

Thionation Reactions of Diacylketene Thioacetals with the Lawesson Reagent and Analogues

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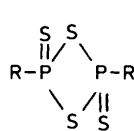
Attempted thionation of diacylketene thioacetals derived from dimedone with dithiadiphosphetane disulphides (the Lawesson reagent and analogues) led to the expected monothioacylketene thioacetals only when the thioacetal sulphur atoms formed part of a dithiolane or dithiane ring. Acyclic analogues readily underwent dealkylation and further reactions, giving a 1,2-dithiole-3-thione derivative as the main isolated product. Reaction of an acyclic ketene thioacetal with P_4S_{10} - Et_3N in acetonitrile at $-30^\circ C$ permitted the isolation of the primary dealkylation product, a dimedonedithiocarboxylate, in 44% yield. A phenoxaphosphorine derivative was isolated as a by-product in the synthesis of bis(phenoxyphenyl)-dithiadiphosphetane disulphide.

Bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulphide (**1a**), commonly known as the Lawesson reagent,¹⁻³ has been widely used as a powerful, mild, and versatile reagent for converting carbonyl into thiocarbonyl groups; the 4-phenoxy analogue (**1b**) has been claimed to be even milder.⁴ The bis(methylthio)dithiadiphosphetane disulphide (**1c**) (Davy's reagent) effects the transformation of carboxylic acids into dithioesters;⁵ it is also a mild and efficient thionating agent for amides and lactams.⁶

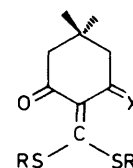
We have used the reagents (**1a** and **b**) to convert twisted 1,1-diacyl-2,2-diaminoethylenes into mono- and di-thio analogues in reasonable yields and with little decomposition.⁷ We now report similar reactions with diacylketene thioacetals (**2a-d**) derived from dimedone. Their propensity for thionation was much less, and side-reactions were more prevalent. Rauchfuss and Zank⁸ have shown by ^{31}P n.m.r. that thionation of benzophenone with (**1a**) leads to mixtures of oligomeric phosphorus derivatives. In our systems it seems that the substrates or their derivatives combine with the thionating agent or its products to form a multitude of labile new products. Chromatographic fractions, which on t.l.c. show mainly one product, display many new spots after careful work-up, and the products described here have mostly been obtained in low yields after lengthy chromatographic separations. The corresponding reactions with tetraphosphorus decasulphide in polar solvents in the presence of a basic catalyst^{9,10} were also examined. Our interest in the expected thione analogues of (**2a-d**) relates to an ongoing study of the effect of thioacyl groups as electron acceptors on rotational barriers in push-pull ethylenes.

Reactions of the thioacetals (**2a** and **b**) with (**1b**) in 1,2-dimethoxyethane at reflux or at room temperature under nitrogen gave the thiones (**2e** and **f**), both in 30% yield after purification by flash chromatography. In the same operations compounds (**3**) and (**6**) were isolated, as described later.

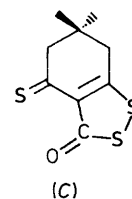
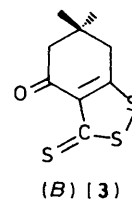
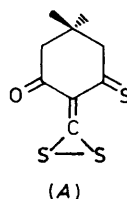
The reactions of (**2c** and **d**) with (**1a** or **b**) in inert solvents (toluene, dimethoxyethane, or tetrahydrofuran) at temperatures from $-30^\circ C$ to reflux led to complex mixtures. Work-up by flash chromatography on silica in general allowed the isolation of only one defined product (**3**) (red crystals) in yields of up to 44%. Mass spectroscopy and elemental analysis gave the molecular formula $C_9H_{10}OS_3$. N.m.r. spectra (Tables 1 and 2) can be reconciled in the first instance with any of the structures (A)-(C). So can a strong i.r. band at 1672 cm^{-1} . Gentric and Saumagne¹¹ report $\bar{\nu}(\text{CO})$ values for a number of 1,2-dithiol-3-



- (1) **a**: R = *p*-MeOC₆H₄
b: R = *p*-PhOC₆H₄
c: R = MeS



- (2) **a**: RR = [CH₂]₂, X = O
b: RR = [CH₂]₃, X = O
c: R = Me, X = O
d: R = CH₂Ph, X = O
e: RR = [CH₂]₂, X = S
f: RR = [CH₂]₃, X = S



ones in the range of $1677\text{--}1693\text{ cm}^{-1}$. However, the u.v. spectrum (Table 3) is much more similar to those reported for simple 1,2-dithiole-3-thiones than to the spectra of the 1-acyl-1-thioacylketene thioacetals (**2e** and **f**) (see later), which could be models for (A). Pfister-Guillouzo *et al.*¹² have recorded the spectra of 5-methyl-1,2-dithiole-3-thione in a variety of solvents and analysed them with the aid of CNDO/S calculations. A weak $n \rightarrow \pi^*$ band is observed at 514 nm in heptane (ϵ 105) and at 470 nm in methanol. Stronger bands are observed in heptane, at 411 (6 400), 333 (5 350), 252 (7 700), and 231 nm (5 500) with a shoulder at 265 nm. With due allowance for the conjugation effect of the carbonyl group expected for structure (B), this spectrum agrees well with that of (3). For unsubstituted 1,2-dithiol-3-one, λ_{max} is 311 nm (2 570);¹³ and it is unlikely that the conjugation with a thiocarbonyl group required for structure (C) would lead to a bathochromic shift of more than 100 nm. Inspection of the 1H and ^{13}C n.m.r. chemical shifts of compounds (**2a-e**) (Tables 1 and 2) leads to the conclusion that the CH₂ groups in structure (A) should have 1H and ^{13}C resonances at *ca.* δ 2.5 and 53 ($CH_2\text{-C=O}$) and 3.1 and 63 ($CH_2\text{-C=S}$), respectively. One of the CH₂ groups in (C) should also have its shift corresponding to $\text{-CH}_2\text{-C=S}$. The observed shifts, δ_H 2.52 and 2.94 and δ_C 44.3 and 53.1, exclude structures (A) and (C). Furthermore, the formation of a 1,2-dithiole-3-

† On leave from P.C.S.I.R., Karachi, Pakistan.

Table 1. ^1H N.m.r. spectra (300 MHz; δ values) of compounds (2), (3) and (7) in CDCl_3

Comp.	$\text{CH}_2\text{C}=\text{O}$	$\text{CH}_2\text{C}=\text{S}$	$\begin{array}{c} \text{S} \\ \\ \text{CH}_2\text{C}=\text{C} \end{array}$	$\text{C}(\text{CH}_3)_2$	SCH_3	$\text{S}-\text{CH}_2$	$\text{C}-\text{CH}_2-\text{C}$	OH	C_6H_5	Others
(2a)	2.52 (s)			1.07 (s)		3.36 (s)				
(2b)	2.45 (s)			1.03 (s)		2.86 (t)	2.32 (quint)			
(2c)	2.55 (s) ^a			1.10 (s)	2.55 (s) ^a					
(2d)	2.46 (s)			1.04 (s)		4.13 (s)			7.27 (m)	
(2e)	2.59 (m)	3.11 (m)		1.04 (s)		3.36 (m)				
(2f)	2.56 (s)	3.05 (s)		1.02 (s)		2.85 (t)	2.40 (quint)			
(3)	2.52 (s)		2.94 (s)	1.16 (s)						
(7)	2.45 (s)			1.10 (s)	2.56 (s)			17.32 (s)		2.66 [s, $\text{CH}_2-\text{C}(\text{OH})=$]

^a Resolved into two singlets (3:2) on addition of benzene.**Table 2.** ^{13}C N.m.r. spectra (75 MHz; δ values) of compounds (2), (3), and (7) in CDCl_3

Comp.	$\text{C}(\text{CH}_3)_2$	$\text{C}(\text{CH}_3)_2$	$\text{CH}_2\text{C}=\text{O}$	$\text{C}=\text{O}$	$\text{CH}_2-\text{C}=\text{S}$	$\text{C}=\text{S}$	$\begin{array}{c} \text{S} \\ \\ \text{CH}_2-\text{C}=\text{C} \end{array}$	$\begin{array}{c} \text{S} \\ \\ \text{CH}_2-\text{C}=\text{C} \end{array}$	$\begin{array}{c} \text{S} \\ \\ \text{CH}_2-\text{C}=\text{C} \end{array}$	$\text{C}=\text{CS}_2$	$\text{C}=\text{CS}_2$	SCH_3	SCH_2	$\text{C}-\text{CH}_2-\text{C}$
(2a)	28.3	31.4	51.3	193.8						185.7	121.8		37.3	
(2b)	28.4	30.4	52.3	194.1						191.4	128.4		31.5	24.7
(2c)	28.1	29.7	52.7	192.5						188.9	124.0	21.5		
(2e)	27.6	31.4	51.7	193.1	63.0	223.9				189.4	133.3		37.8/38.9	
(2f)	27.9	31.6	52.5	195.6	63.5	222.1				193.7	140.1		33.6	26.2
(3)	27.7	35.7	53.1	189.6		211.9	44.3	187.1	134.4					
(7)	28.0	30.4	52.1 ^a	193.6		222.1				<i>b</i>		20.3		

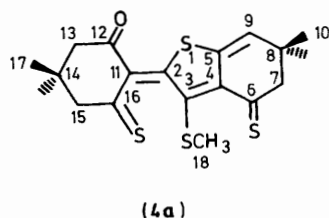
^a $\text{CH}_2-\text{C}(\text{OH})=\text{C}$ at 46.5. ^b $\text{C}-\text{CS}_2\text{CH}_3$ at 119.6.**Table 3.** U.v.-visible absorption spectra of compounds (2)–(4) and (7)

Comp.	Solvent	$\lambda_{\text{max.}}/\text{nm}$ (ϵ)
(2a)	Ethanol	339 (17 400), 308sh (7 300), 244 (11 500)
(2b)	Ethanol	352 (15 000), 298 (5 500), 246 (11 000)
(2c)	Ethanol	390sh (3 300), 347 (5 100), 270 (11 000), 250sh (9 500), 220sh (2 800)
(2e)	Ethanol	570 (36), 399 (15 500), 330sh (2 900), 293 (17 200), 260 (13 500)
	CH_2Cl_2 -hexane (1:9 v/v)	580 (38), 398 (13 200), 325 (2 900), 279 (15 600), 250 (14 500)
(2f)	Ethanol	585 (29), 419 (11 200), 298sh (10 700), 278 (11 300), 252 (5 900), 224sh (8 700)
	CH_2Cl_2 -hexane	594 (37), 418 (9 600), 288sh (11 300), 276 (12 000), 240 (8 200)
(3)	Ethanol	490sh (170), 414 (7 500), 332sh (6 200), 308 (9 000), 256 (11 000), 222 (19 000)
	CH_2Cl_2 -hexane (1:9 v/v)	532 (93), 424 (5 000), 341 (6 100), 307 (7 700), 257 (15 300), 220 (13 500)
(4)	Ethanol	512sh (6 500), 475sh (15 800), 445 (18 000), 325 (8 900), 258sh (4 500), 224 (13 200)
	CH_2Cl_2 -hexane (1:9 v/v)	644 (72), 512sh (6 000), 478sh (14 000), 438 (27 000), 314 (13 000), 244 (9 300)
(7)	Ethanol	420sh (115), 317 (11 700), 295sh (9 600), 251 (8 600)
	CH_2Cl_2 -hexane (1:9 v/v)	520sh (120), 329 (16 000), 249 (12 600)

thione on reaction between a 2-(bismethylthiomethylene)cyclohexanone and P_4S_{10} in boiling xylene has been reported.¹⁴ Therefore, we consider structure (B) well established.

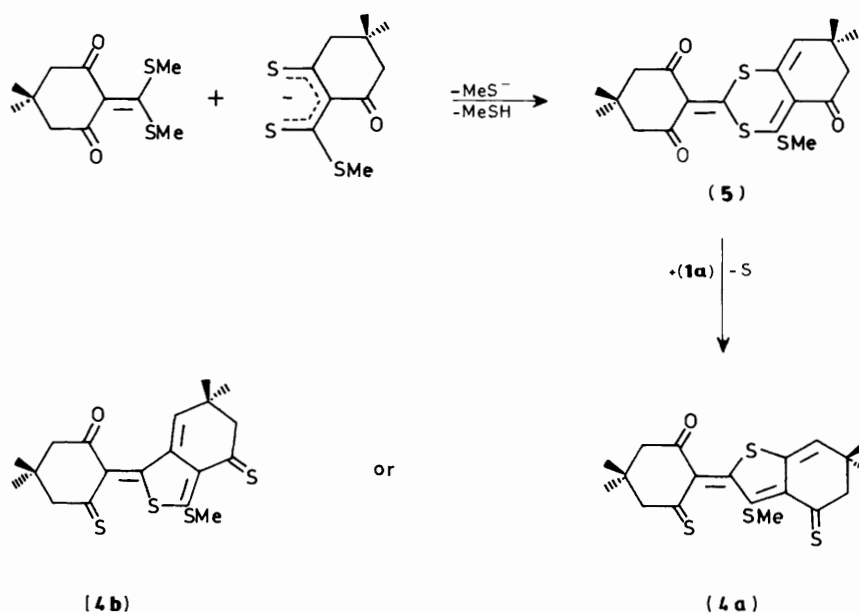
In one experiment, when (2e) reacted with (1b) in dimethoxyethane at room temperature, until t.l.c. indicated complete consumption of starting material (16 h), a new compound (4), was isolated in 3% yield together with 11% of (3). The molecular formula, $\text{C}_{19}\text{H}_{22}\text{OS}_4$, found by high resolution and fast atom bombardment (f.a.b.) mass spectroscopy, indicates that the molecule consists of two dimedone moieties bonded by a $\text{C}_2\text{S}_2\text{Me}$ fragment. The ^1H and ^{13}C n.m.r.

spectra (Scheme 1) show two different pairs of CH_3C groups, one CH_3S group, and three different CH_2 groups. ^1H N.m.r. also shows a vinylic proton (δ 7.54). Two low-field ^{13}C resonances (215.6 and 231.1) indicate $\text{C}=\text{S}$ groups, and one at 192.1, together with a strong i.r. band at 1675 cm^{-1} , a $\text{C}=\text{O}$ group. The presence of a $\text{C}=\text{S}$ group in a more extended planar conjugated system than those of (2d and e) is shown by the weak absorption band ($n \rightarrow \pi^*$) at 644 nm (ϵ 72) in the u.v.-visible spectrum of (4) in a non-hydroxylic solvent. A structure which accounts for these observations could have been formed by reaction between one molecule of (2c) and a partly demethyl-



Position	$\delta(^1\text{H})$	$\delta(^{13}\text{C})$
2		125.6
3		141.1
4		155.4
5		141.0
6		231.1
7/15	2.65/3.00	51.3(7), 58.7 (15)
8		37.6
9	7.54	125.1 ($^1J_{\text{CH}}$ 163.7)
10/17	1.11/1.37	27.3/28.0
11		140.3
12		192.1
13	2.46	43.5
14		34.1
16		215.6
18	2.78	20.1

Scheme 1. Tentative chemical shift assignments for (4a) [and for the corresponding atoms in (4b)]



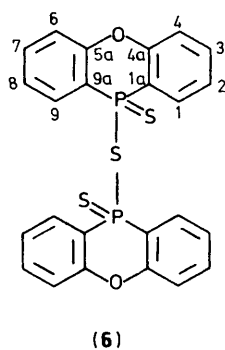
Scheme 2.

ated and thionated ambident anion derived from (2c). The first product could be the dithiane (5) (Scheme 2), which subsequently loses one sulphur atom and is dithionated to give one of the thiophene derivatives (4a or b). Extrusion of one sulphur atom from a dithiane structure to form a thiophene derivative has been observed for 1,2- and 1,4-dithi-ines,¹⁵ and it is also feasible for (5). A decision between structures (4a) and (4b) and analogous structures with permitted C=O and C=S groups could be sought by using the INADEQUATE pulse sequence, but the low yield of the compound made this experiment unfeasible. However, the large differences in ^1H and ^{13}C n.m.r. shifts for the $\text{CH}_2\text{-C=S}$ moieties make it unlikely that they are in the same ring. Furthermore, after 48 h at room temperature, the n.m.r. sample of (4) had developed a new set of signals close to the original ones and with *ca.* 1/3 of their intensity, indicating isomerization about the exocyclic double bond in (4a or b). Inspection of the coupled ^{13}C n.m.r. spectrum of (4) with and without selective decoupling of the vinylic proton resonance (H-9) allowed partial assignment of the ^1H and ^{13}C resonances (Scheme 1); however this does not distinguish between the alternative structures (4a) and (4b).

In several experiments where (1b) was used as the thionating agent, a product isolated by chromatography was eventually

identified as a by-product in the preparation of the reagent. It was obtained in 5–15% yield as light yellow crystals with the molecular formula $\text{C}_{24}\text{H}_{16}\text{O}_2\text{P}_2\text{S}_3$. The spectral data (Scheme 3) indicate a highly symmetrical structure containing four equivalent benzene rings, which according to the ^1H coupling pattern are *ortho*-disubstituted. The assignment of the ^{13}C resonances is based on a two-dimensional ^1H - ^{13}C correlation spectrum (HETCOR). The product is identified as 10,10'-thiobis(phenoxyphosphorine-10-thione) (6), the formation of which in the reaction between diphenyl ether and P_4S_{10} is not unexpected. The C-1a (C-9a) resonance appears as the X part of an ABX spectrum ($^{13}\text{C}^1\text{P}^2$); the J_{AX} and J_{BX} values of 87.3 and -2.7 Hz could be derived by simulation. Three other ^{13}C resonances appear as triplets with splittings of 3–6 Hz; they are interpreted as the X parts of deceptively simple ABX spectra with the phosphorus atoms as nuclei A and B. The mass spectrum is in agreement with the assigned structure, with peaks at 494 (M^{++}), 462 ($M^{++} - \text{S}$), 430 ($M^{++} - 2\text{S}$), 263 ($M^{++} - \text{C}_{12}\text{H}_8\text{OPS}$), 231 (base peak, $\text{C}_{12}\text{H}_8\text{OPS}$), and 199 ($\text{C}_{12}\text{H}_8\text{OP}$). An ^1H n.m.r. spectrum of the crude (1b) showed the characteristic resonance of H-1 (H-9) of (6) with an intensity corresponding to *ca.* 15% of other 2 H signals.

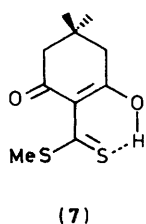
For comparison, some experiments were performed with



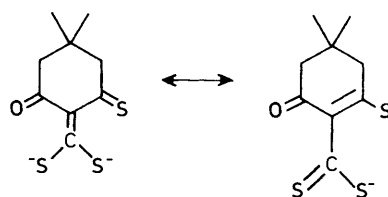
(6)

Scheme 3. Chemical shift assignments for (6)

Position	$\delta(^1\text{H})$	$\delta(^{13}\text{C})$
1,9	7.65 (m)	131.0 (t)
1a,9a		113.8 (X of ABX)
2,8	6.99 (t)	124.3 (t)
3,7	7.43 (d of t)	133.7 (s)
4,6	6.99 (d)	118.0 (t)
4a,5a		153.4 (s)



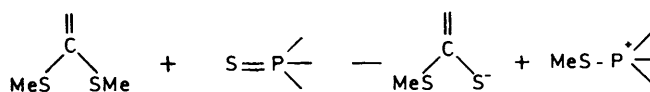
(7)



(8)

P_4S_{10} as thionating agent and (2c) as substrate. Reactions at room temperature in a variety of solvent systems in general led to complex product mixtures, from which only moderate quantities of (3) could be isolated by flash chromatography. However, reaction in acetonitrile-triethylamine (9:1 v/v) at -30°C gave a 44% yield of a new compound, $\text{C}_{10}\text{H}_{14}\text{O}_2\text{S}_2$, as orange-coloured prisms. The composition indicates the presence of a primary demethylation product of (2c), *i.e.* (7). This structure was corroborated by spectroscopic data (Tables 1–3). The ^1H n.m.r. spectrum shows a singlet for one proton at δ 17.32, indicating a strongly hydrogen-bonded hydroxylic proton. Evidently tautomerization is slow, since double ^1H and ^{13}C CH_2 resonances were observed, which coalesced to singlets on addition of a trace of DABCO (1,4-diazabicyclo-[2.2.2]octane). The i.r. spectrum shows a strong band at 1649 cm^{-1} ; the strong peak at m/z 183 in the mass spectrum corresponds to the fragment $M^{++} - \text{SCH}_3$, and the weaker peak at m/z 91 is due to $[\text{CH}_3\text{S}-\text{CS}]^+$. The u.v. spectrum of (7), with a weak band ($n \rightarrow \pi^*$) at 520 nm (ϵ 120) and a strong one ($\pi \rightarrow \pi^*$) at 329 nm (ϵ 16 000), corresponds well to that expected for a conjugated dithiocarboxylic ester. Ethyl dithioacetate shows λ_{max} 460 (ϵ 20) and 306 nm (ϵ 12 300), all in hydrocarbon solvent.¹⁶ In the aprotic reaction medium the anion of (7) must be formed and then protonated during work-up. The structure of (7) was proven by synthesis from dimedone by reaction in dimethylformamide with equivalent amounts of sodium hydride, carbon disulphide, and methyl iodide, in this order. It was isolated in 41% yield after chromatographic separation from (2c) and C-methylated dimedone.

The failure to observe thionation products of (2c and d) indicates that dealkylation is the fastest reaction. The slower reaction with P_4S_{10} permitted the isolation of (7), the first demethylation product of (2c). Since electron-releasing groups in conjugation with a carbonyl group facilitate its thionation, it is possible that thionated products of the anion of (7) are formed in the subsequent steps; one of these could be the intermediate proposed for the formation of (4). A later product in this sequence may be the dianion (8), which is a likely precursor of (3). The formation of (3) requires a two-electron oxidation, and the nature of the oxidant is not clear. Oxygen is



Scheme 4.

excluded since the reactions were performed under nitrogen. A disproportionation of (8) could explain why the yield of (3) never exceeded 50%, but the phosphorus compounds present cannot be excluded as oxidants.

The demethylation probably proceeds by nucleophilic attack by thiophosphoryl groups on the S-methyl groups (Scheme 4), which *per se* is unexpected, since it is known that nitrogen and carbon nucleophiles in general attack the double-bond carbon atom, displacing the SMe groups.^{17,18} However, whereas amines have been shown to attack the double bond carbon of ketene acetals, dimethyl sulphide attacks the sp^3 carbon.¹⁹ This may be explained in terms of the HSAB concept,²⁰ which can also be invoked to explain our dealkylation reactions.

Experimental

The ^1H and ^{13}C n.m.r. spectra were recorded with a Varian XL-300 spectrometer, and the u.v.-visible spectra with a Cary model 219 spectrophotometer.

2,4-Bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulphide (1a)²² and the 2,4-bis(4-phenoxyphenyl) analogue (1b)⁴ were prepared by literature methods. The 2,4-bismethylthio analogue (1c) was a commercial product (Fluka).

2-(4,4-Dimethyl-2,6-dioxocyclohexylidene)-1,3-dithiolane²¹ (2a) and 2-[bis(methylthio)methylene]-5,5-dimethylcyclohexane-1,3-dione²² (2c) were prepared by literature methods. 2-(4,4-Dimethyl-2,6-dioxocyclohexylidene)-1,3-dithiane (2b) was prepared like (2a) and obtained in 74% yield as yellow prisms, m.p. $196\text{--}198^\circ\text{C}$; for ^1H and ^{13}C n.m.r. data see Tables 1 and 2; m/z (70 eV) 256 (100%), 223 (48), 159 (34), 144 (35), 83 (60), 74 (45), 69 (20), 55 (75), and 53 (25); $\bar{\nu}_{\text{C=O}}$ 1615 cm^{-1} .

2-[Bis(benzylthio)methylene]-5,5-dimethylcyclohexane-1,3-

dione (**2d**) was prepared like (**2c**) in 86% yield as yellow-orange crystals, m.p. 99–100 °C, $\bar{\nu}_{C=O}$ 1 615 cm^{-1} .

2-(4,4-Dimethyl-2-oxo-6-thioxocyclohexylidene)-1,3-dithiolane (2e).—Compounds (**2a**) (0.004 mol) and (**1b**) (0.0035 mol) were refluxed under nitrogen in 1,2-dimethoxyethane (10 ml) for 0.5 h. After flash chromatography²³ on silica with hexane–ethyl acetate (85:15 v/v) as eluant, (**2e**) was obtained in 30% yield as dark green prisms, m.p. 157–159 °C; m/z (70 eV) 258 (3%), 230 (99), 174 (25), 170 (27), 82 (66), 70 (44), 69 (36), 55 (67), 45 (57), 41 (86), and 39 (100); $\bar{\nu}_{CO}$ 1 635 cm^{-1} (Found: C, 50.8; H, 5.3; S, 37.4. $C_{11}H_{14}OS_3$ requires C, 51.1; H, 5.5; S, 37.2%).

2-(4,4-Dimethyl-2-oxo-6-thioxocyclohexylidene)-1,3-dithiane (2f).—This was prepared like (**2e**), from (**2b**) by reaction for 4 h at room temperature; yield 30%, dark green prisms, m.p. 140–145 °C; m/z (70 eV) 272 (17%), 239 (45), 230 (21), 225 (75), 106 (20), 83 (50), 70 (25), 58 (22), 55 (62), 49 (35), 45 (55), 41 (100), and 39 (60); $\bar{\nu}_{C=O}$ 1 615 cm^{-1} (Found: C, 52.4; H, 5.9; S, 34.1. $C_{12}H_{16}OS_3$ requires C, 52.9; H, 5.9; S, 35.3%).

4,5,6,7-Tetrahydro-6,6-dimethyl-4-oxo-1,2-benzodithiole-3-thione (3).—Compounds (**2c**) (0.005 mol) and (**1b**) (0.008 mol) reacted in dimethoxyethane (25 ml) under nitrogen for 16 h at ambient temperature. T.l.c. showed that all the thioacetal (**2c**) was consumed, and flash chromatography with light petroleum (gradual elution with toluene as eluant) gave a 40% yield of (**3**) as red prisms, m.p. 167–169 °C; m/z (70 eV) 230 (33%), 82 (70), 77 (34), 69 (34), 55 (55), 45 (41), 41 (70), and 39 (100); $\bar{\nu}_{C=O}$ 1 672 cm^{-1} (Found: C, 46.5; H, 4.3; S, 41.4. $C_9H_{10}OS_3$ requires C, 46.9; H, 4.4; S, 41.8%).

2-(4,4-Dimethyl-2-oxo-6-thioxocyclohexylidene)-5,6-dihydro-6,6-dimethyl-3-methylthio-1-benzothiophen-4(2H)-one (4a).—Compound (**4a**) [or the isomer (**4b**)] was obtained from an experiment analogous to the foregoing in 3% yield as purple crystals, m.p. 171–172 °C; m/z (70 eV) 394 (17%), 379 (100), 331 (33), 171 (23), and 41 (30); $\bar{\nu}_{C=O}$ 1 675 cm^{-1} ; for n.m.r. data, see Scheme 1. (Found: M^+ , 394.055 \pm 0.005; isotopic M^+ /rel. int. 394/100; 395/25; 396/20; 397/4.5. Calc. for $C_{19}H_{22}OS_4$: M^+ 394.055; 394/100; 395/25.0; 396/20.9; 397/4.6).

10,10'-Thiobis(phenoxyphosphorine-10-thione) (6).—Compound (**6**) isolated in varying yield (max. 15%) as pale yellow prisms, m.p. 262–265 °C on flash chromatography of reaction mixtures with (**1b**) as starting material; m/z (70 eV) 494 (8%), 462 (4), 430 (7.2), 263 (3), 231 (100), 199 (30), and 152 (20); for ^1H and ^{13}C n.m.r. data, see Scheme 3 (Found: C, 58.4; H, 3.2; S, 20.4. $C_{24}H_{16}O_2P_2S_3$ requires C, 58.3; H, 3.3; S, 19.5%).

Methyl 2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-enedithiocarboxylate (7).—Dimedone (0.1 mol) in dry dimethylformamide (DMF) (50 ml) was slowly added to a slurry of NaH (0.1 mol) in DMF (50 ml) with stirring at -10°C under N_2 . After complete reaction, CS_2 (0.1 mol) in DMF (20 ml) was added during 15 min, and the red solution was allowed to come to room temperature and was then warmed to 50 °C for 0.5 h. After cooling to -10°C , MeI (0.1 mol) in DMF (50 ml) was

added during 0.5 h; the solution was then allowed to warm up, left overnight, and filtered from the precipitated NaI-DMF complex. Most of the solvent was removed by evaporation; the residue was diluted with water and extracted with CH_2Cl_2 , which was subsequently extracted with several portions of water, aqueous 0.5% HCl, and water again. Flash chromatography of the CH_2Cl_2 solution on t.l.c.-grade silica (Merck 60 H; 'mesh chromatography'²⁴) with toluene–ethyl acetate (9:1 v/v) as mobile phase gave (**7**) as yellow prisms (9.5 g, 41%), m.p. 92–94 °C [with (**2c**) (2.0 g, 8%) and 2,5,5-trimethylcyclohexane-1,3-dione (3.0 g, 20%) as isolated by-products]; m/z (70 eV) 230 (74%), 183 (89), 127 (65), 99 (27), 85 (80), 83 (100), 69 (22), 67 (25), 55 (38), 41 (79), and 39 (30) (Found: C, 51.6; H, 6.0; S, 27.8. $C_{10}H_{14}O_2S_2$ requires C, 52.1; H, 6.1; S, 27.8%).

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