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The Preparation of a Solubilized Form of Lawessons Reagent and Its Thionation Reactions

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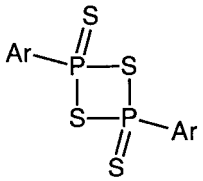
ABSTRACT: *2-tert-Butylanisole and P_4S_{10} react together to give 2,4-bis(3-tbutyl-4-methoxyphenyl) 1,3,2,4-dithiadiphosphetane 2,4-disulfide (LR*) which was characterized by X-ray crystallography. Comparative thionation reactions of LR* and a range of P-S compounds were investigated. It was found that LR*, in many cases, gives better yields of thionated complexes than Lawessons Reagent when the reactions are performed at room temperature.* © 1999 John Wiley & Sons, Inc. Heteroatom Chem 10:651–657, 1999

Lawesson's reagent (LR) (2,4-bis(4-methoxyphenyl) 1,3,2,4-dithiadiphosphetane 2,4-disulfide) has a rich and diverse chemistry [1–3].



LR

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Dedicated to Prof A. Schmidpeter on the occasion of his 70th birthday in recognition of his many significant achievements in phosphorus chemistry.

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We have previously reported [4–6] on the synthesis of NpP_2S_4, $MeONpP_2S_4$ $Fc_2P_2S_4$ and $Fc^*_2P_2S_4$ [Fc, ferrocenyl; Fc*, $(MeC_4H_4)Fe(MeC_4H_3)$] as well as cycloaddition reactions [7–9] of these species, which gives a range of compounds including **1–6**. In this article, we describe the synthesis of LR*, a solubilized analog of LR, together with testing of a range of phosphorus-sulfur compounds (shown below) as thionation reagents.

EXPERIMENTAL

The preparation of NpP_2S_4, $MeONpP_2S_4$ $Fc_2P_2S_4$, and $Fc^*_2P_2S_4$, 1–6, and $dppaS_2$ have been reported previously [7–10]. General experimental conditions and spectroscopic measurements are as previously described [9].

Synthesis of 2,4-bis(3-tbutyl-4-methoxyphenyl) 1,3,2,4-dithiadiphosphetane 2,4-disulfide (LR)*

2-Butylanisole (82.7 g, 504 mmol) and P_4S_{10} (26.9 g, 60.6 mmol) were heated in an oil bath at 120–140°C until no yellow solid remained (ca. 90 minutes). At this stage there was a brown heavy oil in the orange reaction mixture. The mixture was allowed to cool to room temperature and stirred to cause a mass of yellow solid to crystallize. After the addition of ether (100 mL), the solid mass was broken up, and the solid collected by filtration, washed with ether (100 mL), and dried in vacuum to give a yellow solid (37 g). This was dissolved in boiling toluene (100 mL) and rapidly filtered while hot through a Celite pad

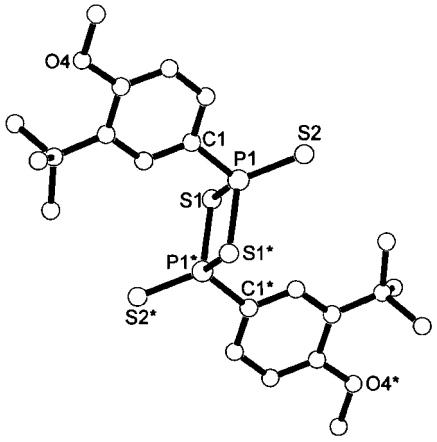


FIGURE 1 Molecular structure of LR*.

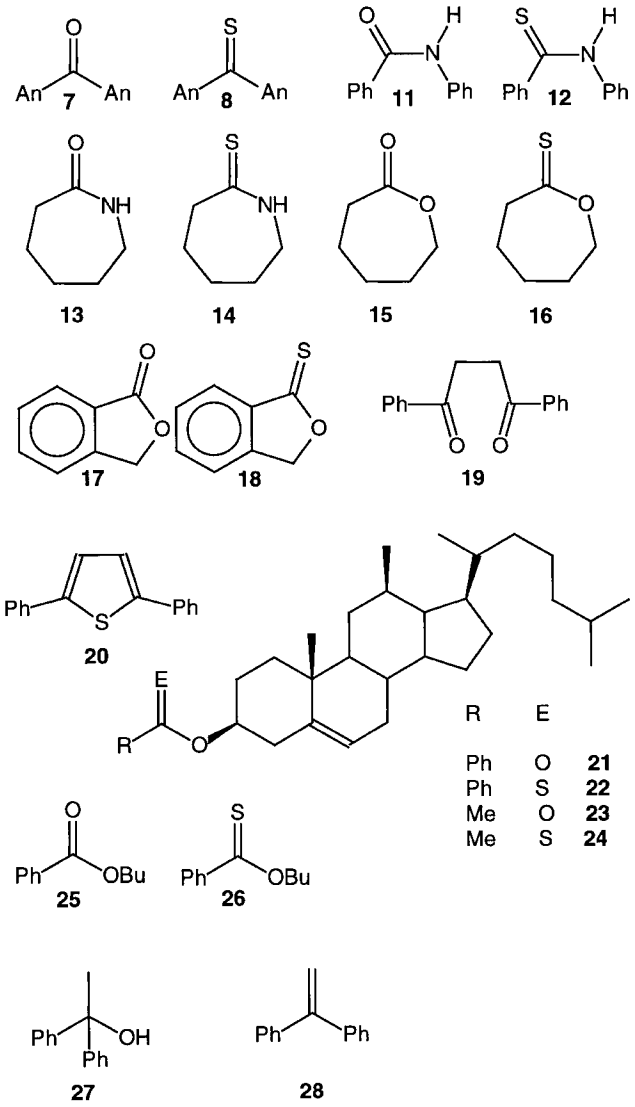
TABLE 1 Selected Bond Lengths (Å) and Angles (°) for LR*

S(1)-P(1)	2.107(2)	P(1)-S(1)-P(1)	87.21(7)
S(1)-P(1*)	2.114(2)	S(1)-P(1)-S(1)	92.79(7)
S(2)-P(1)	1.918(2)	S(1)-P(1)-S(2)	115.93(9)
P(1)-C(1)	1.793(5)	S(1)-P(1)-C(1)	107.1(2)
S(1)..(S1*)	2.91	S(1*)-P(1)-S(2)	116.15(9)
P(1)..(P1*)	3.06	S(1*)-P(1)-C(1)	106.5(2)
		S(2)-P(1)-C(1)	115.7(2)
		P(1)-C(1)-C(2)	120.0(4)
		P(1)-C(1)-C(6)	119.8(4)

TABLE 2 Results of the Screening of Possible Thionation Reagents

Phosphorus Compound	*Ketone*	*Length of Reaction (hours)*	*Yield of Thioketone (%)*
LR	**7**	1	100[a]
LR	**9**	1	78
NpP_2S_4	**7**	1	94
NpP_2S_4	**9**	1	17
$MeONpP_2S_4$	**7**	1	6
$Fc_2P_2S_4$	**7**	1	87[b]
$Fc_2P_2S_4$	**9**	1	66
LR*	**7**	1	98
LR*	**9**	1	100
Ph_3PS	**7**	15.5	0[a]
$dppaS_2$	**7**	16	0[a]
1	**7**	1	44[b]
2	**7**	16	trace[a]
3	**10**	15	98[c,d]
4	**7**	15.5	10
5	**7**	1.5	9
6	**7**	5	37[b,e]

[a]No or very little change found by TLC.
[b]Yield estimated by ^{1}H NMR spectroscopy.
[c]Yield measured by GC-MS.
[d]Yield based on the assumption that three atoms of sulfur per molecule of phosphorus compound are transferred to the substrate in exchange for oxygen atoms.
[e]Product was recrystallized from ethanol.



SCHEME 1 Substrates and thionated products.

into a large Schlenk flask. After the solution was cooled slowly the mother liquor was removed by canular filtration, and the resulting solid was dried in vacuo to give LR* (29.4 g, 57 mmol, 47%). δ_P (ppm) 18.2 s, δ_C (ppm) 162.7, 139.0 (d, 15 Hz), 132.0 (d, 17 Hz), 131.4 (d, 17 Hz), 129.8 (d, 95 Hz), 111.2 (d, 19 Hz), 55.5, 35.6, and 29.6. δ_H (ppm) 8.5 (1H, d, 19 Hz), 8.4 (1H, dd, 16.9 and 8.7 Hz), 7.1 (1H, dd, $^4J[^{31}P\text{-}^1H]$ = 5 Hz and $^3J[^1H\text{-}^1H]$ = 8.6 Hz), 3.97 (3H, s), and 1.47 (9 H, s). IR 3076w, 2997m, 2954s, 2937s, 2906s, 2866s, 2838m, 1584s, 1560m, 1492s, 1483s, 1454s, 1437m, 1391m, 1383m, 1361m, 1308m, 1297m, 1254vs, 1200m, 1181m, 1146m, 1115vs, 1092m, 1020s, 928w, 896w, 878m, 811s, 721m, 679vs, 647s, 599m, 579m, 546m, 533w, 497w, 460vs, 409sh, 367w, and 326w (cm^{-1}). MS(EI) *m/z* 412, 372, 340, 308, 285, 258 (M/2)+, 222, 195, and 158. Mo-

TABLE 3 Reactions of LR, LR*, and $Fc_2P_2S_4$ at Elevated Temperatures

Substrate	Product	Solvent	Yield with Thionation Reagent (%)		
			LR	*$Fc_2P_2S_4$*	*LR**
7	**8**	Petrol	9	1	27
11	**12**	Petrol/Toluene	14	trace	39
13	**14**	Toluene	100	66	—[a]
13	**14**	Toluene	99	90	90
15	**16**	Toluene	60	4	6[b]
17	**18**	Glyme	43	0	65
21	**22**	Glyme	48	0	34
23	**24**	Glyme	35	–	11
25	**26**	Toluene	23	–	41
27	**28**	Toluene	70	76	76

[a]Could not isolated pure by flash column chromatography.
[b]Not isolated pure; yield estimated by ^{1}H NMR spectroscopy or GCMS.

TABLE 4 δ_c NMR Values for Thioester Thiocarbonyl Carbons

Compound	δ_c(C=S) (ppm)
16	227.5
22	219.0
24	210.4
26	211.7
$C_6H_{13}C(S)OEt$	224.6
tert-BuC(S)OBn	224.1
PhC(S)OMe	212.2
PhC(S)OEt	211.4
PhC(S)O^{i}Pr	210.9
PhC(S)OBn	211.2
1-NpC(S)OEt	215.6
2-NpC(S)OEt	211.1

lecular ion found at 258.0307 amu ($^{12}C_{11}{}^1H_{15}{}^{16}O^{31}P^{32}S_2$ requires 258.0302 amu.error of 1.8 ppm). MS(FAB) *m/z* 765, 741, 735, 719, 539, 523, 516, 501, 493, 483, 471, 297, 275, 267, 259, 257 and many peaks below 250. MS(ES+) (*m/z*) 291 $(MeOH_2+[M/2])^+$, 259 $([M/2]H)^+$, and 111. MS(ES-) *m/z* 290, 289 $(MeO+[M/2])^-$, and 157. (Found: C, 51.4; H, 6.0; N, 0.0; S, 24.6, $C_{22}H_{30}O_2P_2S_4$ requires C, 51.2; H, 5.8; N, 0.0; S, 24.8%).

Synthesis of 2,4-bis(3-t-butyl-4-butoxyphenyl) 1,3,2,4-dithiadiphosphetane 2,4-disulfide (LR-t-Bu)

2-*tert*-butyl-1-butoxybenzene (6.65 g, 32 mmol) and P_4S_{10} (1.77 g, 4 mmol) were heated in an oil bath (120–160°C) for 40 minutes. After this time no P_4S_{10} remained, and the mixture was allowed to cool; below 140°C a large amount of crystalline solid formed. After cooling to room temperature the product was collected by filtration and washed with 40–60 petroleum ether (4 mL). δ_P (ppm) 18.4 (s), δ_H (ppm) 8.5 (0.42 H, m), 7.7 (1.37 H, m), 7.1 (0.21 H, m), 6.9 (0.74 H, m), 4.14 (t, 6 Hz) and 4.0 (m). Combined integration height for the last two peaks is (2H), 1.9 to 0.9 multiplets (17 H). MS(EI) *m/z* 300, 229, 181 and 61. IR 2998m, 1585m, 1560m, 1492m, 1483m, 1454m, 1437m, 1392w, 1383m, 1361m, 1308m, 1297m, 1254s, 1201m, 1181m, 1146m, 1114s, 1093s, 1020s, 897w, 878m, 811s, 722s, 679vs, 649s, 599m, 578m, 546m, 532w, 497w, and 460 (cm^{-1}). (Found: C, 59.8; H, 6.6; N, 0.0; S, 21.0 $C_{28}H_{42}O_2P_2S_4$ requires C, 56.0; H, 7.0; N, 0.0; S, 21.3%).

TABLE 5 Room Temperature Thionation Reactions

Substrate	Thionation Reagent	Solvent	Time	Product	Yield
7	LR	Toluene	140 min	NA	0
7	LR*	Toluene	140 min	8	36
7	LR	CH_2Cl_2	15 hours	8	84
7	LR*	CH_2Cl_2	15 hours	8	86
11	LR	Toluene	16 hours	29	28[b]
11	LR	CH_2Cl_2	22 hours	29	75
11	LR*	Toluene	15 hours	29	100
11	LR*	CH_2Cl_2	160 min	29	100
17	LR*	Toluene[d]	7 weeks	NA	0[c]
19	LR	Toluene	65 hours	15	77[a]
19	LR*	Toluene	43 hours	15	77[a]
21	LR*	Toluene	8 days	NA	0[c]
25	LR*	Toluene[d]	7 weeks	NA	0[c]

[a]4% of the furan was present in the thiophene product by GCMS.
[b]Not isolated pure, yield estimated by ^{1}H NMR or GCMS.
[c]Very little or no product detected by TLC.
[d]Stirred in CH_2Cl_2 for 7 days before the addition of toluene (10 mL).

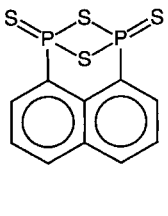
Reactions of Test Compounds with Thionation Reagents

Typically compounds were heated in a solvent with the thionation reagent before being allowed to cool. Flash column chromatography on SiO_2 was used to obtain the product as a pure compound.

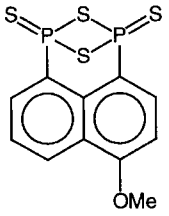
LR* (0.75 g, 3.1 mmol) and **7** (0.63 g, 1.6 mmol) were heated in petroleum ether (100 mL) for 30 minutes, chromatography (CH_2Cl_2/petroleum ether 4:6) gave **8**.

11 (0.615 g, 3.12 mmol) and LR (0.65 g, 1.61 mmol) was heated in petroleum ether (80 mL) mixed with toluene (20 mL) for 90 minutes. Chromatography (CH_2Cl_2/petroleum ether 4:6) gave **12**.

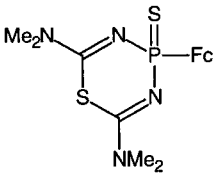
13 (119 mg, 1.05 mmol) and $Fc_2P_2S_4$ (300 mg, 5.36 mmol) were heated in toluene (10 mL) for 55 minutes. Chromatography (CH_2Cl_2) gave **14** as a white solid.



NpP_2S_4



$MeONpP_2S_4$



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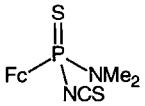

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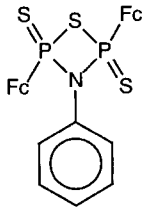

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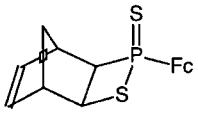

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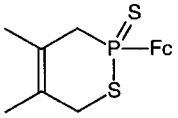

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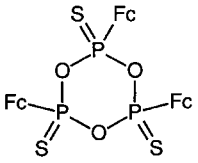

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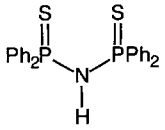
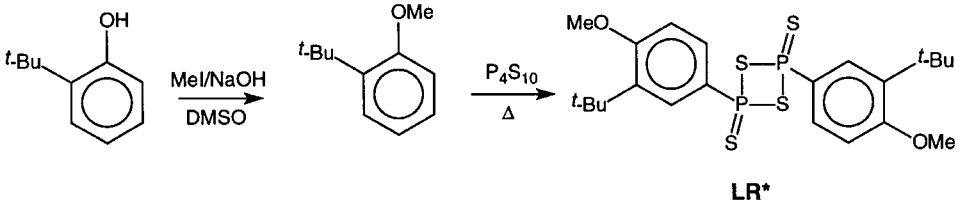


$dppaS_2$

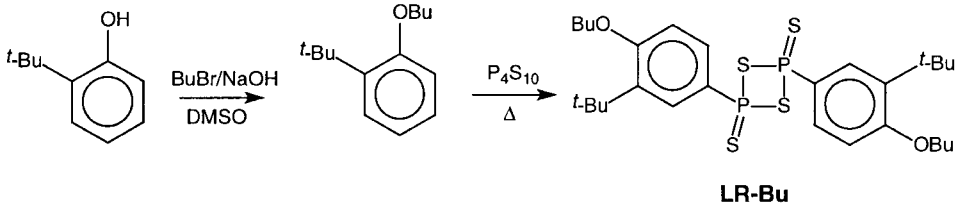
Ph_3PS

STRUCTURE 2



LR*

EQUATION 1



LR-Bu

EQUATION 2

15 (0.4 mL, 0.41 g, 3.6 mmol) and LR (0.78 g, 1.9 mmol) were heated in toluene (10 mL) for 30 minutes. Chromatography (11 g SiO_2, 60 mL petroleum ether followed by 25% ether in petroleum ether) gave **16** as a yellow oil.

17 (149 mg, 1.11 mmol) and LR (240 mg, 0.59 mmol) were heated in glyme (2.5 mL) for 2 hours. After removal of solvent, chromatography (CH_2Cl_2/petroleum ether 1:9) gave **18**.

19 (81 mg, 340 mmol) and LR* (198 mg, 354 mmol) were heated in toluene (6 mL) for 45 minutes. Chromatography (petroleum ether) gave **20**.

21 (288 mg, 588 mmol) and LR (550 mg, 1.36 mmol) in glyme (4 mL) were heated (17 hours) be-

fore the addition of LR (250 mg, 0.62 mmol) after a further heating (24 hours) the solvent was removed; chromatography (petroleum ether) gave **22**.

23 (266 mg, 620 mmol) and LR (593 mg, 1.47 mmol) were heated in glyme (4 mL) for 48 hours. After removal of solvent, the residue was extracted with petroleum ether (7 mL) followed by CH_2Cl_2 (2.5 mL) and these extracts applied to a flash column. Chromatography (petroleum ether) gave **24**.

27 (198 mg, 1.0 mmol) and $Fc_2P_2S_4$ (276 mg, 493 μmol) in toluene (10 mL) were heated (70 minutes). By thin-layer chromatography (TLC), **27** was absent. After filtration through SiO_2 chromatography (3 g SiO_2, petroleum ether) gave 1,1-diphenylethene (**28**) as a yellow oil (138 mg, 766 μmol, 76%). By gas chromatography-mass spectrometry (GC–MS) this was a single compound.

Typical Room Temperature Reaction

18 (75 mg) and LR* (179 mg) were stirred in toluene (10 mL). Chromatography (petroleum ether) gave **15** with a trace of the furan present.

Treatment of LR and LR with Excess* **7** *under Forcing Conditions*

LR (270 mg, 0.67 mmol) and **7** (663 mg, 2.7 mmol) were heated in toluene (11 mL) (18 hours); chromatography (CH_2Cl_2/petroleum ether 4:6) gave **8** as a blue/black solid (566 mg, 2.19 mmol, 82%).

LR* (333 mg, 0.65 mmol) and **7** (670 mg, 2.77 mmol) were heated in toluene (10 mL) for 18 hours, chromatography gave **8** (645 mg, 2.50 mmol, 96%).

Synthesis of **26**

To LR (0.571 g, 1.41 mmol) was added **25** (0.5 mL, 0.505 g, 2.81 mmol) and to this was added toluene (10 mL). This mixture was then refluxed for 30 minutes. After cooling and removal of solvent, chromatography on silica (elution with petroleum ether) gave, after removal of solvent, **26** as a yellow oil (42 mg, 216 mmol, 8%). δ_H (ppm) 8.20 (2H, d, 8 Hz), 7.5 (1H, t, 7 Hz), 7.4 (2H, t, 8 Hz), 4.7 (2H, t, 6.5 Hz), 1.9 (2H, m), 1.6 (2H, m), 1.0 (3H, t, 7 Hz). On irradiation of the peak at 4.7 ppm the multiplet at 1.9 became a triplet (8 Hz). δ_C (ppm), 211.7 (quat), 138.6 (quat), 132.6, 128.7, 128.1, 72.6 (CH_2), 30.4 (CH_2), 19.5 (CH_2), and 13.8. IR (thin film) 3067m, 2959s, 2872s, 1596m, 1451s, 1380m, 1316s, 1272s, 1235s, 1176s, 1156w, 1099m, 1076s, 1052s, 1025s, 927m, 843w, 772s, 732w, 688s, 637m (cm^{-1}). MS(EI) *m/z* 194 (M^+), 161, 139, 121, 105, 77, 56, 51, 41, and 29. Molecular mass measured by HRMS at 194.0765 amu ($^{12}C_{11}{}^{1}H_{14}{}^{16}O^{32}S$ requires 194.0765 amu, within 0.1 ppm). Due to the likely offensive smell and toxic nature of **26**, no microanalysis was attempted.

CRYSTAL DATA

All measurements were performed at room temperature using a Rigaku AFC7S diffractometer, Cu Kα radiation, λ = 1.54178 Å, ω-scans (2ϑ max = 120°). LR* $C_{22}H_{30}O2P_2S_2$ M = 516.7, triclinic, space group P-1 a = 9.597(2), b = 12.089(2), c = 5.986(2) Ă, α = 102.00(2) β = 99.92(2) γ = 95.61(2)°. U = 663 Å^3, Z = 1, D_C = 1.295 gcm^{-3}, F (000) = 272, μ(Cu K_α) = 4.56 mm^{-1}. Crystal dimensions 0.10 × 0.10 × 0.28 mm. Of 2116 measured data, 1979 were unique and 1538 were observed [$I > 3.0\sigma(I)$]. The structure was solved by the heavy atom method and refined using absorption corrected data (psi scans) with the H-atoms in idealized positions to give R = 0.056 and R_W = 0.057. All calculations employed the TeXsan program system [11,12].

RESULTS AND DISCUSSION

As the methyl groups in $Fc_2^*P_2S_4$ greatly increased its solubility compared with $Fc_2P_2S_4$, *tert*-butyl anisole was reacted with P_4S_{10} to give 2,4-bis(3-*tert*-butyl-4-methoxyphenyl) 1,3,2,4-dithiadiphosphetane 2,4-disulfide (LR*) [δ_P 17.2 ppm, ν(P=S) 679 cm^{-1}] a more soluble version of LR. The *tert*-butyl groups prevent the molecules from packing tightly into a crystal lattice; moreover the presence of the large group could provide steric protection for the methoxy group because it has been suggested that the methoxy group in LR is involved in one of the decomposition routes.

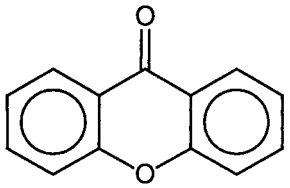
The 2-*tert*-butylanisole was made in good yield by the methylation of 2-*tert*-butylphenol in DMSO using MeI/NaOH [13,14]. The presence of dithiophosphine ylides in solution can be demonstrated by ^{31}P-{^1H} NMR spectroscopy on a mixture of $Fc_2P_2S_4$ and LR*, which results in an AX-type spectrum (δ_P = 16.2, 17.4 ppm, J[^{31}P-^{31}P] 7 Hz) indicating the formation of Fc*P(S)S_2P(S)R [R = $MeOBuC_6H_3$].

The molecular structure of LR* (Figure 1 and Table 1), confirmed its identity and revealed the lack of intermolecular interactions in the solid state, which improves its solubilization. In LR the molecules pack into layers with the aromatic groups parallel with the sulfurs forming layers. It is likely that sulfur sulfur interactions help bind the molecules into the lattice. The nonbonded intramolecular S. .S and P. .P distances are similar to those found in $Fc_2P_2S_4$ but slightly shorter than those in NpP_2S_4 and $MeONpP_2S_4$

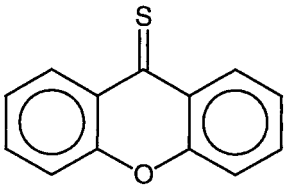
The reaction of 2-butyl-1-butoxybenzene with P_4S_{10} gave (in reasonable yield) 2,4-bis(3-*tert*-butyl-4-butoxyphenyl) 1,3,2,4-dithiadiphosphetane 2,4-disulfide (LR-Bu) [δ_P 18.4 ppm, ν(P=S) 679 cm^{-1}], LR-Bu is less soluble than LR*, and because the synthesis of 2-*tert*-butyl-1-butoxybenzene is more difficult than that of 2-*tert*-butylanisole, very little further work was attempted with LR-Bu.

Lawesson's reagent is employed for thionation of carbonyl compounds [2,3] often at elevated temperatures due to the low solubility of LR. Here the transformation of 4,4′-dimethyoxybenzophenone (**7**) to 4,4′-dimethoxybenzothione (**8**) was used to investigate a selection of phosphorus sulfur compounds (Table 2) as thionation reagents. The phosphorus sulfur compounds were heated with **7** in boiling toluene. Only LR, $Fc_2P_2S_4$, and NpP_2S_4 gave yields of thione (**8**) above 80%. For the dithiadiphosphetane disulfides (LR, LR*, NpP_2S_4, and $Fc_2P_2S_4$) the test reaction was repeated with benzophenone (9) However, because of separation difficulties in the case of 3 the ketone for this preliminary thionation test was xanthone 10.

Clearly many of the sulfur phosphorus compounds are ineffective as thionation reagents, so they were subject to no further testing. The dithiadiphosphetane disulfides with the naphthalene backbone were much less reactive than LR in part one assumes because the two phosphorus atoms are held close together in space.



11



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We also found that when excess 7 was treated with LR or LR* for a long time in refluxing toluene, more than two moles of 8 were formed per mole of thionation reagent. This does suggest that three or four sulfur atoms per molecule can be used in thionation reactions, rather than only two as would be initially expected and as is reported to be the case. This fact also suggests that the oxygen containing phosphorus sulfur side products from LR/LR* are able to act as thionation reagents.

In view of these results, the relative thionating ability of LR, LR*, and $Fc_2P_2S_4$ was tested with a variety of compounds (Scheme 1 and Table 3). By using conditions under which LR gives a moderate yield any differences between the effectiveness of the different thionation reagents is more likely to be noticeable. By reducing the temperature, time of reaction, or polarity of solvent, the yields obtained with LR were often reduced greatly from those stated in the literature. Then using identical conditions (and work-up) the reaction was repeated with LR* (sometimes also with $Fc_2P_2S_4$). All thionated compounds gave satisfactory spectral data. In most cases, LR* was equally effective as a thionation reagent as LR or $Fc_2P_2S_4$, and on some occasions, LR* was better than LR. Cholesterol esters were found to react more slowly with LR* than with LR. This is likely to be due to a steric effect. The formation of thioesters using LR can require high temperatures and long reaction times, so the low yields obtained in the synthesis of **22** and **24** are reasonable. Only limited NMR data had been published for **22**, and for **24** no NMR data was available. The thiocarbonyl δ_c values for **16, 22, 24**, and **26** are similar to those reported for thioesters (Table 4).

Because LR* is more soluble than LR, the use of LR* as a thionation reagent for use at room temperature was investigated (Table 5). Carbonyl compounds were stirred in either toluene or CH_2Cl_2 with either LR or LR*, before the product was isolated by means of chromatography. Xanthone (**11**) was used in these room temperature experiments.

We found that at room temperature, LR* was often more effective as a thionation reagent than LR. Esters and lactones would not react at room temperature with LR*. We also noted that LR in a suspension in CH_2Cl_2 is more effective as a thionation reagent than when in toluene. This could be due to the increased polarity of the solvent. Among the reactions listed in Table 5, it is noteworthy that a thiophene can be formed at room temperature from a 1,4-diketone. These conditions are very mild compared to those often used.

In conclusion, LR* has been shown in most of the examples to be an effective thionation reagent both at room temperature and above. It is likely that LR* can be used as a thionation reagent under mild conditions.

REFERENCES

[1] Cherkasov, R. A.; Kutyrev, G. A.; Pudovik, A. N. Tetrahedron 1985, 41, 2567.
[2] Cava; Levinson, M. I. Tetrahedron 1985, 41, 5061.
[3] Clausen, K.; Thorson, M.; Lawesson, S. O. Tetrahedron 1981, 21, 3635.
[4] Slawin, A. M. Z.; Williams, D. J.; Wood, P. T.; Woollins, J. D. J Chem Soc Chem Commun 1987, 1741.
[5] Foreman, M. R. StJ; Novosad, J.; Slawin, A. M. Z.; Woollins, J. D. J Chem Soc Dalton Trans 1997, 1347.
[6] Foreman, M. R. StJ; Slawin, A. M. Z.; Woollins, J. D. J Chem Soc Dalton Trans 1996, 3653.

[7] Foreman, M. R. St.J.; Slawin, A. M. Z.; Woollins, J. D. J Chem Soc Chem Commun 1997, 855.
[8] Foreman, M. R. StJ.; Slawin, A. M. Z.; Woollins, J. D. Chem Comm 1997, 1269.
[9] Foreman, M. St. J.; Slawin, A. M. Z.; Woollins, J. D. J Chem Soc Dalton Trans 1999, in press.
[10] Woollins, J. D. J Chem Soc Dalton Trans 1996, 2893.
[11] TeXsan, Molecular Structure Corporation, The Woodlands, Texas, 1985, 1992.
[12] Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic data centre, CCDC No 122732. Copies of this information may be obtained free of charge from The Director CCDC, 12 Union Road, Cambridge, CB2 1EZ UK. (Fax: +44 1223 336-033; E-mail *deposit@ccdc.cam.au.uk* or *www: http://www.ccdc.cam.ac.uk*.
[13] Heaney, H.; Ley, S. V. J Chem Soc Perkin Trans 1, 1973, 499.
[14] Gillis, R. G. Tetrahedron Lett 1968, 1413.