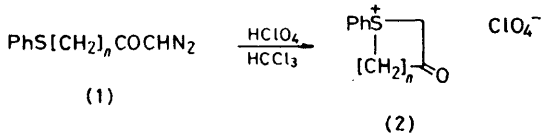
Preparation and Reactions of Novel Cyclic β-Oxosulphonium Salts obtained by the Acid-induced Cyclisation of 1-Diazo-ω-phenylthio-2-alkanones

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 $PhS[CH_2]_nCOCHN_2$ (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 interest [1] 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 sulphides [2] (Scheme 1). The *p*-chlorophenyl analogue of (2d) was similarly prepared.



(1) (2)

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 perchlorate [3]); 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 $PhCH_2SCH_2CH_2COCHN_2$ undergoes cyclisation with aqueous acid, the major product is thiolan-3-one, presumably resulting from debenzylation 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

$PhS[CH_2]_nCOCH_2X$ (3)

a; $n = 1$; $X = \overset{+}{P}Ph_3\ ClO_4^-$
b; $n = 2$; $X = \overset{+}{P}Ph_3\ ClO_4^-$
c; $n = 3$; $X = \overset{+}{P}Ph_3\ ClO_4^-$
d; $n = 4$; $X = \overset{+}{P}Ph_3\ ClO_4^-$
e; $n = 1$; X = Cl
f; $n = 1$; X = SCSOEt
g; $n = 3$; X = SCSOEt
h; $n = 4$; X = SCSOEt
i; $n = 1$; $X = \overset{+}{S}MePh\ ClO_4^-$
j; $n = 1$; X = OAc
k; $n = 1$; X = OCHO
l; $n = 1$; X = OMe
m; $n = 3$; X = OAc

$PhS[CH_2]_3COCH{=}CHCO[CH_2]_3SPh$ (7)

$PhSCH_2COCH_2CH_2X$ (4)

a; $X = \overset{+}{P}Ph_3\ ClO_4^-$
b; X = SCSOEt
c; X = OAc
d; X = NHPh

$PhS[CH_2]_nCO_2Me$ (5)

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

PhSCH(R)COMe (6)

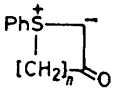
a; R = OAc
b; R = OCHO
c; R = OMe

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

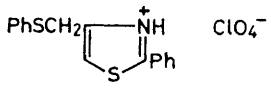
The high reactivity of the thietanium salt (2a) is demonstrated by its reaction with triphenylphosphine in the cold, while heating is required with (2b)—(2d); all four salts react with potassium *O*-ethyl dithiocarbonate at ambient temperatures. The salt (2a) reacts with thioanisole in the cold to provide, 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]

Again, the salt (2a) reacts with thiobenzamide, in the cold, to give the thiazolium salt (9) in a process reminiscent of that between diazo-ketones and thioamides.[8]

When Rosnati treated the acyclic chloro-ketone (3e)



(8)



(9)

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

with potassium acetate, he obtained, as the major product, the acetoxy-ketone (6a) with the isomeric (3j) as the minor product (Table), which he interpreted as indicating the intermediacy of the secondary phenacyl ion, $PhS\overset{+}{C}HCOMe$, arising by rearrangement of the primary carbonium ion obtained from the S_N1 dissociation

TABLE

Reaction of (2a) and (3e) with nucleophiles

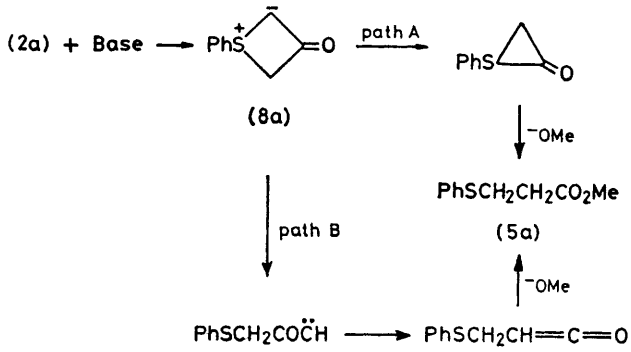
Substrate	Nucleophile	Products
(2a)	KOAc–HOAc	$PhSCH_2COCH_2OAc$ (3j)
(2a)	NaOCHO–HOCHO	$PhSCH_2COCH_2OCHO$ (3k)
		PhSCH(OCHO)Ac (6b)
(3e)	KOAc–HOAc	$PhSCH_2OCOH_2OAc$ (3j)
		PhSCH(OAc)Ac (6a)

of (3e). In contrast, (3j) was the sole product of the reaction of acetate ion with the sulphonium salt (2a), indicating that S_N2 attack had occurred on the salt, in its cyclic form.

One might expect the open-chain forms of the salt (2a) to be favoured by a polar environment. Such appears to be the case, since when the salt (2a) was allowed to react with sodium formate in formic acid, the product of direct nucleophilic attack, (3k) (54%), was accompanied by the isomeric formate, (6b) (36%) (Table). Similar reasoning may be used to rationalise the formation of the methoxy-ketone (6c), which is the minor product (20%) when the salt (2a) reacts with sodium methoxide in the cold; no isomeric methoxy-ketone (3l) was detected.

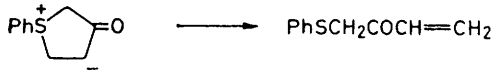
The major product (60%) of the methoxide reaction with (2a) was the ester (5a). It seems reasonable to suppose that, under these strongly basic conditions, the dominant process is proton removal to give the ylide (8a), rearrangement of which may, in principle, occur *via* two paths (Scheme 2). One is the Favorski-type rearrangement (path A) to the cyclopropanone which, under the conditions of the reaction, might be expected to ring-open to the ester (5a); an alternative is spontaneous ring-opening of the ylide (path B) to give the carbene, followed by Wolff rearrangement and addition of methanol to the resulting keten. Attention has been previously drawn to the analogous behaviour of α-diazo-ketones and β-oxosulphonium ylides in undergoing the Wolff rearrangement.[9]

All the reactions of the thiolanium salt (2b) with nucleophiles led to the αβ-unsaturated ketone (11) or to products of its Michael addition. In the first category is the reaction with cold, methanolic sodium methoxide, which provides, in high yield, the vinyl ketone (11), which is most probably formed by rearrangement of



SCHEME 2

the ylide (10) (Scheme 3), obtained either by deprotonation of the salt (2b) or by proton transfer in the presumably more stable ylide (8b). Ring-opening of (10) gives the observed product. The driving force in this process is presumably conjugation of the arising double bond with the carbonyl group in a process that may well be concerted. In the second category are the reactions with potassium acetate, triphenylphosphine, and potassium *O*-ethyl dithiocarbonate. Heating the salt (2b) with potassium acetate in acetic acid provides the β-acetoxy-ketone (4c) together with a much smaller amount of the vinyl ketone (11). As separate experiments showed, the latter undergoes Michael addition with potassium acetate to give the β-acetoxy-ketone (4c). In



(10) (11)

SCHEME 3

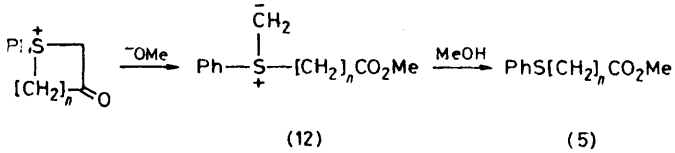
the same way, both triphenylphosphine and potassium *O*-ethyl dithiocarbonate provide the Michael adducts (4a) and (4b), respectively. Both reactions were carried out in dioxan, which is apparently sufficiently basic to generate the ylide (8b) and hence the vinyl ketone (11). The latter then reacts with triphenylphosphine or with potassium *O*-ethyl dithiocarbonate to give the observed Michael adducts.

Salts (2c) and (2d) react with sodium methoxide in methanol to give the esters (5a) and (5b), respectively, in a process which involves the loss of a methylene group. One rationalisation of this result is attack of methoxide at the carbonyl carbon to give the acyclic methylene ylides (12) which are then protonated and demethylated by the solvent (Scheme 4).

In contrast to these high-yield reactions, the salt (2c) provided a complex, tarry mixture when treated with potassium acetate in acetic acid. On the basis of spectroscopic evidence, this appeared to contain (3m),

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 shown [2] that the diacylolefins arise from sulphonium salt–ylide interaction and such could be the case here [(2c) + (8c) ⟶ (7) + $HClO_4$].

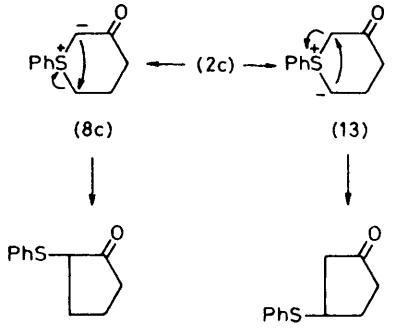
Many of the reactions described above implicate ylides and hence attempts were made to obtain these in a state of purity. The salt (2a) reacted rapidly with triethylamine, a reagent we have used successfully in the past [2] to generate ylides from both acyclic and cyclic β-oxosulphonium salts, but no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



(12) (5)

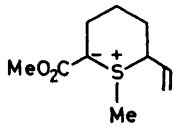
SCHEME 4

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 1 710 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 1 520 and

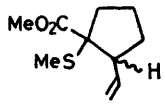


SCHEME 5

1 580 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 recently [11] reported an analogous ring contraction [(14) ⟶ (15)].



(14)



(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 synthesis [15] (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 chloride [16] and addition of these to etheral diazomethane under standard conditions [17] provided the requisite diazo-ketones. The diazo-ketones were further characterized as their adducts with triphenylphosphine.[18]

(a) 1-Diazo-3-phenylthiopropan-2-one (1a) (75%), m.p. 32—33 °C, (lit.,[4,19] a yellow oil) (from diethyl ether), $\nu_{max.}$ 2 100s (diazo) and 1 620s (CO) cm^{-1}; 1-(*triphenylphosphoranylidenehydrazono*)-3-*phenylthiopropan-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. $C_{27}H_{23}N_2OPS$ 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, $\nu_{max.}$ 2 080s (diazo) and 1 630s (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. $C_{28}H_{25}N_2OPS$ 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, $\nu_{max.}$ 2 100s (diazo) and 1 640s (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. $C_{29}H_{27}N_2OPS$ 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, $\nu_{max.}$ 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-*phenylthietanium 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%); $\nu_{max.}$ 1 812s (CO) and 1 080s br (ClO_4^-) cm^{-1}; 3-*oxo*-1-*phenylthiolanium perchlorate* (2b) (85%), m.p. 142—143 °C (Found: C, 43.1; H, 4.1; Cl, 12.7; S, 11.2. $C_{10}H_{11}ClO_5S$ requires C, 43.1; H, 3.9; Cl, 12.7; S, 11.5%); $\nu_{max.}$ 1 748s (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, $COCH_2\overset{+}{S}$), 5.84—6.18 (1 H, m, $\overset{+}{S}CH_2CH_2$), 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%); $\nu_{max.}$ 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, $COCH_2\overset{+}{S}$), 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%); $\nu_{max.}$ 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, $COCH_2S$), 6.0—6.4 (2 H, m, $\overset{+}{S}CH_2CH_2$), 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%); $\nu_{max.}$ 1 730s (CO) and 1 080s br (ClO_4^-) cm^{-1}; τ[$(CD_3)_2SO$] 2.1—3.0 (20 H, m, Ar), 4.53 (2 H, d, $C\overset{+}{H_2}PPh_3$, 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. $C_{28}H_{26}ClO_5PS$ requires C, 62.4; H, 4.8; P, 5.7; S, 5.9%); $\nu_{max.}$ 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%); $\nu_{max.}$ 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, $CH_2\overset{+}{P}$), 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%); $\nu_{max.}$ 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, $CH_2\overset{+}{P}$, 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 thiobenzamide. 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%); $\nu_{max.}$ 1 720s (CO), 1 080s br (ClO_4^-) cm^{-1}; τ [$(CD_3)_2SO$] 1.8—3.1 (10 H, m, Ar), 4.7 (2 H, s, $CH_2\overset{+}{S}$), 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%); $\nu_{max.}$ 3 160—2 800m br ($\overset{+}{N}H$) and 1 080s br (ClO_4^-) cm^{-1}; τ [$(CD_3)_2SO$] 0.81 (1 H, s, $\overset{+}{N}H$), 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 perchorate, 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%); $\nu_{max.}$ 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%); $\nu_{max.}$ 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, A_2 of A_2B_2 m, SCH_2CH_2), 7.01 (2 H, B_2 of A_2B_2, 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%); $\nu_{max.}$ 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, $CH_2CH_2CH_2$), 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. $C_{15}H_{20}O_2S_3$ requires C, 54.8; H, 6.1; S, 29.2%); $\nu_{max.}$ 1 720 (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, CH_2CH_2CO), 8.35 (4 H, m, $CH_2CH_2CH_2CH_2$), 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); $\nu_{max.}$ 1 770—1 730s 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. $C_{12}H_{14}O_3S$ requires C, 60.5; H, 5.9; S, 13.4%); $\nu_{max.}$ 1 740s 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. $C_{10}H_{10}OS$ requires C, 67.4; H, 5.6; S, 18.00%); $\nu_{max.}$ 1 680s (CO) and 1 620s (C=C) cm^{-1}; τ ($CDCl_3$) 2.7 (5 H, s, Ar), 3.2—4.4 (3 H, m, $CH=CH_2$), 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. $C_{16}H_{17}NOS$ requires C, 70.8; H, 6.3; N, 5.2%); $\nu_{max.}$ 3 400m (NH) and 1 700s (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%); $\nu_{max.}$ 1 735s br (CO) cm^{-1}; τ ($CDCl_3$) 2.7 (5 H, s, Ar), 5.4 (2 H, s, $-CH_2O-$), 6.9—7.7 (4 H, m, $CH_2CH_2CH_2$), 7.85 (3 H, s, Me), and 7.8—8.2 (2 H, m, $CH_2CH_2CH_2$).

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. $C_{22}H_{24}O_2S_2$ requires C, 68.8; H, 6.3; S, 16.7%); $\nu_{max.}$ 1 670s (CO) cm^{-1}; τ ($CDCl_3$) 2.74 (10 H, s, Ar), 3.2 (2 H, s, CH=CH), 6.9—7.4 (8 H, m, $CH_2CH_2CH_2$), and 7.9—8.2 (4 H, m, $CH_2CH_2CH_2$). 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. $C_{10}H_{10}O_3S$ requires C, 57.1; H, 4.8; S, 15.2%); $\nu_{max.}$ 1 725s br (CO) cm^{-1}; τ ($CDCl_3$) 2.69 and 2.71 (s, Ar), 1.87 (s, CHOCOH), 1.92 (s, CH_2OCOH), 3.7 (s, CHOCOH), 5.1 (s, CH_2OCOH), 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-phenylthiopropan-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); $\nu_{max.}$ 1 740s (CO) cm^{-1} and methyl 5-(phenylthio)-pentanoate (8c) (60%) $\nu_{max.}$ 1 740s (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-butyllithium (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 1 580m 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 (1 720 cm^{-1}). After 3 d at 18—21 °C the 1 520 cm^{-1} band had disappeared completely and the rearrangement product was 3-*phenylthiocyclopentanone* (72%) (Found: C, 67.6; H, 6.2; S, 16.6. $C_{11}H_{12}OS$ requires C, 68.6; H, 6.3; S, 16.7%); $\nu_{max.}$ 1 720s (CO) cm^{-1}; τ ($CDCl_3$) 2.7 (5 H, s, Ar), 6.8—7.7 (5 H, m, CHS, $CHCH_2CO$, and CH_2CH_2CO), and 7.8—8.4

(2 H, m, $CHCH_2CH_2$); *m/e* 192 ($\overset{+}{M}$, 29%), 136 ($C_8H_8\overset{+}{S}$, 66%), 124 ($C_7H_8\overset{+}{S}$, 100%), 123 ($C_7H_7\overset{+}{S}$, 44%), 110 ($C_6H_6\overset{+}{S}$, 67%), 109 ($C_6H_5\overset{+}{S}$, 80%), and 77 (C_6H_5, 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-phenylthiepan-1-ium-2-ide* (8d) (1.5 g, 47%), m.p. 119—120 °C (Found: C, 69.6; H, 6.9; S, 15.4. $C_{12}H_{14}SO$ requires C, 69.9; H, 6.8; S, 15.5%); $\nu_{max.}$ 1 550s (CO) cm^{-1}; τ ($CDCl_3$) 2.37 (5 H, s, Ar), 6.30 (1 H, s, $\overset{+}{S}\overset{-}{C}HCO$), 6.50 (2 H, m, $\overset{+}{S}CH_2CH_2$), and 7.6—8.4 (6 H, complex, $CH_2CH_2CH_2CH_2CO$); *m/e* 206 (M^+, 38%), 193 ($C_{11}H_{13}OS^+$, 6%), 165 ($C_{10}H_{13}S^+$, 5%), 123 ($C_7H_7S^+$, 100%), 110 ($C_6H_6S^+$, 46%), 109 ($C_6H_5S^+$, 23%), 97 (M^+, $C_6H_5S^+$, 55%), and 77 ($C_6H_5^+$, 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.

[0/1276 *Received*, 13*th August*, 1980]

REFERENCES

[1] B. M. Trost and L. S. Melvin, 'Sulphur Ylides,' Academic Press, 1975; R. Schmid and H. Schmid, *Helv. Chim. Acta*, 1977, **60**, 1361; E. Vedejs, J. P. Hagen, B. L. Roach, and K. L. Spear, *J. Org. Chem.*, 1978, **43**, 1185; E. Vedejs, M. J. Mullins, J. M. Renga, and S. P. Singer, *Tetrahedron Lett.*, 1978, **6**, 519; R. J. Gillespie, A. E. A. Porter, and W. E. Willmott, *J. Chem. Soc., Chem. Commun.*, 1978, **85**; R. M. Acheson and M. W. Cooper, *J. Chem. Soc., Perkin Trans. 1*, 1980, 1185.

[2] W. T. Flowers, G. Holt, and M. A. Hope, *J. Chem. Soc., Perkin Trans. 1*, 1974, 1116.

[3] J. B. Engberts and B. Zwanenburg, *Tetrahedron Lett.*, 1967, 831.

[4] V. Rosnati, G. Pagani, and F. Sannicolo, *Tetrahedron Lett.*, 1967, **46**, 4545.

[5] W. T. Flowers, G. Holt, C. P. Poulos, and K. Poulos, *J. Chem. Soc., Perkin Trans. 1*, 1976, 1757.

[6] K. Kondo and I. Ojima *Chem. Lett.*, 1972, 119.

[7] Von F. Krollpfeiffer, H. Hartmann, and F. Schmidt, *Annalen*, 1949, **563**, 15.

[8] L. C. King and F. M. Miller, *J. Am. Chem. Soc.*, 1949, **71**, 131.

[9] See A. W. Johnson, 'Ylide Chemistry,' Academic Press, 1966, 304, for compilation of references; 'Organic Compounds of Sulphur, Selenium and Tellurium,' ed. D. H. Reid, Specialist Periodical Report, The Chemical Society, London: (*a*) Vol. 1, 1970, 248; (*b*) Vol. 2, 1973, 288; (*c*) Vol. 3, 1975, for compilation of references.

[10] D. Seebach and T. Manfred, *Chem. Ber.*, 1976, **109**, 1601; I. Shionobu, T. Katsuhiko, T. Koji, and T. Genichi, *Agric. Biol. Chem.*, 1976, **40**, 1301.

[11] E. Vedejs, M. J. Arnost, and J. P. Hagen, *J. Org. Chem.*, 1979, **44**, 3230.

[12] S. Gabriel, *Ber.*, 1879, **12**, 1639.

[13] G. Kresze, W. Schramm, and G. Cleve, *Chem. Ber.*, 1961, **94**, 2060.

[14] J. Traynelys and R. F. Love, *J. Org. Chem.*, 1961, **26**, 2728.

[15] M. S. Newman and P. F. Beal, *J. Am. Chem. Soc.*, 1950, **72**, 5163.

[16] B. M. Trost and R. A. Kunz, *J. Org. Chem.*, 1974, **39**, 2648.

[17] See W. E. Bachmann and W. S. Struve, *Org. React.*, 1942, **1**, 38, for compilation of references.

[18] H. J. Bestmann, H. Buckschewski, and H. Leube, *Chem. Ber.*, 1959, **92**, 1345.

[19] V. Rosnati, G. Pagani, and F. Sannicolo, *Gazz. Chim. Ital.*, 1969, **99**, 152.

[20] Krafft Vorster, *Ber*, 1893, **26**, 2815.

[21] J. B. Jones and H. W. Middleton, *Can. J. Chem.*, 1970, **48**, 3819.