me), 2.23 (2 H, m, $J_{4,6}$ *ca.* 4, $J_{4,9}$ *ca.* 7, $J_{5',9}$ *ca.* 4, $J_{5,7}$ *ca.* 2 Hz, 5'-, 5-H), 2.30 (3 H, s, SMe), 2.56 (1 H, m, $J_{H,Me}$ 6.92, $J_{3,4}$ 4.4, $J_{4,9}$ *ca.* 3—4 Hz, 4-H), 3.19 (1 H, m, $J_{8,9}$ 9.8 Hz, 9-H), 4.26 (1 H, octet, $^{?}J_{7,8}$ 4.0 $J_{6,8}$ *ca.* 2 Hz, 8-H), 5.57 (1 H, m, $J_{6,7}$ 5.6 Hz, 6-H), 5.66 (1 H, m, 7-H), and 5.81 (1 H, d, $J_{3,4}$ 4.4 Hz, 3-H); δ_C 16.9 (q), 18.2 (q), 34.0 (t), 36.5 (d), 46.8 (d), 55.7 (d), 131.2 (d), 132.5 (d), 133.2 (d), and 134.6 (s).

(*b*) A solution of methyl but-2-enedithioate and freshly distilled cyclopentadiene (1.04 g, 15.8 mmol) in carbon tetrachloride was generated as described in the previous paper[1] using methyl 3-hydroxybutanedithioate (0.49 g, 3.3 mmol) (reaction time 15 min at −5 °C). The solution was kept at 18 °C and the course of the reaction monitored by n.m.r. The change in the ratio of cyclopentadiene:unsaturated dithioester (**1**):thiopyran adduct (**4**) with time was estimated by n.m.r. integration. The results are summarised in the discussion.

N-(trans-*But*-2-*enethioyl*)*pyrrolidine*.—*N*-(*trans*-But-2-enoyl)pyrrolidine (0.22 g. 1.58 mmol) and 2,4-bis(*p*-methoxyphenyl)-1,3,2,4-dithiadiphosphetan-2,4-diyl disulphide[6] (0.31 g. 0.77 mmol) were heated to 100 °C in HMPA (1.5 ml) for 1 h. After cooling and addition of water the product was isolated with ether to give a solid (0.39 g); recrystallisation from ethanol gave *N*-(*trans*-but-2-enethioyl)pyrrolidine as yellow crystals (0.12 g. 47%), m.p. 101.5—103.5 °C (lit.,[7] 100—101 °C); δ($CDCl_3$) 1.8—2.2 (7 H, m, Me + CH_2), 3.6—4.0 (4 H, m, CH_2N), 6.4 (1 H, br d, *J* 15 Hz, CHCS), 6.85—7.45 (1 H, dq, *J* 15, 6 Hz, =C*H*Me).

N-{3-exo-*Methylbicyclo*[2.2.1]*hept*-5-*en*-2-endo-*yl*-(*thiocarbonyl*)}*pyrrolidine* (**9**).—Cyclopentadiene (8.0 g, 120 mmol), *N*-(*trans*-but-2-enethioyl)pyrrolidine (1.01 g, 6.5 mmol) and anhydrous zinc chloride (1.01 g, 7.4 mmol) were refluxed in dry dichloromethane (20 ml) for 20 h. Water was then added and the product extracted into ether. The etheral solution was washed with water and brine, dried ($MgSO_4$), and evaporated under reduced pressure. Repeated crystallisation of the residue from a small quantity of ethanol gave the crude adduct (0.84 g, 58%), as a mixture of stereoisomers, and recovered starting thioamide (0.06 g, 6%). Evaporation of the resulting filtrate under reduced pressure and trituration with light petroleum (2×) gave a solution which yielded a yellow oil (120 mg) on removal of the solvent under reduced pressure. This was shown by n.m.r. to be enriched in the minor *endo*-methyl-*exo*-thioamide isomer; δ(CCl_4) 0.85 (d, *endo*-Me), 6.15—6.35 (m, =CH). The crude adduct was recrystallised from ethanol to give a solid (0.63 g, 44%), m.p. 121—124 °C, which was shown by n.m.r. to contain a little of the minor isomer (<10%, by integration of the Me doublets at δ 1.1 and 0.85). This material was pure enough for further use. A second recrystallisation gave colourless plates of the *adduct* (**9**), m.p. 127.7—128.5 °C (Found: C, 70.85; H, 8.75; N, 6.4; S, 14.25. $C_{13}H_{19}NS$ requires C, 70.55; H, 8.65; N, 6.35; S, 14.5%); δ † (300 MHz; $CDCl_3$) 1.12 (3 H, d, *J* 6.7 Hz, Me), 1.46 (1 H, dd, $J_{7a,s}$ 8.2, $J_{7s,3n}$ 1.5 Hz, 7-H_s), 1.64 (1 H, d, 7-H_a), 1.93—2.02 (2 H, m, 3-H_n + pyrrolidine β-H), 2.09 (2 H, quintet, pyrrolidine β-H), 2.50 (1 H, br s, 4-H), 2.65 (1 H, tt, *J* 6.7, *ca.* 2.5 Hz, pyrrolidine β-H), 2.73 (1 H, t, *J* 3 Hz, 2-H_x), 3.03 (1 H, br s, 1-H), *ca.* 3.8 (3 H, t + dt, *J* 6.7 Hz, pyrrolidine α-H), 3.92 (1 H, dt, *J* 13.9, 6.7 Hz, pyrrolidine α-H), 5.84 (1 H, dd, $J_{5,6}$ 5.6, $J_{5,4}$ *ca.* 3 Hz, 5-H), and 6.38 (1 H, dd, $J_{1,6}$ *ca.* 3 Hz, 6-H); δ_C 20.28 (q, Me), 23.92 (t, pyrrolidine β-C), 26.32 (t, pyrrolidine β-C), 40.94 (d, C-3), 47.31 (d, C-4), 47.51 (t, C-7), 49.65 (d, C-1), 50.17 (t, pyrrolidine α-C), 54.72 (t, pyrrolidine α-C), 58.56 (d, C-2), 130.63 (d, C-5 or -6), 138.49 (d, C-5 or-6), and 202.38 (s, C=S); *m/z* (e.i.) 221 (M^+, 100%), 155 ($C_8H_{13}NS^+$, 50), 140 ($C_7H_{10}NS^+$, 90), 114 ($C_5H_8NS^+$, 65), and 85 (50); $\lambda_{max.}$ (EtOH) 276 (ε, 15 000), 350 nm (42).

Methylation of the Thioamide (**9**).—A solution of the recrystallised thioamide (**9**) prepared as above (0.29 g, 1.3 mmol) and methyl iodide (4.1 g, 28.9 mmol) in dry dichloromethane (1.8 ml) was kept at 18 °C for 6½ h. Dry ether was added to complete precipitation and the resulting methylthioimmonium iodide was collected by filtration and washed with dry ether to give a white solid (0.44 g. 91%), m.p. 130—142 °C (with decomp.); δ($CDCl_3$) 1.25 (3 H, d, Me),

† In the n.m.r. assignments, the subscripts *s* and *a* refers to *syn* and *anti*, while *x* and *n* refer to *exo* and *endo*, respectively.

1.55—1.8 (3 H, m), 2.0—2.5 (5 H, m), 2.65 (1 H, br s), 2.95 (3 H, s, SMe), 3.5—3.7 (1 H, m,), 4.0—4.45 (4 H, m, $CH_2\overset{+}{N}$), and 6.0—6.5 (2 H, m, AB system, =CH); $\nu_{max.}$($CHCl_3$) 1 560 (m, C=N) cm^{-1}. This material was stored in a desiccator.

3-exo-*Methylbicyclo*[2.2.1]*hept*-5-*ene*-2-endo-*carboxylic Acid* (**10**).—Freshly distilled cyclopentadiene (88 g, 1.3 mol) and *trans*-but-2-enoic acid (6.07 g, 0.07 mol) were refluxed together for 48 h. After cooling, the product was partitioned between ether and dilute aq. $NaHCO_3$. Acidification of the aqueous phase (dilute aq. HCl) and ether extraction gave a pale yellow oil, which crystallised on standing (9.84 g). This was shown by n.m.r. to be a 3:2 mixture of the Diels–Alder adduct (two stereoisomers) and unchanged but-2-enoic acid. Recrystallisation from water and from light petroleum gave the acid (**10**) (1.08 g, 10%), m.p. 93—94 °C (lit.,[4] 96 °C); δ($CDCl_3$) 1.17 (3 H, d, *J* 6 Hz, *exo*-Me), 1.5 (2 H, br s, 7-$H_{s,a}$) 1.6—2.05 (1 H, m, *J* 6 Hz, 3-H), 2.3—2.55 (2 H, t, *J ca.* 4 Hz, 2-H + 4-H), 3.1 (1 H, br s, 1-H), 6.0 (1 H, dd, *J* 6, 3 Hz, 6- or 5-H), and 6.22 (1 H, dd, *J* 6, 3 Hz, 6- or 5-H).

N-(3-exo-*Methylbicyclo*[2.2.1]*hept*-5-*en*-2-endo-*ylcarbonyl*)-*pyrrolidine*.—(*a*) *From the acid* (**10**). A solution of 3-*exo*-methylbicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylic acid (0.2 g, 1.3 mmol) in dry benzene (10 ml) was treated with oxalyl chloride (0.22 g, 1.7 mmol). When the initial exothermic reaction had subsided, the solution was refluxed for 20 min. The solvent was removed under reduced pressure, leaving the crude acid chloride, $\nu_{max.}$(liq. film) 1 805 cm^{-1} (C=O). This was redissolved in dry benezene (1 ml) and added to a stirred solution of pyrrolidine (0.17 g, 2.4 mmol) in toluene at 16 °C. After 16 h, the product was partitioned between water (5 ml) and ethyl acetate (4 × 5 ml), and the combined organic extracts were washed with dilute aq. HCl, water, and brine, dried ($MgSO_4$), and concentrated under reduced pressure, to give the amide, as an almost colourless liquid (220 mg, 82%), which solidified on standing, m.p. 48—50 °C (one spot on t.l.c. [CH_2Cl_2]). Satisfactory analytical data have not been obtained. Attempts to recrystallise this compound were unsuccessful; δ(300 MHz; $CDCl_3$) 1.06 (3 H, d, *J* 7, 2 Hz, *exo* Me), 1.36 (1 H, dd, $J_{7s,a}$ 8.5, $J_{7s,3n}$ *ca.* 2 Hz, 7-H_s), 1.51 (1 H, d, 7-H_a), 1.73—1.95 (4 H, AB multiplet, *J ca.* 13, *ca.* 7 Hz, CH_2), 2.01 (1 H, m, $J_{2x,3n}$ 3.1 Hz, 3-H_n), 2.34 (1 H, t, $J_{1,2x}$ 3.1 Hz, 2-H_x), 2.41 (1 H, br, s 4-H), 2.98 (1 H, br s, 1-H), 3.27—3.46 (AB multiplet, *J ca* 12, *ca.* 7 Hz, CH_2N) + 3.50 (4 H together, dt, *J ca.* 7 Hz, CH_2N), 5.82 (1 H, dd, $J_{5,6}$ 5.4, $J_{4,5}$ 3.1 Hz, 6- or 5-H), and 6.26 (1 H, dd, 6- or 5-H); *m/z* (e.i.) 205 (M^+, 44%), 140 ($C_8H_{14}NO^+$, 100), 124 (41), 98 ($C_5H_8NO^+$, 65), 70 ($C_4H_8N^+$, 49), 69 ($C_4H_5O^+$, 76), and 66 ($C_5H_6^+$, 44); $\nu_{max.}$(liq. film) 1 653—1 645 cm^{-1} (s, C=O).

(*b*) *By hydrolysis of the methylthioimmonium salt*.—To a stirred suspension of the salt (61.4 mg, 0.17 mmol) in aqueous THF (1 ml; 1:1 v/v) at 16 °C, was added triethylamine (22 mg, 0.22 mmol). After 16 h, more water was added and the product extracted with ether. The ethereal solution was washed with water and brine, dried ($MgSO_4$), and concentrated under reduced pressure to give a yellowish oil (40 mg), which was shown by n.m.r. and i.r. to be identical with the compound formed above.

Methyl 3-exo-*Methylbicyclo*[2.2.1]*hept*-5-*ene*-2-endo-*carbodithioate* (**6**).—Hydrogen sulphide was passed into a stirred suspension of the methylthioimmonium salt (274 mg, 0.75 mmol) in dry THF (6.5 ml) containing dry pyridine (130 mg, 1.6 mmol) at −10 to −20 °C for 14 h; the flask was wrapped in foil to exclude light. The suspension was then allowed to warm to −5 °C during 1 h and poured onto a mixture of dilute aq. HCl and ice. The product was extracted into ether and the ethereal solution was washed with water and brine, dried ($MgSO_4$), and concentrated under reduced pressure giving the crude dithioester as a yellow liquid (85 mg, 57%). T.l.c. (light petroleum) showed one main spot (R_F 0.2); δ($CDCl_3$) 1.2 (3 H, d, *J* 8 Hz, *exo* Me), 1.45—2.4 (complex m), 2.5 (1 H, br s, 4-H), 2.55 (3 H, s, SMe), 3.05 (1 H, t, *J ca.* 4 Hz, 2-H_x), 3.3 (1 H, br s, 1-H), 5.9 (1 H, dd, $J_{5,6}$ 6, $J_{1,6\text{ or }4,5}$ 3 Hz, 6- or 5-H), and 6.25 (1 H, dd, *J* 6, 3 Hz, 6- or 5-H); $\nu_{max.}$(Et_2O) 306.5 (strong) and 466 (weak) nm. Further extraction of the aqueous phase with chloroform and removal of the solvent under reduced pressure gave unchanged immonium salt (85 mg, 31% recovery).

The dithioester (**6**) deteriorated rapidly on standing, becoming gummy after a few minutes; trituration of this gum with ether gave a white solid, which only showed n.m.r. absorption between δ 0.8 and 3.6 Periodic monitoring by n.m.r. of a solution of the dithioester in carbon tetrachloride showed only slight polymerisation after 2 days at 16 °C.

Rearrangement of the Dithioester (**6**).—A solution of the dithioester in carbon tetrachloride (*ca.* 0.07 mmol in 1.5 ml) was refluxed for 16 h. The solvent was then removed under reduced pressure leaving a brown liquid, which was shown by n.m.r. to be 4-methyl-2-methylthio-4,5,8,9-tetrahydrocyclopenta[*b*]thiopyran, by comparison with an authentic spectrum. It also had identical mobility on t.l.c.

Reaction of Methyl 3-*Trifluoroacetoxypropanedithioate with* 2,6-*Dimethylpyridine in Cyclopentadiene*.—(*a*) Methyl 3-trifluoroacetoxypropanedithioate[1] (108 mg, 0.46 mmol), 2,6-dimethylpyridine (320 mg, 3 mmol), and a little hydroquinone were dissolved in freshly distilled cyclopentadiene (1 ml, 12 mmol) and left at 18 °C for 48 h. The product was then partitioned between water (5 ml) and ether and the ethereal solution was washed with dilute aq. HCl, saturated aq. $NaHCO_3$, water, and brine, dried ($MgSO_4$), and evaporated, giving a yellow liquid (250 mg). Column chromatography (silica gel; 2 g) using light petroleum to elute bicyclopentadiene and dichloromethane to elute the products was followed by p.l.c., using light petroleum as eluant. The minor, yellow band (R_F 0.3) was extracted from the silica gel using AnalaR carbon tetrachloride and concentrated to a volume of *ca.* 0.5 ml under reduced pressure. The spectral data were consistent with methyl bicyclo[2.2.1]hept-5-ene-2-*endo*-carbodithioate (**13**); δ (300 MHz; CCl_4–CD_2Cl_2) *ca.* 1.3—1.5 (m, 7-H_s, the *a* signal was obscured by impurities), 1.93 (1 H, octet, $J_{3x,3n}$ 11.8, $J_{3n,2x}$ 4.6, $J_{3n,7s}$ 2.1 Hz, 3-H_n), 2.59 (3 H, s, SMe), 2.94 (1 H, br s, 4-H), 3.43 (1 H, br s, 1-H), 3.66 (1 H, quintet, $J_{2x,3x}$ 8.7, $J_{1,2x}$ 3.6 Hz, 2-H_x), 5.85 (1 H, dd, $J_{5,6}$ 5.6, $J_{4,5\text{ or }1,6}$ 3.1 Hz, 6- or 5-H), and 6.20 (1 H, dd, 6- or 5-H); $\lambda_{max.}$(CCl_4) 308.6 (strong), 469 cm^{-1} (weak); $\lambda_{max.}$(Et_2O) 305 (strong), 465 cm^{-1} (weak); $\nu_{max.}$(CCl_4) 1 165w cm^{-1} (C=S). The neat material was found to polymerise rapidly.

The major band gave a colourless oil, which darkened on standing for 18 h at 16 °C. In subsequent preparations, this compound was stored in solution in light petroleum at 4 °C.

(*b*) The reaction was repeated as above, using 295 mg (1.27 mmol) of the trifluoroacetate (reaction time 2 h, 18 °C). Work-up gave a dried light petroleum solution, which was reduced under reduced pressure to a volume of *ca.* 1 ml and treated with dry pyrrolidine (85 mg, 1.2 mmol). After 15 h at 16 °C, the products were partitioned between water (5 ml) and ether and the ethereal solution was washed with water and brine, dried ($MgSO_4$), and concentrated under reduced pressure, giving a yellow oil (230 mg). The mixture was separated by column chromatography (silica gel; 4 g) using light petroleum to elute bicyclopentadiene through to dichloromethane to elute the products. 2-Methylthio-4,5,8,9-tetrahydrocyclopenta[*b*]thiopyran (**14**) was isolated as a colourless liquid (60 mg, 26%); δ (300 MHz; $CDCl_3$) 2.14—2.24 (2 H, dd + m, part of AB system 4- or

4′-H + 5- or 5′-H), 2.33 (3 H, s, SMe), 2.33 (1 H, dd, $J_{4,4'}$ 19.5, $J_{3,4}$ 5.6 Hz, 4- or 4′-H), 2.55 (1 H, octet, $J_{5,5'}$ 16.9, $J_{5',9}$ 8.7, $J_{5',7}$ 1.5 Hz, 5- or 5′-H), 3.00 (1 H, m, $J_{8,9}$ 9.2 Hz, 9-H), 4.21 (1 H, br d, $J_{7,8}$ *ca.* 4, $J_{6,8}$ *ca.* 2 Hz, 8-H), 5.54 (1 H, m, $J_{6,7}$ 7.7, $J_{5,6}$ *ca.* 4 Hz, 6-H), 5.77 (1 H, m, 7-H), and 6.17 (1 H, t, 3-H); δ_C (75.57 MHz) 16.70 (q, SMe), 32.76 (t, CH_2), 39.02 (t, CH_2), 40.55 (d, CH), 54.27 (d, CHS), 126.51 (d, =CH), 131.43 (d, =CH), 132.32 (d, =CH), and 135.11 p.p.m. (s, CS_2); *m/z* (e.i.) 184 (M^+, 100%), 137 (SMe, 12), 119 ($C_4H_7S_2^+$, 19), 93 (CS_2Me, 18), 79 ($C_6H_7^+$, 16), 71 (78), 66 ($C_5H_6^+$, 16), 45 (14), and 39 (15).

N-Bicyclo[2.2.1]hept-5-en-2-yl(thiocarbonyl)pyrrolidine was obtained as a pale yellow oil (100 mg, 41%), containing two stereoisomers, presumably *via* epimerisation of (**13**). Attempts to crystallise this material were unsuccessful.

Acknowledgements

We thank the S.E.R.C. for a Research Studentship (to A. S.) and Lady Richards and her associates for n.m.r. spectra.

References

1 K. R. Lawson, A Singleton, and G. H. Whitham, preceding paper.
2 P. Gosselin, S. Masson, and A. Thullier, *Tetrahedron Lett.*, 1978, 2715; A. Thullier, P. Gosselin, and S. Masson, *ibid.*, 1980, **21**, 2421.
3 P. Beslin, D. Lagain, J. Vialle, and C. Minot, *Tetrahedron*, 1981, **37**, 3839.
4 K. Alder and W. Günzl, *Chem. Ber.*, 1960, **93**, 809.
5 I. Fleming, 'Frontier Orbitals and Organic Chemical Reactions,' Interscience, London, 1976.
6 S. Scheibye, B. S. Pedersen, and S-O. Lawesson, *Bull. Soc. Chim. Belg.*, 1978, **83**, 229; B. S. Pedersen, S. Scheibye, N. H. Nilsson, and S-O. Lawesson, *ibid*, p. 223; B. S. Pedersen, S. Scheibye, K. Clausen, and S-O. Lawesson, *ibid.*, p. 293.
7 Y. Tamaru, T. Harada, and Z. Yoshida, *J. Am. Chem. Soc.*, 1980, **102**, 2392.

Received 9th September 1983; *Paper* 3/1575