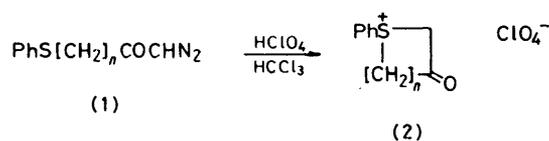


Preparation and Reactions of Novel Cyclic β -Oxosulphonium Salts obtained by the Acid-induced Cyclisation of 1-Diazo- ω -phenylthio-2-alkanones

By William T. Flowers, Ana M. Freitas, Geoffrey Holt,* and, in part, Stuart C. Purkiss, Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD

With perchloric acid, the diazo-ketones $\text{PhS}[\text{CH}_2]_n\text{COCHN}_2$ (1a)—(1d) give the corresponding cyclic β -oxosulphonium salts (2a)—(2d); the *p*-chlorophenyl analogue of (2d) was similarly prepared. The salts (2a), (2c), and (2d) react with triphenylphosphine at C(2) to give the acyclic phosphonium salts (3a), (3c), and (3d) and, analogously, with potassium *O*-ethyl dithiocarbonate to give the corresponding acyclic *O*-ethyl dithiocarbonates (3f), (3g), and (3h). All the reactions of the salt (2b) with nucleophiles gave either 1-phenylthiobut-3-en-2-one (11) or products of its Michael addition. Salts (2c) and (2d) with sodium methoxide in methanol provide, respectively, methyl ω -phenylthio-butanoate and -pentanoate in a process that involves the loss of a methylene group. These and other reactions are considered to proceed *via* ylide intermediates; the intermediate derived by the deprotonation of (2d) being isolated, whereas that from (2c) rearranged to give 3-phenylthiocyclopentanone.

We are prompted by the current interest¹ in the synthetic utility of cyclic sulphonium salts to report that each of the four phenylthio-diazoketones (1a)—(1d), on addition to perchloric acid in chloroform, provides, by intramolecular cyclisation, the corresponding cyclic β -oxosulphonium perchlorates (2a)—(2d) in high yield, paralleling the intermolecular reaction between 2-diazoacetophenones and alkyl aryl and dialkyl sulphides² (Scheme 1). The *p*-chlorophenyl analogue of (2d) was similarly prepared.



a; $n = 1$
b; $n = 2$
c; $n = 3$
d; $n = 4$

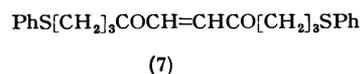
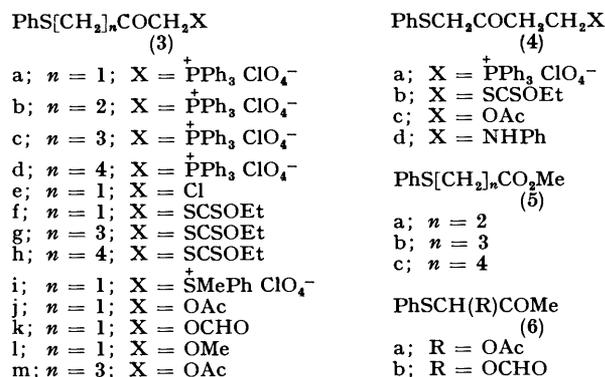
SCHEME 1

All the white, crystalline perchlorates (2a)—(2d) gave satisfactory analyses and are stable when stored in a desiccator, although the thietanone derivative (2a) deteriorates after a few weeks. Each exhibited a strong carbonyl absorption in the i.r. spectra (1 812, 1 748, 1 725, and 1 708 cm^{-1} , respectively) as well as absorptions due to the perchlorate anion (1 080 cm^{-1} , *cf.* 1 250 cm^{-1} for covalent perchlorate³); the ¹H n.m.r. spectra support the proposed structures, though an entirely satisfactory spectrum of (2a) could not be obtained since it reacted with both Me_2SO and MeCN .

This is, we believe, the first reported preparation of monocyclic β -oxosulphonium salts by such a reaction. In contrast, Rosnati *et al.*⁴ treated the diazo-ketone (1a) with hydrogen chloride in ether and obtained the acyclic chloro-ketone (3e), presumably reflecting the greater nucleophilicity of the chloride ion with respect to perchlorate, as we have observed in other cases.⁵ Also, although the diazo-ketone $\text{PhCH}_2\text{SCH}_2\text{CH}_2\text{COCHN}_2$ undergoes cyclisation with aqueous acid, the major

product is thiolan-3-one, presumably resulting from debenylation of the first-formed sulphonium salt.⁶

All the perchlorates (2a)—(2d) react with triphenylphosphine to give stable acyclic phosphonium perchlorates [(2a), (2c), and (2d) giving (3a), (3c), and (3d), respectively]; the salt (3a) was also prepared from the diazo-ketone (1a), triphenylphosphine, and perchloric acid. In the case of the salt (2b), there resulted not the expected phosphonium salt (3b), but the isomeric salt (4a) (see later). Exactly analogous was the reaction of

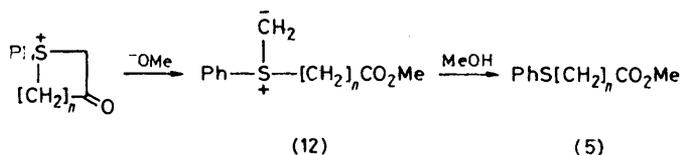


the salts with potassium *O*-ethyl dithiocarbonate, giving the dithiocarbonates (3f), (3g), and (3h), respectively, while (2b) gave (4b).

The high reactivity of the thietanium salt (2a) is demonstrated by its reaction with triphenylphosphine in the cold, while heating is required with (2b)—(2d); all four salts react with potassium *O*-ethyl dithiocarbonate at ambient temperatures. The salt (2a) reacts with thioanisole in the cold to provide, again in high yield, a sulphonium salt (3i), identical with that obtained from the diazo-ketone (1a), perchloric acid, and thioanisole. It is therefore apparent that the reactivity of the thietanium salt (2a) is greater than that of phenacyl halide, since the latter does not react with thioanisole.⁷

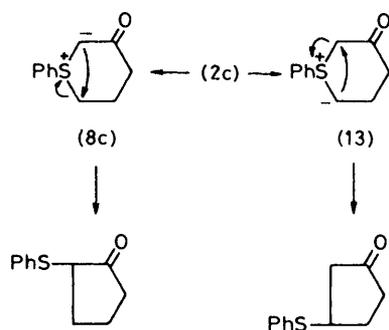
the product of direct nucleophilic attack of acetate ion on the 2-carbon atom, together with isomeric acetates, none of which could be obtained in a state of purity. In addition, there was isolated 21% of the diacylolefin (7); the yield of the latter was raised to 60%, when the salt was treated with potassium phthalimide in acetonitrile and in this case products of nucleophilic intervention were not detected. We have previously shown² that the diacylolefins arise from sulphonium salt-ylide interaction and such could be the case here [(2c) + (8c) \rightarrow (7) + HClO₄].

Many of the reactions described above implicate ylides and hence attempts were made to obtain these in a state of purity. The salt (2a) reacted rapidly with triethylamine, a reagent we have used successfully in the past² to generate ylides from both acyclic and cyclic β -oxosulphonium salts, but no ylide was detectable by



SCHEME 4

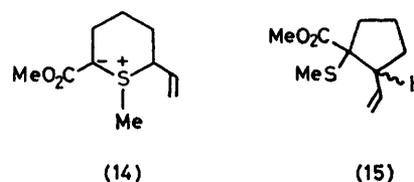
spectroscopy and very similar results were obtained when *n*-butyl-lithium was used as base. The i.r. spectrum of the product, molecular weight *ca.* 790, showed a carbonyl band at 1710 cm⁻¹ indicating that ring-opening had taken place. Surprisingly, very similar material was obtained when the salt (2b) was treated with *n*-butyl-lithium and this material is still under investigation. In this case, however, the freshly prepared reaction mixture gave an indication (i.r.) of an ylide carbonyl group, but this decayed rapidly and trapping experiments with benzaldehyde were unsuccessful. When the salt (2c) was similarly treated, the crude product exhibited i.r. absorptions at 1520 and



SCHEME 5

1580 cm⁻¹, clearly indicative of an ylide;¹⁰ attempts to purify the material led to rapid rearrangement affording a phenylthiocyclopentanone, shown to be the 3-isomer by comparison with the known 2-isomer and synthesis of the unknown 3-isomer by interaction of sodium thiophenolate and cyclopent-2-enone (Scheme 5). The 2-

isomer would be the product of Stevens-type rearrangement of the initial ylide (8c), whereas the 3-isomer presumably arises from the isomeric ylide (13). Vedejs *et al.* have very recently¹¹ reported an analogous ring contraction [(14) \rightarrow (15)].



Finally, the salt (2d), on treatment with *n*-butyl-lithium, gave an isolable ylide (8d) which was sufficiently stable for its structure to be established spectroscopically. Even this material, however, rearranged after some days at ambient temperature, and much more rapidly on heating in chloroform, to give what is apparently a dimer.

EXPERIMENTAL

I.r. spectra were recorded on a Perkin-Elmer 257 instrument, ¹H n.m.r. spectra on Perkin-Elmer R12 and Varian HA spectrometers, and mass spectra on an A.E.I. MS902 spectrometer. All the known compounds gave satisfactory analytical data and spectroscopic data.

In general, reaction times were determined by following the disappearance of the i.r. carbonyl absorption of the reactant.

The Diazo-ketones (1a)–(1d).—(Phenylthio)acetic acid, 3-(phenylthio)propionic acid, and 4-(phenylthio)butanoic acid were prepared by literature procedures.^{12–14} 4-(Phenylthio)pentanoic acid was most conveniently prepared by the Arndt-Eistert synthesis¹⁵ (silver benzoate-triethylamine-methanol) from the diazo-ketone (1c) and subsequent hydrolysis of the resulting ester. All the acids were converted into the corresponding chlorides with thionyl chloride¹⁶ and addition of these to ethereal diazomethane under standard conditions¹⁷ provided the requisite diazo-ketones. The diazo-ketones were further characterized as their adducts with triphenylphosphine.¹⁸

(a) 1-Diazo-3-phenylthiopropion-2-one (1a) (75%), m.p. 32–33 °C, (lit.,^{4,19} a yellow oil) (from diethyl ether), ν_{max} 2100s (diazo) and 1620s (CO) cm⁻¹; 1-(triphenylphosphoranylidenehydrazono)-3-phenylthiopropion-2-one (63%), m.p. 107–109 °C (from diethyl ether) (Found: C, 71.5; H, 4.9; N, 6.3; P, 6.6; S, 6.8. C₂₇H₂₃N₂O₂PS requires C, 71.4; H, 5.1; N, 6.2; P, 6.8; S, 7.0%).

(b) 1-Diazo-4-phenylthiobutan-2-one (1b) (93%), obtained as a yellow oil, ν_{max} 2080s (diazo) and 1630s (CO) cm⁻¹; 1-(triphenylphosphoranylidenehydrazono)-4-phenylthiobutan-2-one (67%), m.p. 103–105 °C (from diethyl ether) (Found: C, 71.6; H, 5.9; N, 6.3; P, 6.5; S, 6.9. C₂₈H₂₅N₂O₂PS requires C, 71.2; H, 6.1; N, 6.0; P, 6.6; S, 6.8%).

(c) 1-Diazo-5-phenylthiopentan-2-one (1c) (91%), obtained as a yellow oil, ν_{max} 2100s (diazo) and 1640s (CO) cm⁻¹; 1-(triphenylphosphoranylidenehydrazono)-5-phenylthiopentan-2-one (80%), m.p. 107–108 °C (from diethyl ether) (Found: C, 71.9; H, 5.7; N, 5.8; P, 6.2. C₂₉H₂₇N₂O₂PS requires C, 72.4; H, 5.6; N, 5.8; P, 6.4%).

(d) 1-Diazo-6-phenylthiohexan-2-one (1d) (95%), obtained as a yellow oil, ν_{max} 2110s (diazo) and 1640s (CO) cm⁻¹; 1-(triphenylphosphoranylidenehydrazono)-6-phenylthio-

hexan-2-one (78%), m.p. 97–98 °C (from diethyl ether) (Found: C, 72.4; H, 5.9; N, 5.6; P, 6.2. $C_{30}H_{29}N_2OPS$ requires C, 72.6; H, 5.8; N, 5.6; P, 6.2%).

Cyclic β-Oxosulphonium Salts (2a)–(2d).—When each of the diazo-ketones (1a)–(1d) (0.01 mol) in chloroform (15 ml) was added, with stirring, during 15 min to 71% (w/w) perchloric acid (0.02 mol) in chloroform (10 ml), nitrogen (ca. 100%) was evolved. The product was filtered off, washed with chloroform, water [omitted in the case of the salt (2a)], and then chloroform again [salt (2a) could only be washed with chloroform as no suitable solvent could be found for the recrystallization]. Recrystallization from acetonitrile–ether provided, respectively, 3-oxo-1-phenylthiethanium perchlorate (2a) (83%), m.p. 132–134 °C (Found: C, 40.8; H, 3.4; Cl, 13.2; S, 11.8. $C_9H_9ClO_5S$ requires C, 40.8; H, 3.4; Cl, 13.4; S, 12.1%); ν_{max} 1 812s (CO) and 1 080s br (ClO_4^-) cm^{-1} ; τ (CD_3CN) 2.4 (5 H, s, Ar), 5.73 (2 H, ABq, J_{AB} 17 Hz, $COCH_2\dot{S}$), 5.84–6.18 (1 H, m, $\dot{S}CH_2CH_2$), and 6.78–7.08 (2 H, m, CH_2CH_2CO); 3-oxo-1-phenylthianium perchlorate (2c) (92%), m.p. 158–159 °C (Found: C, 45.3; H, 4.2; Cl, 12.4; S, 10.7. $C_{11}H_{13}ClO_5S$ requires C, 45.1; H, 4.4; Cl, 12.1; S, 11.0%); ν_{max} 1 725s (CO) and 1 080s br (ClO_4^-) cm^{-1} ; τ (CD_3CN) 2.3 (5 H, s, Ar), 5.72 (2 H, ABq, J_{AB} 14 Hz, $COCH_2\dot{S}$), 6.0–6.4 (2 H, m, CH_2CH_2CO), and 7.5–7.8 (2 H, m, $CH_2CH_2CH_2$); 3-oxo-1-phenylthiepanium perchlorate (2d) (79%), m.p. 148–150 °C (Found: C, 46.7; H, 5.1; Cl, 11.4; S, 10.4. $C_{12}H_{15}ClO_5S$ requires C, 47.0; H, 4.9; Cl, 11.6; S, 10.4%); ν_{max} 1 708s (CO) and 1 080s br (ClO_4^-) cm^{-1} ; τ (CD_3CN) 2.45 (5 H, s, Ar), 5.45 (2 H, s br, $COCH_2\dot{S}$), 6.0–6.4 (2 H, m, $\dot{S}CH_2CH_2$), 7.4–7.9 (2 H, m, CH_2CH_2CO), and 8.4–8.9 (4 H, m, $CH_2CH_2CH_2CH_2$); and 3-oxo-1-(p-chlorophenyl)thiepanium perchlorate (25%), m.p. 137–140 °C (Found: C, 41.9; H, 4.1. $C_{12}H_{14}Cl_2O_5S$ requires C, 42.2; H, 4.1%).

Cyclic β-Oxosulphonium Salts (2a)–(2d) and Triphenylphosphine.—To a stirred suspension of the salt (2a) (0.01 mol) in dioxan (80 ml) at 18–21 °C, was added, in drops, triphenylphosphine (0.015 mol) in dioxan (40 ml). After 3 h the reaction mixture was stored overnight at 0 °C and the crude phosphonium salt separated. To effect a similar reaction of the salts (2b)–(2d) it was necessary to reflux the mixture for 3 h after which the solvent was removed under reduced pressure. The residue, after washing with water (50 ml) was taken up in chloroform (3 × 50 ml) and dried ($MgSO_4$). Removal of the solvent gave an orange oil which was shaken with ether to remove triphenylphosphine, when the crude phosphonium salt solidified (85–95%). Recrystallization from chloroform–ether provided, respectively, (2-oxo-3-phenylthiopropyl)triphenylphosphonium perchlorate (3a), m.p. 153–154 °C (Found: C, 61.2; H, 4.8; Cl, 7.0; P, 5.7; S, 5.9. $C_{27}H_{24}ClO_5PS$ requires C, 61.5; H, 4.6; Cl, 6.7; P, 5.9; S, 6.1%); ν_{max} 1 730s (CO) and 1 080s br (ClO_4^-) cm^{-1} ; τ [(CD_3) $_2$ SO] 2.1–3.0 (20 H, m, Ar), 4.53 (2 H, d, $CH_2^+PPh_3$, J_{HP} 13.5 Hz), and 5.95 (2 H, s, SCH_2CO) [this product was identical in i.r. and n.m.r. spectra with that obtained from the reaction of the diazo-ketone (1a), triphenylphosphine, and perchloric acid]; (3-oxo-4-phenylthiobutyl)triphenylphosphonium perchlorate (4a), m.p. 60–65 °C (Found: C, 62.0; H, 5.1; P, 5.6; S, 6.4. $C_{28}H_{26}Cl-$

O_5PS requires C, 62.4; H, 4.8; P, 5.7; S, 5.9%); ν_{max} 1 715s (CO) and 1080s br (ClO_4^-) cm^{-1} ; τ ($CDCl_3$) 2.1–2.9 (20 H, m, Ar), 6.12 (2 H, s, SCH_2), and 6.2–7.0 (4 H, m, CH_2CH_2P); (2-oxo-5-phenylthiopentyl)triphenylphosphonium perchlorate (3c), m.p. 46–49 °C (Found: C, 63.1; H, 5.2; P, 5.8; S, 5.4. $C_{29}H_{28}ClO_5PS$ requires C, 62.8; H, 5.0; P, 5.6; S, 5.8%); ν_{max} 1 708s (CO) and 1 080s br (ClO_4^-) cm^{-1} ; τ ($CDCl_3$) 2.1–2.9 (20 H, m, Ar), 4.94 (2 H, d, J_{HP} 13.5 Hz, CH_2^+P), 6.98 (2 H, t, $-SCH_2$), and 7.19 (2 H, t, $CH_2CH_2CH_2$); and (2-oxo-6-phenylthiohexyl)triphenylphosphonium perchlorate (3d), m.p. 35–37 °C (Found: C, 63.2; H, 5.0; Cl, 6.7; P, 5.4. $C_{30}H_{30}ClO_5PS$ requires C, 63.3; H, 5.3; Cl, 6.2; P, 5.5%); ν_{max} 1 708s (CO) and 1 080s br (ClO_4^-) cm^{-1} ; τ ($CDCl_3$) 2.1–2.9 (20 H, m, Ar), 5.05 (2 H, d, CH_2^+P , J_{HP} 13.5 Hz), and 7.0–7.4 (4 H, m, $CH_2CH_2CH_2CH_2$).

Cyclic β-Oxosulphonium Salts and Sulphur Nucleophiles.—(a) The salt (2a) with thioanisole and with the thio benzamide. A suspension of the salt (2a) (2.65 g, 0.01 mol) in dry chloroform (85 ml) containing thioanisole (2.48 g, 0.02 mol) was stirred at 18–21 °C for 48 h. The bulk of the solvent was removed under reduced pressure, the solid was separated and washed with water and then with chloroform to give methyl-(2-oxo-3-phenylthiopropyl)phenylsulphonium perchlorate (3i) (93%), m.p. 110–112 °C (from acetonitrile–ether) (Found: C, 49.1; H, 4.5; Cl, 9.1; S, 16.0. $C_{16}H_{17}ClO_5S_2$ requires C, 49.4; H, 4.4; Cl, 9.1; S, 16.5%); ν_{max} 1 720s (CO), 1 080s br (ClO_4^-) cm^{-1} ; τ [(CD_3) $_2$ SO] 1.8–3.1 (10 H, m, Ar), 4.7 (2 H, s, $CH_2\dot{S}$), 5.97 (2 H, s, SCH_2CO), and 6.8 (3 H, s, SMe).

A suspension of the salt (2a) (1 g, 3.78 mmol) in dry dioxan (10 ml) containing thiobenzamide (0.52 g, 3.78 mmol) was refluxed gently for 30 min. Filtration of the slurry, obtained by removal of the bulk of the solvent under reduced pressure, gave 2-phenyl-5-phenylthiomethylthiazolium perchlorate (9) (79%), m.p. 101–102 °C (from dioxan) (Found: C, 50.4; H, 4.0; Cl, 8.9; N, 3.5; S, 16.4. $C_{16}H_{15}ClNO_4S_2$ requires C, 49.1; H, 3.9; Cl, 9.2; N, 3.6; S, 16.6%); ν_{max} 3 160–2 800m br ($\dot{N}H$) and 1 080s br (ClO_4^-) cm^{-1} ; τ [(CD_3) $_2$ SO] 0.81 (1 H, s, $\dot{N}H$), 2.15–3.15 (10 H, m, Ar), 5.74 (1 H, s, $CH=C$), and 6.55 (2 H, s, SCH_2).

(b) The salts (2a)–(2d) with potassium O-ethyl dithiocarbonate. The salt (0.015 mol) and potassium O-ethyl dithiocarbonate (3.25 g, 0.02 mol) were stirred in dry dioxan (30 ml) for 1.5 h. After removal of potassium perchlorate, the solvent was evaporated under reduced pressure. The oily residue was washed with water (50 ml) and extracted with ether (3 × 50 ml). The water-washed, ether extracts were dried ($MgSO_4$) and evaporated to give, as orange oils, respectively, O-ethyl S-(2-oxo-3-phenylthiopropyl)dithiocarbonate (3f) (88%) (Found: C, 50.1; H, 5.0; S, 33.0. $C_{12}H_{14}O_2S_3$ requires C, 50.3; H, 4.9; S, 33.6%); ν_{max} 1 720s (CO) cm^{-1} ; τ ($CDCl_3$) 2.7 (5 H, s, Ar), 5.42 (2 H, q, CH_2Me), 5.9 (2 H, s, $COCH_2S$), 6.17 (2 H, s, $PhSCH_2CO$), and 8.65 (3 H, t, Me); O-ethyl S-(3-oxo-4-phenylthiobutyl)dithiocarbonate (4b) (89%) (Found: C, 52.3; H, 5.5; S, 32.4. $C_{13}H_{16}O_2S_3$ requires C, 52.0; H, 5.3; S, 32.0%); ν_{max} 1 710s (CO) cm^{-1} ; τ ($CDCl_3$) 2.7 (5 H, s, Ar), 5.4 (2 H, q, CH_2Me), 6.35 (2 H, s, SCH_2CO), 6.65 (2 H, A₂ of A₂B₂ m, SCH_2CH_2), 7.01 (2 H, B₂ of A₂B₂, m, CH_2CH_2CO), and 8.63 (3 H, t, Me); and O-ethyl S-(2-oxo-5-phenylthiopentyl)dithiocarbonate (3g) (91%) (Found: C, 53.2; H, 5.7; S, 30.6. $C_{14}H_{18}O_2S_3$ requires C, 53.5; H, 5.8; S, 30.5%); ν_{max} 1 720

(CO) cm^{-1} ; τ (CDCl_3) 2.7 (5 H, s, Ar), 5.40 (2 H, q, CH_2Me), 6.09 (2 H, s, SCH_2CO), 7.09 (2 H, r, SCH_2CH_2), 7.28 (2 H, t, COCH_2CH_2), 8.09 (2 H, q, $\text{CH}_2\text{CH}_2\text{CH}_2$), and 8.63 (3 H, t, Me) which, on standing, deposited off-white crystals, m.p. 41–42 °C, and *O-ethyl S-(2-oxo-6-phenylthiohexyl)dithiocarbonate* (3h) (92%) (Found: C, 55.1; H, 6.0; S, 29.3. $\text{C}_{15}\text{H}_{20}\text{O}_2\text{S}_3$ requires C, 54.8; H, 6.1; S, 29.2%); ν_{max} 1720 (CO) cm^{-1} ; τ (CDCl_3) 2.7 (5 H, Ar), 5.40 (2 H, q, CH_2Me), 6.08 (2 H, s, SCH_2CO), 7.11 (2 H, t, SCH_2CH_2), 7.43 (2 H, t, $\text{CH}_2\text{CH}_2\text{CO}$), 8.35 (4 H, m, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), and 8.36 (3 H, t, Me).

The Salts (2a)–(2c) with Potassium Acetate in Acetic Acid and with Sodium Formate in Formic Acid.—Salt (2a) (4 g, 0.015 mol) and anhydrous potassium acetate (4.44 g, 0.045 mol) were heated in refluxing acetic acid (45.5 ml) for 1 h. After cooling and separation of potassium perchlorate, the solvent was removed under reduced pressure and the residue was neutralized with sodium carbonate solution (2M), the resultant oil was taken up in ether, washed with water, dried (MgSO_4), and the extract concentrated before distillation under reduced pressure to give 2-oxo-3-phenylthiopropyl acetate (3j) (81%), b.p. 190–195 °C at 4 mmHg (lit.¹⁹ 120–122 °C at 0.4 mmHg); ν_{max} 1770–1730s br (CO); identical (i.r. and n.m.r. spectra) with that described by Rosnati *et al.*¹⁹

With the salts (2b) and (2c) a reaction time of 2.5 h was required. Salt (2b) then provided, after distillation, 3-oxo-4-phenylthiobutyl acetate (4c) (64%), b.p. 155–160 °C at 0.2 mmHg (Found: C, 60.8; H, 5.7; S, 13.1. $\text{C}_{12}\text{H}_{14}\text{O}_3\text{S}$ requires C, 60.5; H, 5.9; S, 13.4%); ν_{max} 1740s br (CO) cm^{-1} ; τ (CDCl_3) 2.7 (5 H, s, Ar), 5.7 (2 H, t, CH_2O), 6.3 (2 H, s, SCH_2), 7.1 (2 H, t, COCH_2CH_2), and 8.05 (3 H, s, COMe) and 1-phenylthiobut-3-en-2-one (11) (19%), b.p. 114–120 °C at 0.2 mmHg (Found: C, 67.5; H, 5.8; S, 18.00. $\text{C}_{10}\text{H}_{10}\text{OS}$ requires C, 67.4; H, 5.6; S, 18.00%); ν_{max} 1680s (CO) and 1620s (C=C) cm^{-1} ; τ (CDCl_3) 2.7 (5 H, s, Ar), 3.2–4.4 (3 H, m, $\text{CH}=\text{CH}_2$), and 6.15 (2 H, s, SCH_2). The latter with potassium acetate, under the conditions described above, gave (4c), in near-quantitative yield, identical with that described above. The vinyl ketone (11) with aniline in ethanol gave 4-phenylamino-1-phenylthiobutan-2-one (4d) (51%), m.p. 82–84 °C [from ether-light petroleum (b.p. 40–60 °C)] (Found: C, 70.7; H, 6.6; N, 4.7. $\text{C}_{16}\text{H}_{17}\text{NOS}$ requires C, 70.8; H, 6.3; N, 5.2%); ν_{max} 3400m (NH) and 1700s (CO) cm^{-1} ; τ (CDCl_3) 2.7 (5 H, s, PhS), 3.0–3.6 (6 H, m, PhNH), 6.4 (2 H, s, SCH_2), 6.6–7.0 (2 H, m, CH_2NH), and 7.2 (2 H, t, COH_2CH_2).

The product from the interaction of salt (2c) and potassium acetate, under similar conditions, was much more complex. The neutral ether-extract, on concentration to low bulk, deposited a solid 'A' which was separated and the residual oil chromatographed on a column of silica gel (80 × 3 cm). Starting with light petroleum (b.p. 40–60 °C) as eluant, and then using mixtures increasingly rich in toluene and ultimately using toluene itself, gave, as identifiable products only, diphenyl disulphide (6%) (lit.²⁰ m.p. and mixed m.p. 61 °C), a further quantity of the solid 'A', and an oil which, although not analytically pure, appeared, on the basis of spectroscopic data, to be 2-oxo-5-phenylthiopentyl acetate (3m) (10%); ν_{max} 1735s br (CO) cm^{-1} ; τ (CDCl_3) 2.7 (5 H, s, Ar), 5.4 (2 H, s, $-\text{CH}_2\text{O}-$), 6.9–7.7 (4 H, m, $\text{CH}_2\text{CH}_2\text{CH}_2$), 7.85 (3 H, s, Me), and 7.8–8.2 (2 H, m, $\text{CH}_2\text{CH}_2\text{CH}_2$).

The solid 'A' was identified as 1,4-bis-(3-phenylthiopropyl)but-2-ene-1,4-dione (7) (17%), m.p. 84–85 °C (from

ethanol–water) (Found: C, 68.5; H, 6.4; S, 16.6. $\text{C}_{22}\text{H}_{24}\text{O}_2\text{S}_2$ requires C, 68.8; H, 6.3; S, 16.7%); ν_{max} 1670s (CO) cm^{-1} ; τ (CDCl_3) 2.74 (10 H, s, Ar), 3.2 (2 H, s, $\text{CH}=\text{CH}$), 6.9–7.4 (8 H, m, $\text{CH}_2\text{CH}_2\text{CH}_2$), and 7.9–8.2 (4 H, m, $\text{CH}_2\text{CH}_2\text{CH}_2$). The solid (7) was obtained in a much improved yield (60%) when equimolar proportions of the salt (2c) and potassium phthalimide were heated in refluxing acetonitrile for 4 h.

When the salt (2a) (2 g, 7.56 mmol) was stirred with sodium formate (1.52 g, 22.34 mmol) in formic acid (25 ml), the reaction proceeded in the cold (18–21 °C) to give an oil which, on the basis of its ^1H n.m.r. spectrum, was identified as a mixture of the isomers 2-oxo-3-phenylthiopropyl formate (3k) (54%) and 2-oxo-1-phenylthiopropyl formate (6b) (36%) (Found: C, 57.4; H, 4.9; S, 15.3. $\text{C}_{10}\text{H}_{10}\text{O}_3\text{S}$ requires C, 57.1; H, 4.8; S, 15.2%); ν_{max} 1725s br (CO) cm^{-1} ; τ (CDCl_3) 2.69 and 2.71 (s, Ar), 1.87 (s, CHOCO), 1.92 (s, CH_2OCO), 3.7 (s, CHOCO), 5.1 (s, CH_2OCO), 6.32 (SCH_2), and 7.79 (s, COMe).

Salts (2a)–(2d) with Sodium Methoxide in Methanol.—To a solution of sodium methoxide in methanol [from sodium (0.173 g, 7.56 mmol) and dry methanol (30 ml)] was added slowly a suspension of the salt (2a) (2 g, 7.56 mmol) in the same solvent (60 ml) and the mixture was stirred at 18–21 °C for 2 h under nitrogen. After neutralizing the mixture with acetic acid, the solvent was removed under reduced pressure and the residue was extracted with chloroform. The extract was washed, successively, with sodium hydrogencarbonate (2M) and water (50 ml), dried (MgSO_4), and evaporated to provide a yellow oil, which, on the basis of its ^1H n.m.r. spectrum, was identified as a 3 : 1 mixture of methyl-3-(phenylthio)propionate (5a) (60%) and 1-methoxy-1-phenylthiopropion-2-one (6c) (20%) identical (i.r. and n.m.r. spectra) with those described by Rosnati *et al.*¹⁹

Under similar conditions (2b) gave 1-phenylthiobut-3-en-2-one (11) (86%) as previously described.

The salts (2c) and (2d) failed to react in the cold, but in refluxing methanol the reaction was complete in 6 h and gave, respectively, methyl 4-(phenylthio)butanoate (8b) (63%), b.p. 137–138 °C at 2 mmHg (lit.²¹ 112 °C at 0.07 mmHg); ν_{max} 1740s (CO) cm^{-1} and methyl 5-(phenylthio)pentanoate (8c) (60%) ν_{max} 1740s (CO) cm^{-1} . These esters were identical (i.r. and n.m.r. spectra) with those obtained from the appropriate acids and methanol in the presence of sulphuric acid.

Salts (2a)–(2d) with n-Butyl-lithium.—To a stirred suspension of each salt (16.0 mmol) in tetrahydrofuran (TNF) (50 ml) in an atmosphere of nitrogen was added n-butyl-lithium (18.0 mmol) in hexane (9 ml) at 0 °C during 10 min. After a further 10 min the solvent was removed under reduced pressure and residue 'A' was stirred with water (50 ml) before extraction with chloroform (3 × 50 ml). The water-washed and dried (MgSO_4) extract was concentrated under reduced pressure to provide the crude product 'B'.

Compound (2c) provided a residue 'A', i.r. ν 1520s br and 1580m cm^{-1} , suggesting the presence of the ylide (8c). However, extraction with chloroform gave the product 'B' whose i.r. spectrum showed an additional carbonyl band (1720 cm^{-1}). After 3 d at 18–21 °C the 1520 cm^{-1} band had disappeared completely and the rearrangement product was 3-phenylthiocyclopentanone (72%) (Found: C, 67.6; H, 6.2; S, 16.6. $\text{C}_{11}\text{H}_{12}\text{OS}$ requires C, 68.6; H, 6.3; S, 16.7%); ν_{max} 1720s (CO) cm^{-1} ; τ (CDCl_3) 2.7 (5 H, s, Ar), 6.8–7.7 (5 H, m, CHS, CHCH_2CO , and $\text{CH}_2\text{CH}_2\text{CO}$), and 7.8–8.4

(2 H, m, CHCH₂CH₂); *m/e* 192 (*M*⁺, 29%), 136 (C₈H₈S⁺, 66%), 124 (C₇H₈S⁺, 100%), 123 (C₇H₇S⁺, 44%), 110 (C₆H₆S⁺, 67%), 109 (C₆H₅S⁺, 80%), and 77 (C₆H₅⁺, 50%).

The salt (2d) gave product 'B' as a yellow oil which rapidly solidified (m.p. 95–102 °C), which, on recrystallization from acetonitrile–ether gave 3-oxo-1-phenylthiopyran-1-ium-2-ide (8d) (1.5 g, 47%), m.p. 119–120 °C (Found: C, 69.6; H, 6.9; S, 15.4. C₁₂H₁₄SO requires C, 69.9; H, 6.8; S, 15.5%); ν_{\max} 1550s (CO) cm⁻¹; τ (CDCl₃) 2.37 (5 H, s, Ar), 6.30 (1 H, s, SCHCO), 6.50 (2 H, m, SCH₂CH₂), and 7.6–8.4 (6 H, complex, CH₂CH₂CH₂CH₂CO); *m/e* 206 (*M*⁺, 38%), 193 (C₁₁H₁₃OS⁺, 6%), 165 (C₁₀H₁₃S⁺, 5%), 123 (C₇H₇S⁺, 100%), 110 (C₆H₆S⁺, 46%), 109 (C₆H₅S⁺, 23%), 97 (*M*⁺, C₆H₅S⁺, 55%), and 77 (C₆H₅⁺, 16%). This ylide, on storage in chloroform solution, was transformed, during 5 d (20–21 °C), into what appears to be an unsymmetrical dimer, m.p. 95–97 °C (from acetonitrile–ether). The structure of this product is still under investigation.

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