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ADDITION REACTIONS OF SOME SIMPLE THIOALDEHYDES

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Abstract - When generated at 100 °C, aliphatic and aromatic thioaldehydes without electronic bias are shown to undergo addition reactions to both aliphatic and aromatic 1,3-dienes. The reaction is shown to have application in an intramolecular example.

INTRODUCTION

Early attempts to prepare thioaldehydes invariably led to the isolation of oligomeric and polymeric species.[1] These often had the desired empirical formula, strongly suggesting that the elusive monomeric thioaldehydes were indeed being formed, but were not stable under the reaction and isolation conditions. It was not until 1960 that the first stable, monomeric compound containing the thioformyl group was reported.[2] The significant feature which conferred stability upon this thioaldehyde was the conjugation of the carbon-sulphur double bond with an electron-rich pyrrole ring. This stabilisation by an electron-rich centre was soon reproduced in other systems, and so now several such thioaldehydes are known.[3]

Thioaldehydes without this electronic stabilisation have only been isolated in a few cases. Thiobenzaldehyde and thioacrolein have been isolated at liquid nitrogen temperatures,[4,5] and thioformaldehyde[6] and thioacrolein[7] in the gas phase at above 380 °C. Recently the preparation of 2,4,6-tri-*t*-butylthiobenzaldehyde as a stable, purple solid under ambient conditions was reported,[8] which represents a new class of thioaldehydes stabilised only by steric crowding of the thiocarbonyl group. In none of these cases were the reactions of the prepared thioaldehydes investigated.

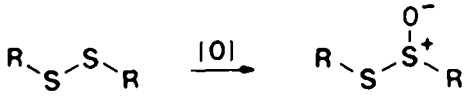
Our interest in the generation and reactivity of thioaldehydes not stabilised by electronic factors derives from their recurrence in the literature as proposed intermediates despite the scarcity of experimental evidence concerning the reactions of their thioformyl group. Electron-deficient thioaldehydes have unequivocably been generated and their Diels-Alder reactions with electron-rich 1,3-dienes described.[9] Other reports mention the isolation of products which strongly suggest the intermediacy of a thioaldehyde,[10] and the nature of the isolated product provides information on the thioaldehyde's reactivity.

We have shown previously[11] that thiobenzaldehyde and thioacetaldehyde may be generated by thermolysis of the appropriate thiosulphinate, and that such thioaldehydes can be trapped with

a variety of reagents. Here, the reactivities of simple thioaldehydes are further presented.

RESULTS AND DISCUSSION

Symmetrical alkyl thiosulphinates are readily prepared by oxidation of the corresponding disulphide (scheme 1).[12] Thus, S-ethyl ethanethiosulphinate (1) was prepared from diethyl disulphide.[13]

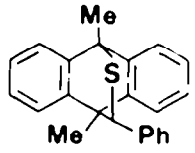


(1) R = Et

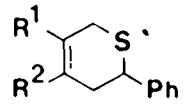
Scheme 1

[The boiling point for thiosulphinate (1) observed (47 °C at 0.5 mmHg) was below that in the literature[13] (67 °C at 0.5 mmHg), which instead corresponds to the boiling point of S-ethyl ethanethiosulphonate[14] (56 °C at 0.2 mmHg).] On the other hand, it was found more convenient to prepare S-benzyl phenylmethanethiosulphinate (2) by oxidation of benzyl mercaptan.[15]

Thiobenzaldehyde (3), generated by the thermolysis[16] of thiosulphinate (2) in toluene, was trapped efficiently by anthracene (scheme 2), 9,10-dimethylanthracene and 2,3-dimethylbutadiene, giving adducts (4), (5) and (6) respectively. Benzene was found to be



(5)



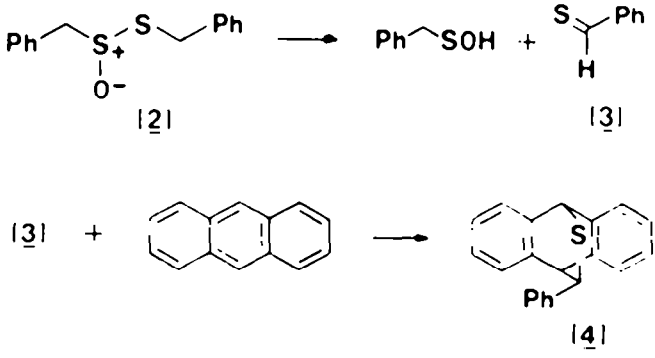
(6) $R^1 = R^2 = Me$

(7) $R^1 = H$, $R^2 = OEt$

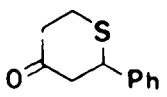
(8) $R^1 = OEt$, $R^2 = H$

as good a solvent as toluene, but dimethylformamide reduced the yield of adduct (4) from 97% to 33%. 9,10-Diacetoxyanthracene, which had to be used in dimethylformamide, gave no adduct when thiobenzaldehyde (3) was generated in its presence, and was recovered unchanged. Reaction times greater than one hour reduced the yield of adduct (4) as did using only one equivalent of the diene trap.

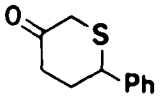
When the unsymmetrical 2-ethoxybutadiene was used as trap, dihydrothiopyrans (7) and (8) were formed, which were hydrolysed to thianones (9) and (10). The yield of thianones (9) and (10) based on thiosulphinate (2) was 31% and



Scheme 2



[9]



[10]

13% respectively. As expected, the regioselectivity observed in this reaction of thiobenzaldehyde is poorer than when strongly electron-deficient thioaldehydes, which have a more effectively polarised thiocarbonyl system, react with the same diene at room temperature.[9] The regioselectivity is also in the opposite sense to these cases. Nevertheless, the thermolysis reaction does produce the desired adducts of thiobenzaldehyde unlike the photochemical reaction,[9] and suggests that the difference in temperatures may be crucial to making thiobenzaldehyde usefully reactive.

When the thermolysis of thiosulphinate (2) was performed in toluene in the absence of a trap, a blue colour was observed and the visible spectrum of the solution (figure) corresponds closely to the spectrum of thiobenzaldehyde at 77 K obtained by the pyrolysis of benzyl allyl sulphide.[5] This supports the reaction pathway of scheme 2, where thiobenzaldehyde (3) is formed as a discrete species which then reacts with the diene trap.

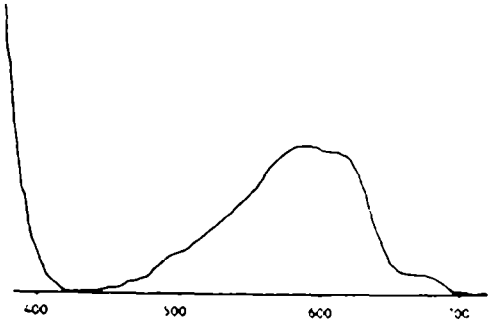
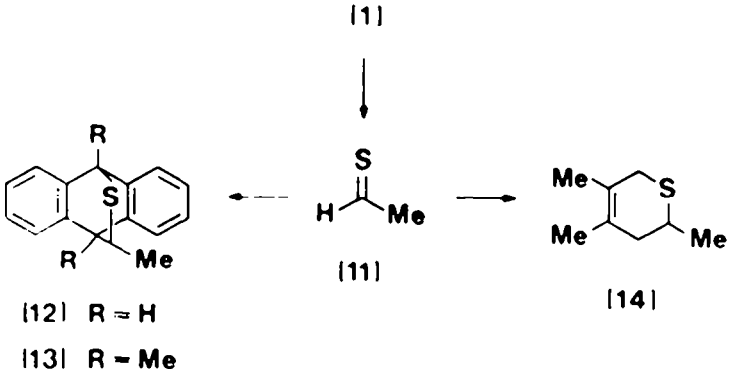


Figure. Visible spectrum of thiobenzaldehyde (3) generated by thermolysis of thiosulphinate (2) in toluene. (Wavelengths in nm)

In a similar manner, thioacetaldehyde (11) was generated from thiosulphinate (1), and adducts (12), (13) and (14) isolated when anthracene, 9,10-dimethylanthracene and 2,3-dimethylbutadiene, respectively, were used as traps (scheme 3).

The anthracene adduct of thiobenzaldehyde (4) itself proved to be an efficient and clean source of thiobenzaldehyde (3). Heating adduct (4) in toluene in the presence of 2,3-dimethylbutadiene cleanly gave anthracene and dihydrothiopyran (6) (scheme 4). However, the anthracene adduct of thioacetaldehyde (12) was far more resistant to thermolysis. Adduct (13) was expected to be more labile to heat, since the retro Diels-Alder reaction would eliminate the steric interaction



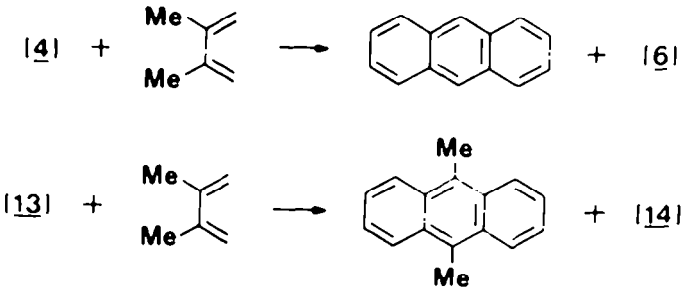
[12] R = H

[13] R = Me

[11]

[14]

Scheme 3

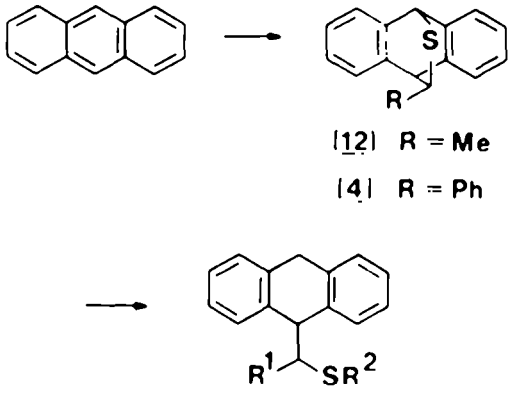


Scheme 4

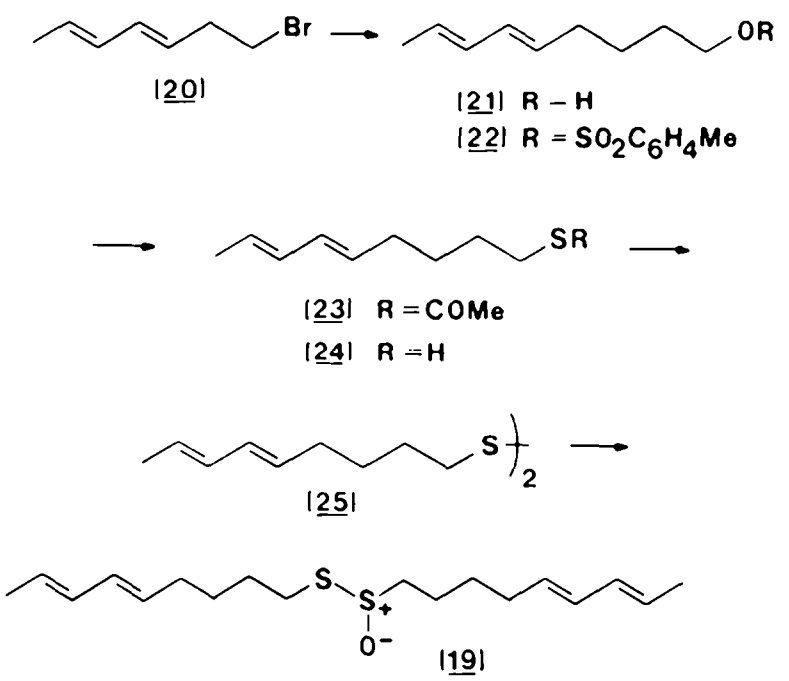
between the thioacetaldehyde methyl group and the anthracene methyl group, which is not present in adduct (12), and this was borne out in practice (scheme 4). A similar strategy of dienophile protection by 9,10-dimethylanthracene has been employed in the reactions of nitrosocarbonyl compounds.[17]

Adducts between thioaldehydes and anthracenes, such as (4), (5), (12) and (13), have a carbon-sulphur bond which is doubly benzylic. Reductive cleavage of such a bond after adduct formation provides a novel entry into 9-substituted 9,10-dihydroanthracenes from the parent anthracene (scheme 5). The reduction was found to proceed smoothly and in high yield with sodium in liquid ammonia[18] in the case of thioacetaldehyde adduct (12), giving thiol (15), which was acetylated to derivative (16). However, thiobenzaldehyde adduct (4) gave thiol (17), which was characterised as acetyl derivative (18), only when the reduction temperature was lowered to -78 °C. In refluxing ammonia, only 9,10-dihydroanthracene was recovered: a triply benzylic carbon-carbon bond being cleaved in addition to the carbon-sulphur bond.

An intramolecular Diels-Alder trapping of an aliphatic thioaldehyde



Scheme 5

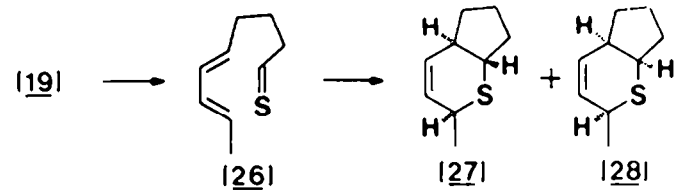


(20) (21) R – H (22) R = $SO_2C_6H_4Me$ (23) R = COMe (24) R = H (25) (19)

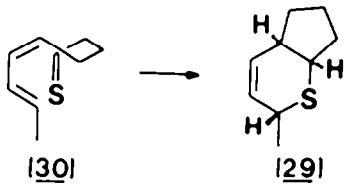
Scheme 6

was performed successfully. Thiosulphinate (19) was prepared from bromodiene (20) (scheme 6). The method of Descoins and Henrick[19] was used to prepare bromodiene (20) and 300 MHz proton n.m.r. spectroscopy showed a ratio of 85:15 of (3E, 5E) to (3Z, 5E) isomers, which remained constant in the subsequent transformations. The bromodiene (20) was converted into the Grignard reagent, which was treated with ethylene oxide to give alcohol (21) on work up. Tosylation of alcohol (21) was best carried out by forming the sodium salt in tetrahydrofuran, followed by reaction with toluene-4-sulphonyl chloride[20] to give derivative (22). This was superior to the alternative procedure of stirring alcohol (21) with toluene-4-sulphonyl chloride in pyridine.[21] Displacement of the tosylate group with potassium thioacetate[22] in dimethylformamide gave thioacetate (23) in excellent yield. Anhydrous potassium thioacetate was prepared from thioacetic acid and potassium hydride in tetrahydrofuran. This procedure was more satisfactory than displacement of the tosylate group with thiourea in dimethylsulphoxide followed by alkaline hydrolysis of the S-alkyl thiouronium salt.[23] Thioacetate (23) was hydrolysed to thiol (24), which was oxidised to the disulphide (25). Disulphide (25) was oxidised with one equivalent of m-chloroperbenzoic acid to thiosulphinate (19), which was not purified, but showed an absorption band in the infra-red spectrum at 1075 cm^{-1}, indicative of thiosulphinate S=O stretch. The crude thiosulphinate (19) was heated in toluene in order to produce thioaldehyde (26), and thiabicyclononenes (27) and (28) were isolated in 40% yield, based on disulphide (25), in a ratio of 1:1 (scheme 7). The yield takes into account disulphide (25) containing 15% of (5Z, 7E) isomers.

Bicyclononenes (27) and (28) could only be separated by capillary gas liquid chromatography, which also showed the presence of 5% of a third, so far unidentified component. This may be an isomer such as bicyclononene



Scheme 7

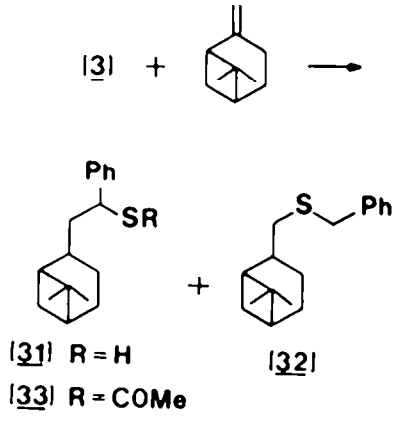


Scheme 8

(29), derived from the (5Z, 7E) thioaldehyde (30) (scheme 8).

The successful intramolecular trapping of a thioaldehyde shows that this is a feasible ring-forming reaction.

Thiobenzaldehyde (3), generated by the thermolysis of thiosulphinate (2), gave a mixture of adducts (31) and (32) with β-pinene, in a ratio of 2:1 (scheme 9). The two products arise from different orientations of thiobenzaldehyde addition with respect to β-pinene. Diastereomer mixture (31) gave an acetyl derivative mixture (33) upon acetylation while sulphide (32) was recovered unchanged after the same treatment.



Scheme 9

An attempted 'ene' reaction with cyclododecene only gave back the olefin in quantitative yield.

CONCLUSION

The success encountered in trapping thiobenzaldehyde (3) and thioacetaldehyde (11) from the thermolyses of thiosulphinates (2) and (1) with both aromatic and aliphatic dienes in high yields suggests that these reactions could be exploited with a variety of structural and electronic elements in the diene and dienophile not used previously.

The reversible trapping of thioaldehydes on aromatic dienes represents a valuable synthetic supplement to the straightforward thermolyses of thiosulphinates. The regeneration of the thioaldehyde takes place with the formation of the relatively inert anthracene or 9,10-dimethylanthracene as the only other product, avoiding sulphenic acids and water which are produced in thiosulphinate thermolysis, and avoiding potentially destructive irradiation intrinsic to the photochemical methods of preparation.

These results, in conjunction with the successful intramolecular trapping of a thioaldehyde with a 1,3-diene system and the preliminary investigation into the 'ene' reaction, contribute towards exploring the limits of thioaldehyde reactivity and towards establishing simple thioaldehydes as potentially useful synthetic intermediates in carbon-carbon bond forming reactions.

EXPERIMENTAL

Melting points were recorded on a Kofler hot stage apparatus and are uncorrected. Ultra violet-visible spectra were measured on a Perkin-Elmer 555 spectrophotometer. N.m.r. spectra were obtained on a Bruker WH 300 spectrometer and chemical shifts (δ) are presented in p.p.m. downfield from TMS. Infra-red spectra were measured on a Perkin-Elmer 297 spectrophotometer. Mass spectra were recorded using a VG Micromass ZAB 1F or 16F spectrometer.

Preparation of 9,10-Dihydro-9,10-(2-phenyl-1-thiaethano)anthracene (4). S-Benzyl phenylmethanethiosulphinate (2) (262 mg; 1.00 mmol) and anthracene (1.78 g; 10.0 mmol) in dry toluene (15 ml) were stirred and heated at 98-100 °C under dry nitrogen for 1.0 h. Cooling the solution to room temperature precipitated out anthracene (1.16 g; 65%) as white flakes, which was filtered off. The filtrate was evaporated and the solid obtained separated by flash chromatography[24] (70% 40-60 pet ether, 30% benzene), giving anthracene (268 mg; 15%) as a white solid and adduct (4) (580 mg; 97%) as a white solid. Recrystallisation of the adduct (4) (toluene-hexane) gave white prisms, m.p. 160-163 °C (decomp.), (Found: C, 84.20; H, 5.40; S, 10.90. $C_{21}H_{16}S$ requires C, 83.96; H, 5.37; S, 10.67%), $\lambda_{max}(CH_3CN)$ 212 (36000) and 279 (3000) nm, ν_{max}(KBr) 3025 and 1450 cm^{-1}, $\delta(CD_3SOCD_3)$ 4.57 and 4.69 (2 x 1H, 2 x d, J 2.5 Hz, Ar_2CHCH + $Ar_2CHCH(Ph)S$), 5.59 (1H, s, Ar_2CHS), 6.77-6.88 (3H, m, ArH), 7.05 (1H, m, ArH), 7.10-7.29 (6H, m, ArH), 7.42 (1H, m, ArH) and 7.48-7.55 (2H, m, ArH), and m/e 178 (100) and 121 (29).

Preparation of 9,10-Dihydro-9,10-dimethyl-9,10-(2-phenyl-1-thiaethano)-anthracene (5). S-Benzyl phenylmethanethiosulphinate (2) (257 mg; 0.98 mmol) and 9,10-dimethylanthracene[25] (2.02 g; 9.8 mmol) in dry toluene (15 ml) were stirred and heated at 96-99 °C under dry nitrogen for 20 h. Cooling the solution to room temperature precipitated 9,10-dimethylanthracene (1.11 g; 55%) as yellow crystals, which was filtered off. The filtrate was evaporated and the solid obtained separated by flash chromatography (70% 40-60 pet ether, 30% benzene), giving 9,10-dimethylanthracene (509 mg; 25%) and adduct (5) (557 mg; 87%). Recrystallisation of the adduct (toluene-hexane) gave pale green needles, m.p. 140-150 °C (decomp.), (Found: C, 84.11; H, 6.42; S, 9.56. $C_{23}H_{20}S$ requires C, 84.10; H, 6.14; S, 9.76%), $\lambda_{max}(CH_3CN)$ 280 (2900) nm, ν_{max}(KBr) 3065-2900 and 1450 cm^{-1}, $\delta(CD_2Cl_2)$ 1.74 and 2.33 (2 x 3H, 2 x s, 2 x CH_3), 4.24 (1H, s, PhCHS), 6.55 (2H, br s, ArH) and 7.02-7.50 (11H, m, ArH), and m/e 206 (100), 191 (32) and 121 (29).

Preparation of 3,6-Dihydro-4,5-dimethyl-2-phenyl-2H-thiopyran (6). S-Benzyl phenylmethanethiosulphinate (2) (262 mg; 1.00 mmol) and 2,3-dimethylbutadiene (1.64 g; 20.0 mmol) in dry toluene (15 ml) were sealed in a tube and stirred and heated at 96-99 °C for 20 h. Evaporation and flash chromatography (70% 40-60 pet ether, 30% benzene) gave thiopyran (6) (385 mg; 95%) as a colourless oil, b.p. 130-135 °C at 0.4 mmHg (Kugelrohr), (Found: C, 76.45; H, 7.80; S, 15.54. $C_{13}H_{16}S$ requires C, 76.41; H, 7.89; S, 15.69%), ν_{max}(film) 3100-2820, 1500 and 1450 cm^{-1} $\delta(CDCl_3)$ 1.73 and 1.78 (2 x 3H, 2 x br s, $CH_3C{=}CCH_3$), 2.40-2.49 and 2.53-2.65 (2 x 1H, 2 x m, $PhCHCH_2$), 2.93 and 3.48 (2 x 1H, 2 x m, SCH_2C-), 3.98 (1H, dd, J 6, 9 Hz, PhCHS) and 7.25-7.38 (5H, m, ArH), and m/e 204 (60, M^+) and 122 (100).

Preparation of Thianones (9) and (10). S-Benzyl phenylmethanethiosulphinate (2) (524 mg; 2.00 mmol) and 2-ethoxybutadiene[26] (3.92 g; 40.0 mmol) in dry toluene (30 ml) were stirred and heated at 98-101 °C in a sealed tube for 1.0 h. Evaporation gave a pale yellow oil which was dissolved in THF (20 ml) and 2.0 M hydrochloric acid (10 ml) added. The mixture was refluxed for 10 min, diluted with water (50 ml) and extracted into ether (3 x 100 ml). The combined extracts were washed with water (2 x 100 ml) and saturated brine (50 ml), dried (Na_2SO_4) and evaporated, giving a yellow oil. Flash chromatography (dichloromethane) gave a 7:3 mixture of 2-phenylthian-4-one (9)[27] and 6-phenylthian-3-one (10) (338 mg; 44%) as a colourless oil, $\nu_{max}(CHCl_3)$ 1710 and 700 cm^{-1}, $\delta(CD_2Cl_2)$ 2.55-3.12 5.7H, m), 3.67 (0.3H, d, J 13 Hz, one of $COCH_2S$), 4.24 (0.7H, dd, J 11.4, 3.4 Hz, $COCH_2CH(Ph)S$), 4.35 (0.3H, dd, J 10.6, 3.2 Hz, $COCH_2CH_2CH(Ph)S$) and 7.26-7.43 (5H, m, ArH), and m/e 192 (41, M^+) and 104 (100). Analytical gas chromatography (10% OV 17 column; 3.5 mm internal diameter; 1.5 m length; 200 °C) showed two peaks, ratio 72:28 in order of elution.

Thermolysis of S-Benzyl Phenylmethanethiosulphinate without a Trap. S-Benzyl phenylmethanethiosulphinate (2) (262 mg; 1.00 mmol) in dry toluene (15 ml) was heated at 98-100 °C under dry nitrogen. After 5 min, a portion of the solution (1.0 ml) was withdrawn, diluted three-fold with toluene and the u.v.-visible spectrum showed λ_{max} 580-590 and 610 (shoulder) nm.

Preparation of 9,10-Dihydro-9,10-(2-methyl-1-thiaethano)anthracene (12). 77% S-Ethyl ethanethiosulphinate (1)[13] (695 mg; 3.9 mmol) and anthracene (8.9 g; 50 mmol) in dry toluene (75 ml) were sealed in a tube and stirred and heated at 97 °C for 14 h. Cooling precipitated anthracene (6.37 g; 71%) as white flakes, which was filtered off. Evaporation of the filtrate and flash chromatography (70% 40-60 pet

ether, 30% benzene) gave anthracene (1.36 g; 15%) and adduct (12) (1.53 g; 82%) as a pale yellow solid. Recrystallisation of adduct (12) (toluene-hexane) gave white crystals, m.p. 169-171 °C, (Found: C, 79.96; H, 5.75; S, 13.20. $C_{16}H_{14}S$ requires C, 80.63; H, 5.92; S, 13.45%), λ_{max}(CH_3CN) 225 (8200) and 278 (2700) nm, ν_{max}(KBr) 3070-2860, 1470 and 1455 cm^{-1}, δ(CD_3COCD_3) 1.11 (3H d, J 6 Hz, CH_3CH), 3.44 (1H, qd, J 6, 3 Hz, CH_3CHS), 4.54 (1H, d, J 3 Hz, Ar_2CHCH), 5.25 (1H, s, Ar_2CHS), 7.10-7.23 (4H, m, ArH) and 7.32-7.43 (4H, m, ArH), and m/e 238 (5, M^+) and 178 (100).

Preparation of 9,10-Dihydro-9,10-dimethyl-9,10-(2-methyl-1-thiaethano)anthracene (13).
94% S-Ethyl ethanethiosulphinate (1) (231 mg; 1.57 mmol) and 9,10-dimethylanthracene (3.09 g; 15.0 mmol) in dry toluene (25 ml) were sealed in a tube and stirred and heated at 99-101 °C for 1.0 h. Cooling precipitated 9,10-dimethylanthracene (1.11 g; 36%) as yellow prisms, which was filtered off. The filtrate was evaporated and the solid residue separated by flash chromatography (70% 40-60 pet ether, 30% benzene), giving 9,10-dimethylanthracene (1.24 g; 40%) as a yellow solid and adduct (13) (632 mg; 78%) as a pale yellow solid, m.p. 128-133 °C (decomp.), (Found: C, 81.40; H, 7.05; S, 11.70. $C_{18}H_{18}S$ requires C, 81.15; H, 6.81; S, 12.04%), λ_{max}(CH_3CN) 278 (2300) nm, νmax(KBr) 3075-2895, 1455, 790, 765, 740, 710, 655 and 625 cm^{-1}, δ(CD_2Cl_2) 0.98 (3H, d, J 6.6 Hz, CH_3CH), 2.04 and 2.21 (2 x 3H, 2 x s, 2 x $ArCCH_3$), 3.24 (1H, q, J 6.6 Hz CH_3CHS) and 7.16-7.43 (8H, m, ArH), and m/e 267 (15, M+1$^+$), 207 (100), 206 (44) and 193 (24). All attempts at recrystallisation gave crystals of lower m.p.

Preparation of 3,6-Dihydro-2,4,5-trimethyl-2H-thiopyran (14).
77% S-Ethyl ethanethiosulphinate (1) (181 mg; 1.0 mmol) and 2,3-dimethylbutadiene (1.64 g; 20.0 mmol) in dry toluene (10 ml) were sealed in a tube and stirred and heated at 95-97 °C for 20 h. Evaporation and flash chromatography (90% 40-60 pet ether, 10% benzene) gave thiopyran (14) (235 mg; 83%) as a mobile, colourless oil, b.p. 70-87 °C at 17 mmHg (Kugelrohr), (Found: C, 67.74; H, 9.91; S, 22.64. $C_8H_{14}S$ requires C, 67.54; H, 9.92; S, 22.54%), ν_{max}(film) 2960-2820 and 1450 cm^{-1}, δ($CDCl_3$) 1.27 (3H, d, J 7 Hz, CH_3CH), 1.63 and 1.69 (2 x 3H, 2 x br s, $CH_3C{=}CCH_3$), 1.93-2.06 and 2.17-2.26 (2 x 1H, 2 x m, CH_3CHCH_2), 2.78-2.95 (2H, m, one of $=CCH_2S$ + CH_3CHS) and 3.33 (1H, m, one of $=CCH_2S$), and m/e 142 (100, M^+).

Heating 9,10-Dihydro-9,10-(2-phenyl-1-thiaethano)anthracene (4).
Adduct (4) (300 mg; 1.00 mmol) and 2,3-dimethylbutadiene (840 mg; 10.2 mmol) in dry toluene (10 ml) were sealed in a tube and stirred and heated at 98-99 °C for 1.0 h. The solution was evaporated and the residue separated by flash chromatography (80% 40-60 pet ether, 20% benzene), giving anthracene (165 mg; 92%) and thiopyran (6) (188 mg; 92%).

Heating 9,10-Dihydro-9,10-dimethyl-9,10-(2-methyl-1-thiaethano)anthracene (13).
Adduct (13) (266 mg; 1.00 mmol) and 2,3-dimethylbutadiene (830 mg; 10.1 mmol) in dry toluene (10 ml) were sealed in a tube and stirred and heated at 129-131 °C for 24 h. The solution was evaporated and the residue separated by flash chromatography (90% 40-60 pet ether, 10% benzene), giving 9,10-dimethylanthracene (142 mg; 69%) as a green-yellow solid and thiopyran (14) (69 mg; 49%) as a colourless oil.

Reduction of 9,10-Dihydro-9,10-(2-methyl-1-thiaethano)anthracene (12).
Adduct (12) (119 mg; 0.50 mmol) was stirred in liquid ammonia (25 ml) at -33 °C under argon and sodium added portionwise until the solution remained blue. Methanol (3.0 ml) was added, decolourising the solution which was then evaporated. The residue was dissolved in water (20 ml) and ether (40 ml), the aqueous phase extracted into ether (2 x 40 ml) and the combined ethereal solutions dried (Na_2SO_4) and evaporated, giving a pale yellow oil. Chromatography (SiO_2, 70% pet ether, 30% benzene) gave 1-(9,10-dihydro-9-anthryl)ethanethiol (15) (99 mg; 84%) as a colourless oil, ν_{max}(film) 3070-2820, 2570, 1480 and 1450 cm^{-1}, δ(CD_2Cl_2) 1.27 (3H, d, J 7 Hz, CH_3CH), 1.43 (1H, d, J 6 Hz, SH), 3.27 (1H, m, SCH), 3.85 (1H, d, J 18 Hz, one of Ar_2CH_2), 3.93 (1H, d, J 7 Hz, Ar_2CHCH), 4.25 (1H, d, J 18 Hz, one of Ar_2CH_2) and 7.23-7.42 (7H, m, ArH), and m/e 179 (100).

Acetylation of 1-(9,10-Dihydro-9-anthryl)ethanethiol (15).
Thiol (15) (80 mg; 0.33 mmol) in dichloromethane (6 ml) was stirred at 27 °C with acetyl chloride (0.2 ml; 2.8 mmol) and pyridine (1.0 ml) added. After 20 min, water (5 ml) was added, the aqueous phase acidified to pH 1 with 2 M hydrochloric acid, and the organic layer separated. The aqueous phase was extracted with dichloromethane (2 x 10 ml) and the combined organic solutions dried (Na_2SO_4) and evaporated. Flash chromatography (20% 40-60 pet ether, 80% benzene) gave S-[1-(9,10-dihydro-9-anthryl)ethyl] thioacetate (16) (52 mg; 55%) as a colourless oil, ν_{max} ($CHCl_3$) 3020, 1690 (C=O) and 1455 cm^{-1}, δ(CD_2Cl_2) 1.13 (3H, d, J 7 Hz, CH_3CH), 2.21 (3H, s, CH_3CO), 3.81-3.93 (2H, m, one of Ar_2CH_2 + CH_3CHS), 4.13 (1H, d, J 6 Hz, Ar_2CHCH), 4.25 (1H, d, J 18 Hz, one of Ar_2CH_2) and 7.19-7.42 (8H, m, ArH), and m/e 283 (11, M+1$^+$), 207 (17) and 179 (100).

Reduction of 9,10-Dihydro-9,10-(2-phenyl-1-thiaethano)anthracene (4).
Adduct (4) (151 mg; 0.50 mmol) in liquid ammonia (20 ml) was cooled to -78 °C under argon, and while stirring, sodium was added portionwise until the solution remained blue. The solution was then stirred for 3 h at -78 °C, methanol (2.0 ml) added discharging the

blue colour, and the mixture evaporated. The residue was dissolved in water (150 ml) and ether (150 ml), the aqueous phase separated and extracted with ether (2 x 100 ml) and the combined ethereal solutions dried (Na_2SO_4) and evaporated. Flash chromatography (75% 40-60 pet ether, 25% benzene) gave (9,10-dihydro-9-anthryl)(phenyl)-methanethiol (17) (101 mg; 67%) as a colourless oil, ν_{max}($CHCl_3$) 3020, 1485 and 1455 cm^{-1}, δ(CD_2Cl_2) 1.98 (1H, d, J 5 Hz, SH), 3.60 and 3.70 (2 x 1H, 2 x d, J 18 Hz, Ar_2CH_2), 4.28 (1H, dd, J 7, 5 Hz, CHCHSH), 4.35 (1H, d, J 7 Hz, Ar_2CHCH) and 6.90-7.47 (13H, m, ArH), and m/e 268 (3) and 178 (100).

Acetylation of (9,10-Dihydro-9-anthryl)-(phenyl)methanethiol (17). Thiol (17) (76 mg; 0.25 mmol) in dry dichloromethane (10 ml) was stirred at 22 °C with acetyl chloride (0.2 ml; 2.8 mmol) and pyridine (0.3 ml) added. After 15 min, water (5 ml) was added, the aqueous phase acidified to pH 1 with 2 M hydrochloric acid, and the organic layer separated. The aqueous phase was extracted with dichloro-methane (2 x 10 ml) and the combined organic solutions washed with saturated brine (5 ml), dried (Na_2SO_4) and evaporated. Flash chromatography (40% 40-60 pet ether, 60% benzene) gave S-α-(9,10-dihydro-9-anthryl)benzyl thioacetate (18) (80 mg; 92%) as a white solid. Recrystallisation (toluene-hexane) gave white crystals, m.p. 105-108 °C, (Found: C, 79.98; H, 5.89; S, 9.44. $C_{23}H_{20}OS$ requires C, 80.19; H, 5.85; S, 9.31%), ν_{max}($CHCl_3$) 3020, 1690 (C=O) and 1455 cm^{-1}, δ(CD_2Cl_2) 2.37 (3H, s, CH_3CO), 2.96 and 3.49 (2 x 1H, 2 x d, J 19 Hz, Ar_2CH_2), 4.43 and 4.87 (2 x 1H, 2 x d, J 6 Hz, PhCHS + Ar_2CHCH), 6.55 (2H, m, ArH), 6.99-7.30 (10H, m, ArH) and 7.50 (1H, m, ArH), and m/e 179 (100).

Preparation of 5,7-Nonadien-1-ol (21). Freshly distilled 1-bromo-5,7-hepta-diene (20) (9.71 g; 55.5 mmol) in dry ether (50 ml) was added under dry nitrogen to magnesium turnings (1.35 g; 55.6 mmol) in dry ether (50 ml) over 15 min, maintaining gentle refluxing. The mixture was refluxed for 1 h, cooled to 0 °C, and ethylene oxide (11 ml; 9.9 g; 225 mmol) in dry ether (20 ml) at 0 °C added over 10 min. The solution was heated, and solvent distilled off reducing the volume of the solution (to 80 ml) over 20 min. Dry benzene (100 ml) was added and the mixture refluxed gently. After 45 min, the solution had set to a clear gel, so it was allowed to stand at room temperature under dry nitrogen for 14 h. Adding water (3 ml) turned the gel fluid and ammonium chloride (10 g; 187 mmol) in water (50 ml) was added too, followed by 2 M hydrochloric acid to dissolve the precipitate. The aqueous phase was separated, extracted into ether (2 x 100 ml) and the combined organic solutions dried (Na_2SO_4) and evaporated, giving a pale yellow oil. Distillation under reduced pressure gave a colourless oil, b.p. 48-60 °C at 0.008 mmHg, which was purified by flash chromatography (CH_2Cl_2 followed by 90% CH_2Cl_2, 10% EtOAc), giving 5,7-nonadien-1-ol (21)[28] (1.33 g; 17%) as a colourless oil, ν_{max}(film) 3340 br, 3020, 2930, 2860, 1455, 1440, 1060 and 985 cm^{-1} and m/e 140 (7, M^+), 139 (21), 123 (24), 111 (33), 99 (44), 85 (56), 83 (71), 81 (74), 71 (59), 67 (46), 55 (84), 43 (100) and 41 (68). (E, E)-5,7-Nonadien-1-ol δ($CDCl_3$) 1.42-1.64 (5H, m, $-CCH_2CH_2CH_2CH_2OH$), 1.75 (3H, d, J 6 Hz, $CH_3C=$), 2.11 (2H, q, J 6 Hz, $-CHCH_2CH_2$), 3.66 (2H, t, J 6 Hz, CH_2CH_2OH), 5.58 (2H, m, CH-C-C-CH) and 5.93-6.09 (2H, m, -CH-CH-).

Preparation of 5,7-Nonadien-1-yl Toluene-4-sulphonate (22). 50% Sodium hydride dispersion in oil (530 mg; 11.04 mmol NaH) was washed under dry nitrogen with 40-60 pet ether (2 x 4 ml) and dry THF (20 ml) added. 5,7-Nonadien-1-ol (21) (1.27 g; 9.07 mmol) in dry THF (20 ml) was added, and the mixture stirred under dry nitrogen at 60 °C for 16 h. The suspension was cooled in a bath at -5 °C and toluene-4-sulphonyl chloride (1.90 g; 9.97 mmol) in dry THF (20 ml) added over 10 min. The mixture was stirred at 7-12 °C for 6 h, ether (50 ml) added, and the solution washed with ice-water (3 x 30 ml), dried (Na_2SO_4) and evaporated. The pale orange oil was separated by flash chromatography (50% 40-60 pet ether, 50% CH_2Cl_2 followed by 90% CH_2Cl_2, 10% EtOAc), giving toluene-4-sulphonyl chloride (92 mg; 5%) as white needles, 5,7-nona-dien-1-yl toluene-4-sulphonate (22) (1.74 g; 65%) as a colourless oil, (M^+ 294.1290. $C_{16}H_{22}O_3S$ requires 294.1290), ν_{max}(film) 3020, 2940, 2860, 1600, 1450, 1360, 1190, 1175, 1050, 980, 955 br, 930, 810, 730 and 660 cm^{-1}, and m/e 294 (3, M^+), 122 (51), 107 (24) 94 (100), 93 (64), 91 (59), 79 (91), 67 (12), 65 (19), 55 (16) and 41 (21); (E, E)-5,7-nonadien-1-yl toluene-4-sulphonate δ($CDCl_3$) 1.42 and 1.65 (2 x 2H, 2 x m, $-CCH_2CH_2CH_2CH_2O$), 1.74 (3H, d, J 6 Hz, $CH_3CH=$), 2.03 (2H, q, J 6 Hz, $=CHCH_2CH_2$), 2.48 (3H, s, CH_3Ar), 4.04 (2H, t, J 6 Hz, CH_2CH_2O), 5.45 (1H, m, $-CHCH_2CH_2$), 5.59 (1H, m, $CH_3CH=$), 5.91-6.05 (2H, m, -CH-CH-) and 7.58 (4H, 'ABq', ArH), and 5,7-nonadien-1-ol (21) (224 mg; 18%) as a colourless oil.

Preparation of S-(5,7-Nonadien-1-yl) Thioacetate (23). 5,7-Nonadien-1-yl toluene-4-sulphonate (22) (1.3 g; 4.4 mmol) and potassium thioacetate (1.0 g; 8.8 mmol) in dry DMF (15 ml) were stirred under nitrogen at 20-21 °C. After 20 h, water (100 ml) was added and the turbid white solution extracted into ether (3 x 100 ml). The combined organic solutions were washed with water (2 x 100 ml), dried (Na_2SO_4) and evaporated. The pale yellow oil was purified by flash chromatography (70% 40-60 pet ether, 30% CH_2Cl_2), giving S-(5,7-nonadien-1-yl) thioacetate (23) (840 mg; 95%) as a

mobile, colourless oil, (M^+ 198.1075. $C_{11}H_{18}OS$ requires 198.1078), ν_{max}(film) 3020, 2930, 2860, 1695 (C=O), 1355, 1135, 985, 730 and 625 cm^{-1}, and m/e 198 (12, M^+), 155 (42), 121 (17), 101 (44), 87 (54), 79 (35), 55 (24) and 43 (100); S-[(E, E)-5,7-nonadien-1-yl] thioacetate $\delta(CDCl_3)$ 1.40-1.62 (4H, m, $-CCH_2CH_2CH_2CH_2S$), 1.73 (3H, d, J 6 Hz, CH_3CH-), 2.08 (2H, q, J 6 Hz, $-CHCH_2CH_2$), 2.33 (3H, s, CH_3CO), 2.88 (2H, t, J 6 Hz, CH_2CH_2S), 5.56 (2H, m, CH=C-C-CH) and 6.00 (2H, m, -CH-CH-).

Hydrolysis of S-(5,7-Nonadien-1-yl) Thioacetate (23).

2.0 M Potassium hydroxide in methanol (5.5 ml; 11 mmol KOH) was added to S-(5,7-nonadien-1-yl) thioacetate (23) (1.01 g; 5.10 mmol) in methanol (5 ml) and the solution stirred under nitrogen at 19-21 °C for 16 h, cooled and 2.0 M hydrochloric acid (5.5 ml; 11 mmol HCl) added slowly, taking the pH to 1. Water (30 ml) was added and the mixture extracted into ether (3 x 40 ml), the combined extracts dried (Na_2SO_4) and evaporated. Flash chromatography (90% 40-60 pet ether, 10% benzene) gave 5,7-nonadiene-1-thiol (24) (559 mg; 70%) as a colourless oil, (M^+ 156.0973. $C_9H_{16}S$ requires 156.0973), ν_{max}(film) 3020, 2930, 2860, 1445 br and 985 cm^{-1}, and m/e 156 (26, M^+), 155 (100), 127 (26), 113 (11), 101 (44), 95 (27), 93 (24), 87 (41), 81 (58), 79 (44), 67 (36), 55 (39) and 41 (18); (E, E)-5,7-nonadiene-1-thiol $\delta(CDCl_3)$ 1.32-1.70 (5H, m, $-CCH_2CH_2CH_2-CH_2SH$), 1.74 (3H, d, J 6 Hz, CH_3CH-), 2.08 (2H, q, J 6 Hz, $-CHCH_2CH_2$), 2.55 (2H, q, J 6 Hz, CH_2CH_2SH), 5.58 (2H, m, CH=C-C-CH) and 6.02 (2H, m, -CH-CH-).

Preparation of Di-5,7-nonadien-1-yl Disulphide (25).

Thiol (24) (559 mg; 3.58 mmol) was added over 3 min to 96% sodium hydroxide (146 mg; 3.50 mmol) and potassium iodide (21 mg) in water (2 ml) cooled in an ice-water bath. A white precipitate fell out. Dioxan (1 ml) was added, the mixture warmed to 18 °C, and iodine (450 mg; 1.77 mmol) added with stirring. The precipitate dissolved, an oil separated and after 15 min, a little thiol (24) in dioxan (0.5 ml) was added to discharge the colour of the solution. Water (20 ml) and ether (30 ml) were added, the aqueous phase separated, extracted with ether (2 x 30 ml) and the combined organic solutions dried (Na_2SO_4) and evaporated. Flash chromatography (90% 40-60 pet ether, 10% CH_2Cl_2) gave di-5,7-nonadien-1-yl disulphide (25) (285 mg; 51%) as a colourless oil, ν_{max}(film) 3020, 2930, 2860, 1445 br and 985 cm^{-1}, and m/e 328 (6, $M+NH_3+1^+$), 310 (1, M^+) and 155 (100); (E, E)-5,7-nonadien-1-yl disulphides $\delta(CDCl_3)$ 1.51 (2H, m, two of $-CCH_2CH_2CH_2CH_2S$), 1.65-1.81 (5H, m, CH_3CH- + two of $-CCH_2CH_2CH_2CH_2S$), 2.10 (2H, q, J 6 Hz, $-CHCH_2CH_2$), 2.69 (2H, m, CH_2S), 5.48-5.74 (2H, m, CH=C-C-CH) and 5.95-6.08 (2H, m, -CH-CH-).

Preparation and Thermolysis of S-(5,7-Nonadien-1-yl) 5,7-Nonadiene-1-thiosulphinate (19).

Disulphide (25) (112 mg; 0.36 mmol) in dichloromethane (5 ml) was cooled to -20 °C under dry nitrogen and while stirring, 80-90% m-chloroperbenzoic acid (73 mg; 0.34-0.38 mmol) in dichloromethane (2 ml) was added over 15 min, causing a white solid to precipitate. The mixture was stirred at -20 °C for a further 15 min, at -10 °C for 20 min, and at 19 °C for 30 min, the solid dissolving. 2% Sodium hydrogen carbonate solution (2 ml) was added and the mixture stirred vigorously for 10 min. The aqueous layer was separated, extracted into dichloromethane (2 ml) and the combined organic solutions stirred vigorously with 0.5% sodium hydrogen carbonate solution (2 ml) for 10 min. The aqueous layer was again separated and extracted into dichloromethane (2 ml). The combined organic solutions were dried (Na_2SO_4) and evaporated, giving a colourless oil (124 mg), $\nu_{max}(CH_2Cl_2)$ 1075 and 990 cm^{-1}, which was dissolved in dry toluene (6 ml) and sealed in a tube. Stirring and heating at 96-97 °C for 45 min, cooling and evaporation gave a yellow liquid. Chromatography (90% 40-60 pet ether, 10% CH_2Cl_2) gave 3-methyl-2-thiabicyclo[4.3.0]non-4-enes (27) and (28) (38 mg; 40%) as a colourless oil, $\nu_{max}(CH_2Cl_2)$ 3020, 2970, 2880 and 1450 cm^{-1}, and $\delta(CDCl_3)$ 1.35 and 1.43 (3H, 2 x d, J 7, 7 Hz, CH_3CH), 1.55-1.70 (2H, m, two of $CH_2CH_2CH_2$), 1.73-2.17 (4H, m, four of $CH_2CH_2CH_2$), 2.45-2.59 (1H, m, -CCHCHS), 3.22-3.32 (1H, m, -CCHCHS), 3.38-3.56 (1H, m, -CCHS) and 5.62-5.83 (2H, m, CH=CH). Capillary gas liquid chromatography (S.G.E. Superox 0.1 vitreous silica capillary column; 0.33 mm internal diameter, 25 m length; 130→170 °C) showed three peaks: in order of elution, one bicyclononene m/e 154 (57, M^+), 139 (13), 125 (12), 121 (42), 118 (18), 105 (11), 97 (10), 94 (57), 79 (100) and 39 (36), other bicyclononene m/e 154 (100, M^+), 139 (45), 125 (93), 111 (42), 105 (23), 97 (49), 79 (76) and 39 (41), and impurity m/e 152 (100), 137 (19), 123 (66), 121 (37), 110 (34), 97 (27), 91 (73), 45 (45) and 39 (45).

β-Pinene 'Ene' Reaction.

S-Benzyl phenylmethanethiosulphinate (2) (263 mg; 1.00 mmol) and (1)-β-pinene (1.36 g; 10 mmol) in dry toluene (15 ml) was heated at 95-99 °C for 20 h under dry nitrogen, cooled and the solution evaporated. Flash chromatography (95% 40-60 pet ether, 5% benzene) gave (2-pinen-10-yl)(phenyl)methanethiol (31) (193 mg; 37%) as a colourless oil, (M^+ 258.1443. $C_{17}H_{22}S$ requires 258.1442), $\nu_{max}(CHCl_3)$ 3000-2840, 1495 and 1455 cm^{-1}, $\delta(CD_2Cl_2)$ 0.77 and 0.85 (3H, 2 x s, CH_3C), 0.98 and 1.18 (1H, 2 x d, J 8 Hz, SH), 1.28 (3H, 2 x s, CH_3C), 2.03-2.43 (7H, m), 2.51-2.72 (2H, m), 4.05-4.18 (1H, m, PhCHSH), 5.23 and 5.38 (1H, 2 x m, =CH) and 7.20-7.38 (5H, m, ArH), and m/e 258 (100, M^+), 189

(90) and 91 (78), and benzyl (2-pinen-10-yl) sulphide (32) (99 mg; 19%) as a colourless oil which turned pink on standing, (M^+ 258.1443. $C_{17}H_{22}S$ requires 258.1442), ν_{max}($CHCl_3$) 3000-2840, 1495 and 1455 cm^{-1}, δ(CD_2Cl_2) 0.88 (3H, s, CH_3), 1.18 (1H, d, J 8 Hz) 1.32 (3H, s, CH_3), 2.13 and 2.22 (2 x 1H, 2 x m), 2.28-2.33 (2H, m), 2.40-2.47 (1H, m), 2.98 (2H, m, $-CCH_2S$), 3.62 (2H, s, $PhCH_2S$), 5.38 (1H, m, -CH) and 7.20-7.33 (5H, m, ArH), and m/e 258 (5, M^+), 134 (40), 119 (50) and 91 (100)

Acetylation of (2-Pinen-10-yl)(phenyl)-methanethiol (31).
Thiol (31) (118 mg; 0.46 mmol) in pyridine (2 ml) was stirred with acetyl chloride (0.2 ml; 2.8 mmol) in dichloromethane (6 ml) at 27 °C for 15 min. Water (5 ml) was added, the aqueous phase acidified to pH 1 with 2 M hydrochloric acid and the organic layer separated. The aqueous phase was extracted with dichloromethane (2 x 10 ml) and the combined organic solutions dried (Na_2SO_4) and evaporated. Flash chromatography (70% 40-60 pet ether, 30% benzene) gave S-α-(2-pinen-10-yl)-benzyl thioacetate (33) (80 mg; 59%) as a colourless oil, ν_{max}($CHCl_3$) 3040-2840 and 1690 (C=O) cm^{-1}, δ($CDCl_3$) 0.67 and 0.76 (3H, 2 x s, CH_3CCH_3), 0.90 and 1.04 (1H, 2 x d, J 8 Hz), 1.24 (3H, s, CH_3CCH_3), 1.95-2.35 (9H, m, CH_3CO + aliphatic CH), 2.58-2.64 (2H, m), 4.64-4.74 (1H, m, PhCHS), 5.13 and 5.26 (1H, 2 x br s, -CH) and 7.18-7.33 (5H, m, ArH), and m/e 300 (1, M^+), 224 (69), 181 (65) and 123 (100).

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REFERENCES

1. A.Wagner and A.Schönberg, in 'Methoden der Organischen Chemie (Houben-Weyl),' Georg Thieme Verlag, Stuttgart, 1955, vol. IX, p. 695.
2. R.B.Woodward et al., J.Am.Chem.Soc., 1960, 82, 3800.
3. S.McKenzie and D.H.Reid, J.Chem.Soc. Chem.Commun., 1966, 401; J.G.Dingwall, D.H.Reid and K.Wade, J.Chem.Soc.(C), 1969, 913; S.McKenzie and D.H.Reid, J.Chem.Soc. (C), 1970, 145; R.K.Mackie, S.McKenzie, D.H.Reid and R.G.Webster, J.Chem.Soc.Perkin Trans.I, 1973, 657; J.Dabrowski and K.Kamieńska-Trela, Org.Mag.Resonance, 1972, 4, 421; S.C.Tang, G.N.Weinstein and R.H. Holm, J.Am.Chem.Soc., 1973, 95, 613; D.M.McKinnon and J.M.Buchshriber, Can.J.Chem., 1971, 49, 3299; H.Davy and J.Vialle, Bull.Soc.chim. France, 1975, 1435; H.Yoshida, H.Matsuura, T.Ogata and S.Inokawa, Bull.Chem.Soc.Japan, 1975, 48, 2907; M.Muraoka, T.Yamamoto and T.Takeshima Chem.Letters, 1982, 101.
4. H.G.Giles, R.A.Marty and P.de Mayo, J.Chem.Soc.Chem.Commun., 1974, 409.
5. H.G.Giles, R.A.Marty and P.de Mayo, Can.J.Chem., 1976, 54, 537.
6. B.Solouki, P.Rosmus and H.Bock, J.Am. Chem.Soc., 1976, 98, 6054.
7. H.Bock, S.Mohmand, T.Hirabayashi and A.Semkow, J.Am.Chem.Soc., 1982, 104, 312.
8. R.Okazaki, A.Ishii, N.Fukuda, H. Oyama and N.Inamoto, J.Chem.Soc. Chem.Commun., 1982, 1187.
9. E.Vedejs, T.H.Eberlein and D.L.Varie, J.Am.Chem.Soc., 1982, 104, 1445.
10. D.R.Dice and R.P.Steer, Can.J.Chem., 1974, 52, 3518; A.G.Anastassiou, J.C.Wetzel and B. Chao, J.Am.Chem.Soc., 1976, 98, 6405; E.Vedejs, M.J.Arnost, J.M.Dolphin and J.Eustache, J.Org.Chem., 1980, 45, 2601.
11. J.E.Baldwin and R.C.G.Lopez, J.Chem. Soc.Chem.Commun., 1982, 1029.
12. D.R.Hogg, in 'Comprehensive Organic Chemistry,' ed. D.Barton and W.D. Ollis, Pergamon Press, Oxford, 1979, vol. 3, p. 261.
13. L.D.Small, J.H.Bailey and C.J. Cavallito, J.Am.Chem.Soc., 1947, 69, 1710.
14. L.D.Small, J.H.Bailey and C.J. Cavallito, J.Am.Chem.Soc., 1949, 71, 3565.
15. F.D'Angeli, C.Di Bello, F.Filira and C.Toniolo, Gazzetta, 1967, 97, 798.
16. E.Block, J.Am.Chem.Soc., 1972, 94, 642; E.Block and J.O'Connor, J.Am.Chem. Soc., 1974, 96, 3929.
17. G.W.Kirby, Chem.Soc.Rev., 1977, 6, 1.
18. W.E.Truce, D.P.Tate and D.N.Burdge, J.Am.Chem.Soc., 1960, 82, 2872.
19. C.Descoins and C.A.Henrick, Tet. Letters, 1972, 2999.
20. D.H.G.Crout, M.V.M.Gregorio, U.S. Müller, S.Komatsubara, M.Kisumi and I.Chibata, Eur.J.Biochem., 1980, 106, 97.
21. L.F.Fieser and M.Fieser, 'Reagents for Organic Synthesis,' John Wiley and Sons, New York, 1967, vol. I, p. 1180.
22. J.H.Chapman and L.N.Owen, J.Chem. Soc., 1950, 579.
23. H.-L.Pan and T.L.Fletcher, Chem.and Ind., 1968, 546.

24. W.C.Still, M.Kahn and A.Mitra, J. Org.Chem., 1978, 43, 2923.

25. J.E.Corrie, G.W.Kirby and R.P.Sharma J.Chem.Soc.Chem.Commun., 1975, 915.

26. H.B.Dykstra, J.Am.Chem.Soc., 1935, 57, 2255.

27. J.Davies and J.B.Jones, J.Am.Chem. Soc., 1979, 101, 5405.

28. G.Ohloff, C.Vial, F.Näf and M.Pawlak Helv.Chim.Acta, 1977, 60, 1161.