

STUDIES ON ORGANOPHOSPHORUS COMPOUNDS—XL†

REACTIONS OF KETONES WITH 2,4-BIS(4-METHOXYPHENYL)- 1,3,2,4-DITHIADIPHOSPHETANE 2,4-DISULFIDE

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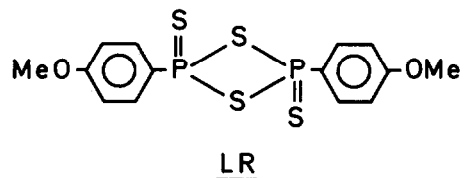
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(Received in the U.K. 23 July 1981)

Abstract—Cyclohexanone and cyclopentanone react with 2,4-bis-4-methoxyphenyl-1,3,2,4-dithiadiphosphetane 2,4-disulfide (Lawesson Reagent (LR)) at 80° with formation of new spiro-1,3,5,2-trithiaphosphorines **1** and **2**, respectively. 2-Methyl and 2-phenylcyclohexanone also react with LR at 80° producing the enethiols **3** and **4**, which on storage are transformed into the sulfides **5** and **6**. Unsaturated cyclohexanones **7–9** are transformed into the corresponding thioketones **10–12** after reactions with LR at 60° for a few hours. 2-Hydroxyketones react with LR with formation of 1,3,2-oxathiaphospholes and similarly a 2-aminoketone gave a 1,3,2-thiazaphosphole. Aromatic ketones, reacted with LR to give corresponding thioketones. Thiofluorenone dimerized to form the cyclic disulfide **31**, as proved by X-ray analyses.

Syntheses of aliphatic thioketones from the corresponding ketones and H₂S/HCl have been attempted since the end of the last century,^{1,2} and during the last few years new synthetic methods have been developed.^{3–10} Detailed UV, ESR and NMR investigations have been performed^{11–14} and also complex reactions of α,β -unsaturated thioketones have been reported.¹⁵

The advantage of the Lawesson reagent, LR, as a thiation agent has been demonstrated for a great variety of carbonyl compounds¹⁶ also including a limited number of ketones.^{17,18} Therefore, we also felt prompted to study reactions of LR with alicyclic ketones and α -hydroxy and α -amino ketones, as reported in this paper.



Thiofluorenone is known to dimerize but the structure of the dimer has been discussed without convincing proof.^{19–21} Here we also present the X-ray analyses of spiro[9H-fluorene-9,3'(10'bH)-fluoreno[9,1-cd][1,2]dithiin] obtained from treatment of fluorenone with LR.

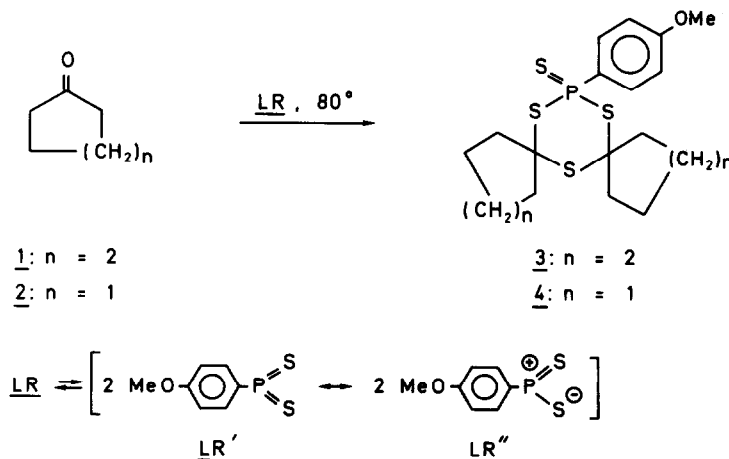
†For part XII see R. Shabana, J. B. Rasmussen and S.-O. Lawesson, *Bull. Soc. Chim. Belg.* **90**, 103 (1981).

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RESULTS AND DISCUSSION

Cyclohexanone and cyclopentanone react with LR at 80° in toluene and the new and unexpected 1,3,5,2-trithiaphosphorins **3** and **4** can be isolated in 50–60% yields. Compound **3** (or **4**) is an addition product of 2



moles of 1 (or 2) and one mole of LR' (LR''). 3 and 4 were characterized by ^1H , ^{13}C and ^{31}P NMR, IR, MS and elemental analyses. In the ^1H NMR spectra all methylene groups except one absorb between 1.3 and 2.8 ppm. In 4 one CH_2 -signal is shifted downfield to 3.3 ppm and this shift might be induced by the vicinity of the P=S sulfur atom.^{22,23} The ^{31}P NMR chemical shifts are δ 60.3 and 59.4 for 3 and 4, respectively.

In the ^{13}C NMR spectrum the quaternary carbon atoms (S-C-S) absorb at 66.1 ppm (3) and 68.2 ppm (4) and $^2J_{\text{PC}}$ is 4.0 Hz. The IR spectra of 3 and 4 are practically superimposable, but no specific P-S or P=S vibrations can be assigned. The mass spectrum of 4 shows *m/e* 402 corresponding to M^+ and the most important fragmentation consists of loss of one or two cyclopentanethione moieties ($\text{M}^+ - 100$ and $\text{M}^+ - 200$).

The formation of 3 and 4 is assumed to involve thiation of 1 and 2 to the corresponding cycloalkane-thiones which are known to trimerize within a few hours.²⁴ However, no trimer was isolated. As the thiation reactions of LR seem to be very complex, no detailed mechanistic suggestions are presented but it should be noted that we have been unable to reproduce published ^{31}P NMR data²⁶ of LR. A spectrum (CDCl_3) showed more than 10 peaks, indicating different P-containing species (LR, LR', LR'' and others). LR' and LR'' have never been isolated but a recent paper²⁵ reports on tricoordinated, pentavalent phosphorus compounds as intermediates and these could easily account for the formation of 3 and 4.

2-Methylcyclohexanone 5 and 2-phenylcyclohexanone 6 react with LR at 80° within 3 hr to form the enethiols 7 and 8 of the corresponding thioketones. The formation of the enethiols is in accordance with the result of the reaction of dibenzylketone with LR which led to 1,3-diphenyl-1-propene-2-thiol.¹⁸ Several other benzylic ketones, i.e. benzylethylketone and benzylmethylketone, were reacted with LR but no products could be isolated. After some days at room temp the oily enethiols 7 and 8 showed precipitation and column chromatography yielded the sulfides 9 and 10 as confirmed by spectroscopy and elemental analyses.

The structures 7 and 8 are mainly based on the fact that an SH is found at δ 2.65 and 2.70 for 7 and 8,

respectively. The four methylene groups result in two multiplets at δ 1.80 and 2.30 in all compounds 7-10 and no vinylic signals were found which proves the position of the double bond. The mass spectra of 7 and 8 showed M^+ as the base peak and intense peaks were found at $\text{M}^+ - \text{SH}$.²⁷ Compounds 7 and 8 are both reddish oils as already described by Mayer²⁸ and the colour is believed to be due to a small content of the thioketone. It is suggested that the formation of 9 and 10 involves an attack of the enethiol on a thioketone molecule and after loss of H_2S the sulfide is formed. A similar mechanism has been suggested for the addition of enethiols to ketones.²⁹

Compounds 9 and 10 gave intense peaks for the molecular ions but this could not exclude the disulfides as these are known to lose sulfur upon electron impact.³⁰ Elemental analyses of 9 and 10 showed that only one sulfur atom was present. ^1H and ^{13}C NMR spectra of the sulfides were practically identical with those of the enethiols except for the fact that the SH-absorption disappeared in the ^1H NMR spectrum.

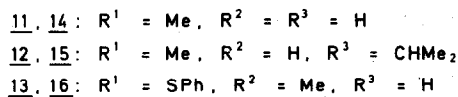
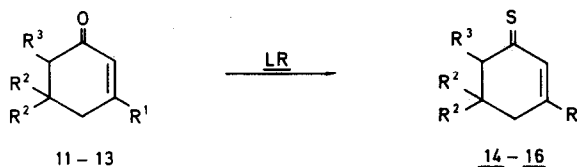
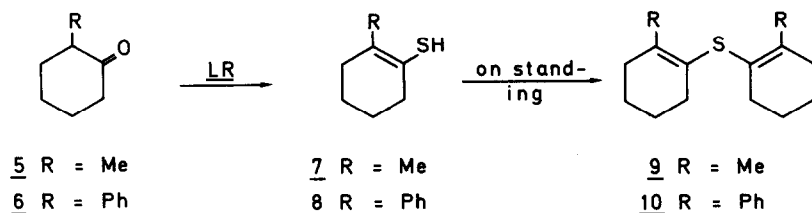
For some ketones our attempts to use LR as thiation agent failed. In the case of 2,2,5,5-tetramethylcyclopentanone and di-*t*-butylketone no thioketones could be isolated after reaction with an excess of LR at 140° for 24 hr. The sterical hindrance at the carbonyl group is believed to prevent the reaction.

Also several simple ketones, i.e. octanone and diisopropylketone, were reacted with LR but in our hands no products could be isolated.

The α,β -unsaturated cycloalkanethiones, 14-16, were obtained in good yields from the corresponding ketones and LR after reaction at 60° for a few hours.

The thioketones are red or violet and only the vinylous dithioester 16 was stable upon standing in the cold. The thiocarbonyl carbons absorbed in the region 230-245 ppm which, as expected,³¹ is at somewhat higher field than saturated aliphatic thioketones.¹⁸ The mass spectra of 14-16 showed M^+ to be the base peak in all cases.

Acyclic α,β -unsaturated ketones, such as 1,3-diphenyl-2-propen-1-one (chalcone), react with LR at 60° in toluene but very complex reaction mixtures were obtained and no products could be isolated and



characterized.¹⁵ When the reaction was carried out at low temperature in CH_3CN a 1:1 adduct between LR' and chalcone could be isolated in a high yield, and from the NMR spectra it is concluded that a mixture of **17** and **18** is present.¹⁷ The ^1H NMR spectrum shows four signals at δ 4.71 and four signals at δ 5.51 integrating as one proton totally. This is interpreted as the signals of C(4)-H of **17** and C(6)-H of **18**. Both these protons show a coupling of 3.3 Hz to the ^1H at C(5) and a coupling of 6.0 Hz to the ^{31}P nucleus. The ^{13}C NMR spectrum (20 MHz) is very complex but it shows two doublets for C4/C6 at δ 46.2 and δ 47.1 and also at δ 105.3 and δ 107.3 two doublets are observed. These are assigned C(5) in **17** and **18** (J_{PC} 10.6 and 9 Hz, respectively).

α -Hydroxy- and α -aminoketones **19–21** react with LR with formation of the oxathiaphospholes **22–23** and the thiazaphosphole **24**, respectively.

The yields were low (10–35%) and in the case of 5-hydroxy-4-octanone (butyroid) the main product was **25**. In the ^{13}C NMR spectrum of **22**, C(4) and C(5) absorb at δ 141.9 (6.0) and 132.2 (6.5) with the coupling constants to ^{31}P given in the brackets. In **23** the values are δ 144.3 (5.9) and 126.1 (6.5).

The structure of **25** is furnished by the ^1H NMR spectrum where the C(5)-H absorbs at 5.0 ppm. In case the double bond was located at C(5) a ^1H on C(4) would resonate at δ 4.3.³² Because of two asymmetric centres in **25** (C(5) and P) and because of the possibilities of *Z*, *E*-isomerism **25** is found to be present as a mixture of isomers which could not be separated in our hands. Also **24** is a mixture of isomers (asymmetric centres at N and P). The ^{31}P NMR shifts ranged from 90 ppm (**24**) to 111 ppm (**22**) which is in accordance with literature values.³³

LR is in most cases the reagent of choice when preparing pyranthiones from pyranones.³⁴ Xanthone **26** yielded xanthione **27** quantitatively upon treatment with LR at 80° . We have earlier reported¹⁸ that benzanthrone **28** gave a dimer of the corresponding thioketone when reacted with LR . We have now been able to show that

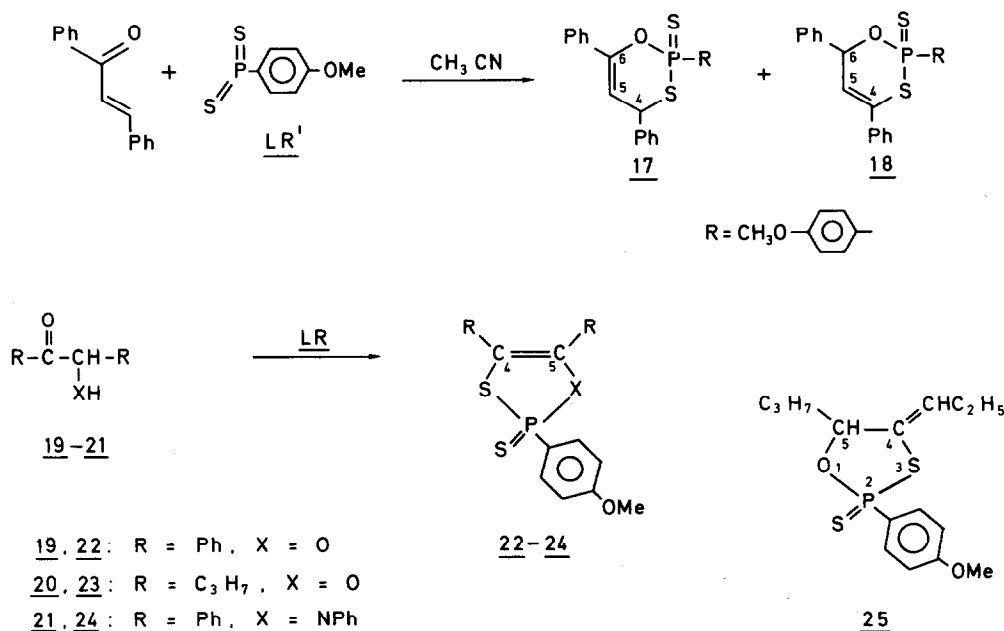
the product is, in fact, a monomeric thioketone as the ^{13}C NMR spectrum of **29** shows a thiocarbonyl signal at 215 ppm which is so broad that we were not able to identify it in the usual way. However, integration in the region 225–200 ppm showed it to be present at the value which is predicted by the linear relation correlating the $>\text{C}=\text{O}$ carbon of a ketone and the $>\text{C}=\text{S}$ of the corresponding thioketone.¹⁸ As a ^1H NMR spectrum recorded at -15° shows a broadening of all the ^1H peaks we assume that some kind of association of the molecules is taking place at low temperature.

When fluorenone **30** is allowed to react with LR at 80° the initial product is the dark green thioketone **31**.¹⁹ When the reaction mixture is allowed to stand overnight the colour changes from green to yellow and column chromatography yields 5% of **32** and also 55% of the yellow dimeric thiofluorenone **33**²¹ the structure of which was determined by X-ray diffraction methods; details of the analysis are given in Experimental. Figure 1 is an ORTEP drawing of the molecule, showing the atomic labelling. Pertinent structural parameters are listed in Table 1.

The dimer molecule consists of two fluorenylidene groups linked by a disulfide bridge between the aliphatic carbon atoms in 9-position (C13 and C26) and also by a bond between the carbon atom in 9-position (C13) in one group and a carbon atom in 1-position (C24) in the other. The disulfide linkage is therefore a part of a 6-membered ring which bridges the fluorenylidene groups.

The bonding parameters observed for the fluorenylidene groups fall into the range of accepted values for such an aromatic ring system. The atoms comprising one of the fluorenylidene groups (C1–C13) are co-planar within the experimental error whereas there is a significant degree of puckering at C26 of the other fluorenylidene group. Atom C26 is displaced by 0.14 Å from the least squares plane calculated through atoms C14, C19, C20 and C25. The dihedral angle between the two tricyclic rings is 84° .

The conformation about the disulfide bond in the 6-



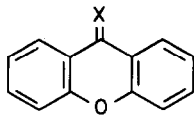
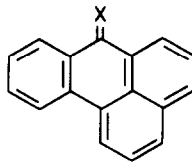
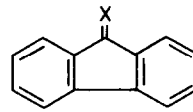
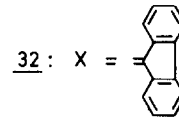
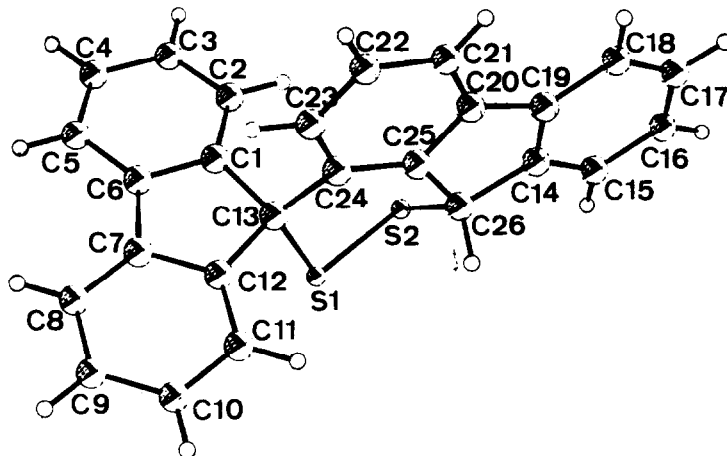
26: X = O27: X = S28: X = O29: X = S30: X = O31: X = S32: X =

Fig. 1. ORTEP plot of spiro[9H-fluorene-9,3'(10'bH)-fluoreno[9,1-cd][1,2]dithiin].

Table 1. Structural data for **31**. The numbering of atoms is given in Fig. 1. Estimated standard deviations (in parentheses) are calculated from the correlation matrix

Bond lengths (Å)				Bond angles (°)			
C6	C7	1.456 (4)	C1	C6	C7	109.0 (2)	
C1	C13	1.526 (3)	C6	C7	C12	108.8 (2)	
C12	C13	1.525 (3)	C7	C12	C13	110.1 (2)	
C19	C20	1.466 (3)	C12	C13	C1	101.7 (2)	
C14	C26	1.509 (3)	C13	C1	C6	110.5 (2)	
C25	C26	1.511 (3)	C14	C19	C20	109.2 (2)	
C13	C24	1.530 (3)	C19	C20	C25	108.5 (2)	
C13	S1	1.856 (2)	C20	C25	C26	109.1 (2)	
C26	S2	1.823 (2)	C25	C26	C14	103.7 (2)	
S1	S2	2.047 (1)	C26	C14	C19	108.7 (2)	
Average C(Ar)-C(Ar) 1.389(19) ^a				C13	S1	S2	103.9 (1)
				S1	S2	C26	93.9 (1)
				S2	C26	C25	110.3 (1)
				C26	C25	C24	129.9 (2)
				C25	C24	C13	124.4 (2)
				C24	C13	S1	113.7 (2)
				Average C(Ar)-C(Ar)-C(Ar) 120(1) ^a			
Torsion angles (°)							
C1	C6	C7	C12	1.8 (3)			
C6	C7	C12	C13	-1.7 (3)			
C7	C12	C13	C1	0.9 (2)			
C12	C13	C1	C6	0.2 (2)			
C13	C1	C6	C7	-1.2 (2)			
C14	C19	C20	C25	-0.1 (3)			
C19	C20	C25	C26	5.8 (3)			
C20	C25	C26	C14	-8.8 (2)			
C25	C26	C14	C19	8.7 (2)			
C26	C14	C19	C20	-5.6 (3)			
C26	C25	C24	C13	-10.6 (4)			
C25	C24	C13	S1	13.1 (3)			
C24	C13	S1	S2	-42.9 (2)			
C13	S1	S2	C26	63.2 (1)			
S1	S2	C26	C25	-63.4 (2)			
S2	C26	C25	C24	43.1 (3)			

^aStandard deviation of mean value.

membered ring connecting the two fluorenylidene groups is constrained, in part, by the aromatic character of the C24–C25 bond. The sulfur atoms, S1 and S2, are respectively displaced 0.18 Å below and 0.98 Å above the least squares plane through atoms C13, C24, C25 and C26. The torsion angle about the S–S linkage is 63.2°.

In a separate experiment pure **33** was heated to 180° in the high boiling solvent Marlotherm S (b.p. 390°) and after separation by column chromatography a mixture of rubicene **35** and 9,9'-bis-9H-fluorenylidene **32** was isolated and characterized.

The presence of **32** and **35** was shown by hplc using authentic samples for comparison. Also a mass spectrum of the mixture showed *m/e* 328 and 326, and the mass spectrum of **32** does not give rise to a peak at *m/e* 326.

In a previous paper¹⁸ we reported that 2- and 4-benzoylpyridine upon treatment with LR did not yield the corresponding thiones. This is explained by the fact that LR reacts with the pyridine nucleus at 20° to form the betaine **34**³⁵ which was characterized by ¹H NMR. When **34** is heated to 80° with an excess of LR the reaction mixture turns green, but there are no spectroscopic proofs for the presence of the >C=S group, as attempts to set the thiobenzoylpyridine free by treatment with base led to polymerization.

EXPERIMENTAL

¹H, ¹³C and ³¹P NMR spectra, IR, UV and mass spectra were obtained as earlier described.^{36,37} Elemental analyses were carried out by Novo Microanalytical Laboratory, NOVO Industri A/S, Novo Allé, DK-2880 Bagsvaerd, supervised by Dr. R. E. Amsler or by Løvens Kemiske Fabrik, DK-2750 Ballerup. Silica gel 60 (Merck) was used for column chromatography. M.p.s and b.p.s are uncorrected. Starting materials were commercial or prepared as follows: LR available from Fluka AG, Buchs, Switzerland, or from Aldrich Chemical Co or prepared according to Ref. 18, 12,³⁸ 13,³⁹ 19–21,⁴⁰ and 28⁴¹ were prepared according to literature references.

X-Ray data. Crystals of dimeric thiofluorenone were obtained

by recrystallization from CH₂Cl₂. The specimen used for the X-ray experiments had dimensions 0.3 × 0.3 × 0.4 mm. Data were collected on a SYNTEX P1 four-circle diffractometer using graphite crystal monochromated MoK α radiation ($\lambda = 0.71069$ Å). Cell parameters were determined by a least squares fit to the diffractometer settings for 15 general reflections. Intensity data were recorded using the $\theta/2\theta$ scanning mode with a scan speed (2θ) of 3° min⁻¹ and a scan range from 0.9° below 2θ (α_1) to 1.1° above 2θ (α_2). The background counts were taken for 0.35 times the scan time at each end of the scan. Reflections in one quadrant of reciprocal space up to $\sin \theta/\lambda = 0.65$ Å⁻¹ were measured. Out of the 3146 reflections recorded 2676 with $I > 2.5\sigma$ (I) were retained for the structure analysis. Corrections were made for Lorentz and polarization effects, but not for absorption. Scattering factors used were those of Ref. 42 for S and C and of Ref. 43 for H. Descriptions of the computer programmes applied are given in Refs. 44 and 45.

Crystal data. Spiro[9H-fluorene-9,3'(10'bH)-fluorene]9,1-cd][1,2]dithiin, C₂₆H₁₆S₂, monoclinic. $a = 11.989(2)$ Å; $b = 11.564(1)$ Å; $c = 14.038(1)$ Å; $\beta = 100.77(1)^\circ$; $V = 1912.0(4)$ Å³, ($t = 19^\circ$). $M = 392.53$; $Z = 4$; $F(000) = 816$; $\mu(\text{MoK}\alpha) = 2.82$ cm⁻¹, $D_x = 1.364$ g cm⁻³. Space group $P 2_1/n$ (No. 14).

Structure determination. The structure was determined by direct methods and refined by standard Fourier and least-squares calculations. The refinements converged to a conventional R -factor of 0.036, $R_w = 0.040$ and $S = (\sum w\Delta F^2 / (\sum (n - m)))^{1/2} = 1.63$. The final atomic parameters are listed in Table 2. A list of observed and calculated structure factors is available from the authors.

General procedure for the reaction of ketones with LR

Ketone (0.01 mol) and 2.02 g (0.005 mol) of LR were heated in 10 ml of anhydrous benzene/toluene with stirring until no more of the starting material could be detected (tlc). After cooling to room temp the reaction mixture was evaporated on silica gel under reduced pressure and applied to a silica gel column using the eluent stated below. The reaction conditions (°C, hr) and the physical, spectroscopic and analytical data are given below. The ligroun used distilled below 45°. Chemical shifts of the 4-methoxyphenyl group: ¹H NMR (CDCl₃): δ 7.8 (2H, dd, ³J_{PH} 14, J_{HH} 9), 6.9 (2H, dd, ⁴J_{PH} 4, J_{HH} 9), 3.5 (3H, s) OCH₃. ¹³C NMR (CDCl₃): δ 164.1 (⁴J_{PC} 3 Hz), 134.8–135.5 (²J_{PC} 12–13 Hz), 124.0–130.5 (¹J_{PC} 74–112 Hz), 112.5–114.2 (²J_{PC} 17 Hz), 55.5 (–) OCH₃.

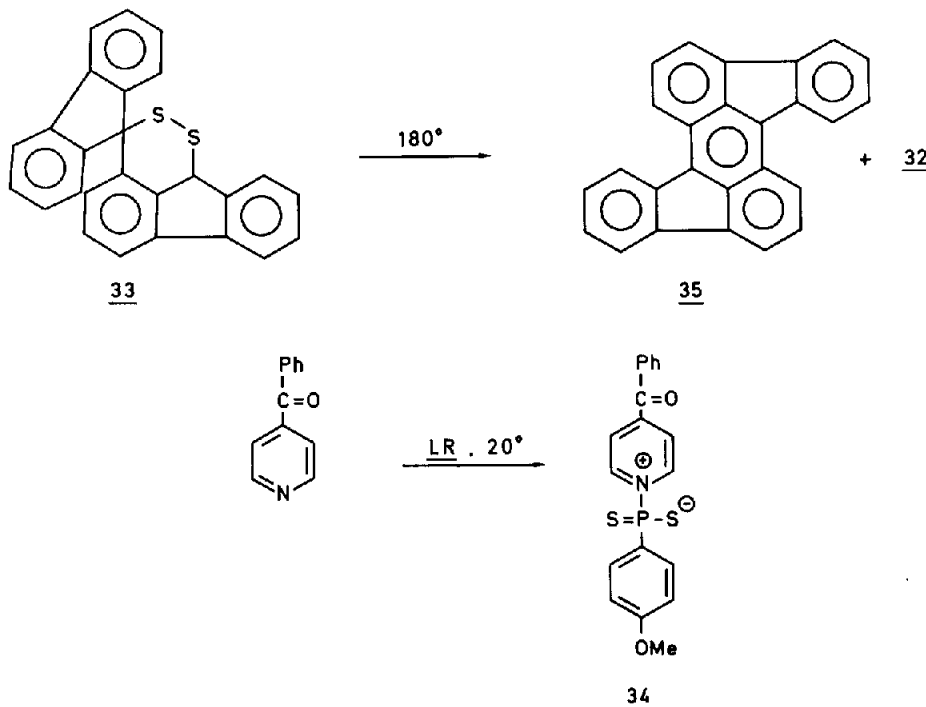


Table 2. Fractional atomic coordinates and thermal parameters with estimated standard deviations for 33. The anisotropic temperature factor is given by $\exp -2\pi^2 (U_{11}a^2 + U_{22}b^2 + U_{33}c^2 + 2U_{12}ab + 2U_{13}ac + 2U_{23}bc) + \dots$.

Atom	X	Y	Z	U11	U22	U33	U12	U13	U23
S1	.95499(5)	.68405(5)	.81377(4)	.0452(3)	.0375(3)	.0418(3)	.0071(3)	.0186(2)	.0017(3)
S2	.97897(5)	.68428(5)	.96150(4)	.0366(3)	.0462(3)	.0433(3)	.0036(3)	.0119(2)	.0015(3)
C1	.9204(2)	.9205(2)	.7825(2)	.0379(11)	.0335(12)	.0434(12)	.0012(9)	.0145(9)	-.0008(10)
C2	.9745(2)	.9790(2)	.8639(2)	.0567(14)	.0423(13)	.0508(14)	-.0052(12)	.0191(12)	-.0087(11)
C3	1.0313(2)	1.0813(2)	.8513(2)	.0657(16)	.0465(15)	.0720(18)	-.0121(13)	.0213(14)	-.0176(14)
C4	1.0313(2)	1.1249(2)	.7598(2)	.0629(17)	.0345(13)	.0929(22)	-.0090(12)	.0325(16)	-.0026(14)
C5	.9766(2)	1.0674(2)	.6784(2)	.0551(15)	.0433(14)	.0700(17)	.0064(12)	.0269(14)	.0148(13)
C6	.9212(2)	.9630(2)	.6896(2)	.0373(11)	.0378(12)	.0506(13)	.0066(10)	.0162(10)	.0063(11)
C7	.8617(2)	.8818(2)	.6185(2)	.0378(11)	.0473(14)	.0428(12)	.0100(10)	.0109(10)	.0051(11)
C8	.8435(2)	.8817(3)	.5179(2)	.0524(15)	.0704(19)	.0435(14)	.0099(14)	.0117(12)	.0094(13)
C9	.7874(3)	.7903(3)	.4681(2)	.0641(17)	.0892(23)	.0416(14)	.0142(17)	.0032(13)	-.0020(16)
C10	.7470(2)	.6994(3)	.5166(2)	.0579(16)	.0759(20)	.0556(16)	.0050(15)	-.0044(13)	-.0220(16)
C11	.7626(2)	.6985(2)	.6176(2)	.0500(14)	.0521(15)	.0564(15)	-.0005(12)	.0065(11)	-.0045(13)
C12	.8205(2)	.7898(2)	.6678(2)	.0397(12)	.0426(13)	.0408(12)	.0042(10)	.0075(10)	-.0009(10)
C13	.8559(2)	.8063(2)	.7770(2)	.0379(11)	.0341(11)	.0402(11)	.0009(10)	.0105(9)	.0019(10)
C14	.7998(2)	.6411(2)	1.0632(2)	.0421(12)	.0401(12)	.0430(12)	-.0062(10)	.0166(10)	.0003(10)
C15	.8440(2)	.5695(2)	1.1388(2)	.0519(14)	.0492(14)	.0513(14)	.0009(12)	.0160(11)	.0062(12)
C16	.7927(2)	.5666(3)	1.2199(2)	.0586(16)	.0676(18)	.0440(13)	-.0089(14)	.0107(12)	.0143(13)
C17	.6989(2)	.6349(3)	1.2242(2)	.0532(15)	.0776(18)	.0442(14)	-.0185(14)	.0202(12)	-.0028(14)
C18	.6548(2)	.7083(2)	1.1489(2)	.0432(12)	.0588(16)	.0536(14)	-.0076(11)	.0219(11)	-.0062(12)
C19	.7047(2)	.7110(2)	1.0670(2)	.0389(11)	.0407(13)	.0455(12)	-.0054(10)	.0153(10)	-.0023(10)
C20	.6771(2)	.7787(2)	.9774(2)	.0356(11)	.0394(12)	.0500(13)	-.0040(9)	.0152(10)	-.0044(10)
C21	.5941(2)	.8616(2)	.9484(2)	.0411(13)	.0541(15)	.0630(16)	.0056(11)	.0221(11)	-.0024(13)
C22	.5926(2)	.9181(2)	.8614(2)	.0420(13)	.0528(15)	.0715(17)	.0129(12)	.0137(12)	.0048(13)
C23	.6746(2)	.8954(2)	.8057(2)	.0447(13)	.0457(14)	.0560(14)	.0067(11)	.0125(11)	.0100(12)
C24	.7589(2)	.8126(2)	.8339(2)	.0359(10)	.0358(11)	.0412(11)	-.0002(10)	-.0002(10)	-.0015(10)
C25	.7556(2)	.7507(2)	.9179(2)	.0320(10)	.0351(11)	.0454(12)	-.0015(9)	-.0015(9)	-.0028(10)
C26	.8305(2)	.6531(2)	.9642(2)	.0417(12)	.0368(12)	.0451(12)	.0010(10)	.0010(10)	.0003(10)

Table 2. (Contd)

Atom	X	Y	Z	B	Atom	X	Y	Z	H
H2	.972	.984	.929	4.0	H3	1.072	1.122	.908	4.0
H4	1.071	1.197	.753	4.0	H5	.977	1.098	.612	4.0
H8	.872	.946	.483	4.0	H9	.775	.790	.398	4.0
H10	.706	.635	.480	4.0	H11	.735	.634	.653	4.0
H15	.909	.521	1.135	4.0	H16	.825	.517	1.275	4.0
H17	.664	.631	1.281	4.0	H18	.589	.758	1.153	4.0
H21	.539	.880	.989	4.0	H22	.533	.975	.839	4.0
H23	.673	.938	.745	4.0	H26	.818	.576	.928	4.0

Compound 3. 15 - (4 - Methoxyphenyl) - 7,14,16 - trithia - 15 - phosphadispiro[5.1.5.3]hexadecane 15-sulfide, 80°, 1 hr. Eluent $\text{CH}_2\text{Cl}_2/\text{ligroin}$ 1:1 v/v. Yield 1.10 g (51%). Oil. Analysis correct for $\text{C}_{19}\text{H}_{27}\text{OPS}_4$ (C, H). MS [*m/e* (%), rel int]: 430 (60, M), 316 (81), 203 (64), 202 (94), 200 (100). $^1\text{H NMR}$ (CDCl_3): δ 1.2–2.8 (20H, m) 10 CH_2 , 4- $\text{CH}_2\text{OC}_6\text{H}_4$ as above. $^{13}\text{C NMR}$ (CDCl_3): δ (J_{PC} if any): 66.1 (4.0) two S–C–S, 42.1 (broad), 24.8, 22.4, 21.9. 4- $\text{CH}_2\text{OC}_6\text{H}_4$ as above. $^{31}\text{P NMR}$ (CDCl_3): δ 60.3.

Compound 4. 13 - (4 - Methoxyphenyl) - 6,12,14 - trithia - 13 - phosphadispiro[4.1.4.3]tetradecane 13-sulfide, 80°, 1 hr. Eluent $\text{Et}_2\text{O}/\text{ligroin}$ 1:9 v/v. Yield 1.25 g (62%). M.p. 132–134°. Analysis correct for $\text{C}_{17}\text{H}_{23}\text{OPS}_4$ (C, H). MS [*m/e* (%), rel int]: 402 (60, M), 302 (81), 202 (95), 200 (100). $^1\text{H NMR}$ (CDCl_3): δ 1.6–2.8 (14H, m) 7 CH_2 , 3.25 (2H, m) CH_2 , 4- $\text{CH}_2\text{OC}_6\text{H}_4$ as above. $^{13}\text{C NMR}$ (CDCl_3): δ (J_{PC} if any): 68.2 (4.0) two S–C–S, 45.3 (6.2), 43.7, 24.3, 22.4. 4- $\text{CH}_2\text{OC}_6\text{H}_4$ as above. $^{31}\text{P NMR}$ (CDCl_3): δ 59.4.

Compound 7. 2 - Methyl - 1 - cyclohexenethiol, 80°, 2 hr. Eluent: $\text{CH}_2\text{Cl}_2/\text{ligroin}$ 1:1 v/v. Yield 0.85 g (66%). Oil (reddish). $^1\text{H NMR}$ (CDCl_3): δ 1.0–2.5 (11H, m) all others than SH, 2.75 (s, SH). $^{13}\text{C NMR}$ (CDCl_3): δ 136.2, 124.6, 32.9, 31.6, 24.2, 23.1, 21.3.

Compound 8. 2 - Phenyl - 1 - cyclohexenethiol, 80°, 3 hr. Eluent $\text{Et}_2\text{O}/\text{ligroin}$ 5:95 v/v. Yield 0.68 g (28%). Oil (reddish). MS [*m/e* (%), rel int]: 190 (100, M), 157 (27), 147 (32), 129 (30), 115 (21), 91 (37). $^1\text{H NMR}$ (CDCl_3): δ 1.80 (4H, m), 2.35 (4H, m), 2.65 (1H, s) SH, 7.30 (5H, s) Ph. $^{13}\text{C NMR}$ (CDCl_3): δ 143.2, 133.2, 128.4, 128.1, 126.9, 123.8, 34.6, 32.8, 23.8, 23.2.

Compound 9. Bis(2 - methyl - 1 - cyclohexene) sulfide. M.p. 101° (Et_2O). MS [*m/e* (%), rel int]: 222 (100, M), 207 (20), 165 (18), 151 (21), 129 (20), 128 (24), 127 (28). $^1\text{H NMR}$ (CDCl_3): δ 1.55 (4H, m), 1.82 (3H, s) CH_3 , 2.01 (4H, m). $^{13}\text{C NMR}$ (CDCl_3): δ 136.0, 124.8, 32.5, 31.6, 24.0, 23.3.

Compound 10. Bis(2 - phenyl - 1 - cyclohexene) sulfide. M.p. 86–8° (ligroin). Analysis correct for $\text{C}_{24}\text{H}_{26}\text{S}$ (C, H, S). MS [*m/e* (%), rel int]: 346 (100, M) all others <3%. $^1\text{H NMR}$ (CDCl_3): δ 1.65 (4H, m), 2.25 (4H, m), 7.10 (5H, s) Ph. $^{13}\text{C NMR}$ (CDCl_3): δ 143.6, 141.3, 128.6, 128.2, 127.7, 127.6, 33.6, 32.9, 23.8, 23.0.

Compound 14. 3 - Methyl - 2 - cyclohexenethione, 60°, 1 hr. Eluent: $\text{Et}_2\text{O}/\text{ligroin}$ 5:95 v/v. Yield (1.10 g (86%)). Violet oil. MS [*m/e* (%), rel int]: 126 (100, M), 111 (27), 98 (36), 93 (52), 91 (36). $^1\text{H NMR}$ (CDCl_3): δ 1.6–2.5 (7H, m), 3.00 (2H, m), 6.70 (1H, q, J_{HH} 1.5 Hz). $^{13}\text{C NMR}$ (CDCl_3): δ 237.3 (C=S), 154.6 (C-3), 137.8 (C-2), 46.0, 31.4, 24.5, 23.4.

Compound 15. 3 - Methyl - 6 - (1 - methylethyl) - 2 - cyclohexenethione, 60°, 1 hr (N_2). Eluent: $\text{Et}_2\text{O}/\text{ligroin}$ 2:98 v/v. Yield 0.41 g (25%). Violet oil. MS [*m/e* (%), rel int]: 168 (93, M), 153 (81), 126 (60), 125 (54), 93 (48), 92 (60), 91 (100). $^1\text{H NMR}$ (CDCl_3): δ 0.8–1.6 (7H, m), 1.7–2.6 (9H, m), 6.65 (1H, br. s.). $^{13}\text{C NMR}$ (CDCl_3): δ 241.5 (C=S), 152.0 (C-3), 138.2 (C-2), 59.2, 29.9, 28.7, 23.9, 23.7, 21.3, 18.8.

Compound 16. 5,5 - Dimethyl - 3 - phenylsulfenyl - 2 - cyclohexenethione, 60°, 0.75 hr. Eluent: $\text{Et}_2\text{O}/\text{ligroin}$ 1:3 v/v. Yield: 2.01 g (81%). M.p. 74–7° (Et_2O) red needles. Analysis correct for $\text{C}_{14}\text{H}_{16}\text{S}_2$ (C, H, S). MS [*m/e* (%), rel int]: 248 (100, M), 233 (20), 215 (6), 200 (13), 171 (16), 155 (11), 141 (18), 124 (20). $^1\text{H NMR}$ (CDCl_3): δ 1.00 (6H, s), 2.30 (2H, s), 2.70 (2H, s), 6.30 (1H, br. s.), 7.2 (5H, s). $^{13}\text{C NMR}$ (CDCl_3): δ 229.6 (C=S), 158.9 (C-3), 135.0 (C-2), 130.1, 129.7, 127.8, 59.4, 34.2, 27.3 (double int).

Compounds 17 and 18. 2.08 g of 1,3 - diphenyl - 1 - propen - 3 - one (chalcone) (0.01 mole) and 2.02 g of LR (0.005 mole) were dissolved in 8 ml of anhydrous CH_3CN . After stirring for 4 hr the precipitate was filtered off. Yield 3.35 g (82%). M.p. 126–128° (dec. green colour appears). $^1\text{H NMR}$ (CDCl_3): δ 3.90 (3H, s) OCH_3 , 4.71 (0.5H, dd, J 3.3 and 6.0 Hz), 5.51 (0.5H, dd, J 3.3 and 6.0 Hz), 5.95 (1H, d, J 3.3 Hz), 6.9–7.8 (14H, m) arom.

Compound 22. 4,5 - Diphenyl - 2(4 - methoxyphenyl) - 1,3,2 - oxathiaphosphole 2-sulfide, 80°, 12 hr. Eluent: $\text{Et}_2\text{O}/\text{ligroin}$ 1:1 v/v. Yield 1.20 g (30%). M.p. 116–118° (Et_2O). Analysis correct for $\text{C}_{21}\text{H}_{17}\text{O}_2\text{PS}_2$ (C, H, P, S). MS [*m/e* (%), rel int]: 396 (100, M), 380 (10), 264 (13), 210 (48). $^1\text{H NMR}$ (CDCl_3): δ 3.80 (3H, s), 6.95 (2H, dd, J_{PH} 3 Hz, J_{HH} 8 Hz), 7.25 (10H, m), 8.10 (2H, dd, J_{PH} 15 Hz, J_{HH} 8 Hz). $^{13}\text{C NMR}$ (CDCl_3): δ (J_{PC} if any): 163.7 (3.5), 141.9 (6.0), 133.9 (15.1), 132.2 (6.5), 130–127 6 c's, 125.2 (74.5), 132.2 (6.5), 130.2 (9.6), 114.0 (17.0), 55.3. $^{31}\text{P NMR}$ (CDCl_3): δ 103.4.

Compound 23. 4,5 - Dipropyl - 2(4 - methoxyphenyl) - 1,3,2 - oxathiaphosphole 2-sulfide, 80°, 1.5 hr. Eluent: $\text{CH}_2\text{Cl}_2/\text{ligroin}$ 1:1 v/v. Yield 0.33 g (10%) and 62 g (20%) of 23 (see below). Oil. MS [*m/e* (%), rel int]: 328 (100, M), 299 (41), 187 (20), 180 (33). $^1\text{H NMR}$ (CDCl_3): δ 1.00 (6H, two t) two CH_3 , 1.62 (4H, m) two CH_2 , 2.40 (4H, two t) $-\text{CH}_2-\text{C}-$, 3.90 (3H, s), 7.: (2H, dd, J_{PH} 3 Hz, J_{HH} 8 Hz), 7.97 (2H, dd, J_{PH} 15 Hz, J_{HH} 8 Hz). $^{13}\text{C NMR}$ (CDCl_3): δ (J_{PC} if any): 163.6 (3.0), 144.3 (5.9), 133.7 (15), 126.7 (125.5), 126.1 (6.5), 113.9 (16.5), 55.6, 30.3 (9.0), 29.9 (8.1), 22.3, 20.4, 13.4 (two CH_3). $^{31}\text{P NMR}$ (CDCl_3): δ .

Compound 24. 3,4,5 - Triphenyl - 2 - (4 - methoxyphenyl) - 1,3,2 - thiazaphosphole, 110°, 12 hr. Eluent: $\text{Et}_2\text{O}/\text{ligroin}$ 1:4 v/v. Yield 1.64 g (35%). M.p. 165–68° ($\text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2$). MS [*m/e* (%), rel int]: 471 (15, M), 455 (100), 180 (89). $^1\text{H NMR}$ (CDCl_3): δ 3.85 (3H, s), 6.8–7.3 (17H, m), 8.00 (2H, m). $^{13}\text{C NMR}$: Not interpreted due to mixture of isomers. $^{31}\text{P NMR}$ (CDCl_3): δ 91.3 and 86.3 (~4:1).

Compound 25. 2 - (4 - Methoxyphenyl) - 5 - propyl - 4 - propylidene - 1,3,2 - oxathiaphosphole 2-sulfide. As above (19). Oil. MS [*m/e* (%), rel int]: 328 (100, M), 295 (21), 187 (32). $^1\text{H NMR}$ (CDCl_3): δ 0.95 (6H, m) two CH_3 , 1.20–2.20 (6H, m) three CH_2 , 3.85 (3H, s) OCH_3 , 5.05 (1H, m) OCH , 5.55 (1H, m) $-\text{CH}=\text{}$, 6.80 (2H, m), 7.75 (2H, m). $^{13}\text{C NMR}$: Not interpreted due to mixture of isomers. $^{31}\text{P NMR}$ (CDCl_3): δ 100.8 and 98.7 (1:1).

Compound 27. 9H - Xanthene - 9 - thione, 80°, 0.5 hr. Eluent: $\text{Et}_2\text{O}/\text{ligroin}$ 2:98 v/v. Yield 2.01 g (94%). M.p. 157° ($\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ 4:1 v/v). Lit.²⁶ m.p. 158–59°.

Compound 29. 7H - Benz[de]anthracene - 7 - thione, 60°, 2 hr. Eluent: CH_2Cl_2 . Yield 2.20 g (90%). Brown powder. M.p. 132–34° (d). Lit.¹⁸ m.p. 132°.

Compound 31. 9H - Fluorene - 9 - thione, 80°, 10 hr (N_2). Intermediate work-up! Eluent: $\text{CH}_2\text{Cl}_2/\text{ligroin}$ 1:9 v/v. Yield: 1.40 g (71%). Green needles, m.p. 75° (ligroin). Lit.¹⁹ m.p. 75°.

Compound 32. 9,9' - Bis - 9H - fluorenylidene. Isolated with 33 (see below). Yield 0.16 g (5%). Orange needles. M.p. 188–89° (CH_2Cl_2). Lit.¹⁹ m.p. 188°. $^1\text{H NMR}$ (360 MHz, CDCl_3): δ 7.21 (H-2, H-7), 7.33 (H-3, H-6), 7.70 (H-4, H-5), 8.38 (H-1, H-8). $^{13}\text{C NMR}$ (90.52 MHz, CDCl_3): δ 141.32 (C-11, C-12), 141.02 (C-9), 138.29 (C-10, C-13), 129.14 (C-3, C-6), 126.81 (C-2, C-7), 126.72 (C-1, C-8), 119.86 (C-4, C-5).

Compound 33. Spiro[9H - fluorene - 9,3'(10'6'H) - fluoreno[9,1-cd][1,2]dithiin]. 1.80 g of 26 (0.01 mol) and 2.02 g of LR (0.005 mol) were heated to 100° for 10 hr under stirring. The mixture was allowed to cool to room temp and in the presence of air. Eluent: $\text{CH}_2\text{Cl}_2/\text{ligroin}$ 1:9 v/v. Yield: 1.20 g 29 (61%) (and 0.16 g 28 (see above)). M.p. 226–30° (d) ($\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$). Lit.²⁰ m.p. 229–31°.

Compound 34. 20°, 1 hr. Solvent CH_3CN or CH_2Cl_2 . Addition of Et_2O and/or ligroin yielded 3.01 g (78%) of the betaine. M.p. 114° (decompose, blue colour appears). Hygroscopic. $^1\text{H NMR}$ (CDCl_3): δ 3.65 (3H, s), 6.7 (2H, m), 7.5–8.1 (11H, m).

Compound 35. Rubicene, 0.18 g of 33 was dissolved in 2 ml of Marlotherm S (b.p. 390°, commercially available from Chemische Werke HÜLS, D-4660 Gelsenkirchen-Buer) and heated for 8 hr to 180° with stirring. After cooling to room temp the reaction mixture was applied to a silica gel column using $\text{CH}_2\text{Cl}_2/\text{ligroin}$ (4:1 v/v) as eluent. From the fractions containing Marlotherm 0.045 g of red and yellow needles precipitated. Hplc experiments proved the structures to be 32 and 35 as the retention times were identical with those of authentic samples.

Acknowledgements—We thank Prof. P. de Mayo for samples of 2,2,5,5 - tetramethylcyclopentanone and di - *t* - butylketone. We are grateful to Prof. H. Fritz, Ciba-Geigy, Basel, for running high-field NMR spectra. Samples of rubicene and 9,9' - bis - 9H - fluorenylidene from Prof. A. Schönberg are greatly acknowledged. A gift of Marlotherm S from HÜLS AG, Gelsenkirchen-Buer is highly appreciated. We thank the Faculty of Science for a grant to S.S and Danida for a fellowship to R.S.

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