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First isolation of 1,3,2-dithiaphosphetane 2-sulfide

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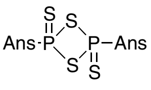
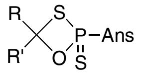
Abstract—The treatment of *tert*-alkyl phenyl thioketones with Lawesson's reagent (LR) gave two diastereomeric 1,3,2-dithiaphosphetane 2-sulfides in high yields. The structure of one of the major diastereomers was determined by X-ray crystallography. The reaction of 2-adamantanethione with LR yielded the corresponding spiro-1,3,2-dithiaphosphetane 2-sulfide derivative in 87% yield.

Lawesson's reagent (LR) has been used extensively not only for the conversion of a wide variety of carbonyl compounds to thiocarbonyl compounds but also for the synthesis of phosphorus- and sulfur-containing heterocycles.[1] The mechanism for the thionation of carbonyl groups has been proposed to proceed via 1,3,2-oxathiaphosphetane derivatives **1** as Wittig-type intermediates.[1] The reactions of thiocarbonyl compounds with LR are, similarly, expected to form the sulfur-analog of **1**, dithiaphosphetane derivatives **2**. However, in the reaction of ketones with LR, while some intermediately formed thioketones react with LR to give 1,3,5,2-trithiaphosphorinane derivatives **3** by a formal [2+2+2] cycloaddition of two C=S groups and one P=S group,[2] the formation of the 1,3,2-dithiaphosphetane 2-sulfide **2** has not been reported. Indeed, 1,3,2-dithiaphosphetanes are a rare class of heterocyclic compounds. As far as we know, there are only two compounds that contain this ring system. They are mono(dithiocarbamato) complex **4**[3] and tris(dithiocarbamato) complex **5**,[4] which have hexacoordinated phosphorus centers. We report here the first isolation of 1,3,2-dithiaphosphetane 2-sulfides, **7**, **8**, and **11**, by reaction of thioketones **6** and **10** with LR, in addition to their characterization.

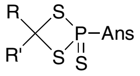


Ans = *p*-MeOC$_6$H$_4$

LR



1



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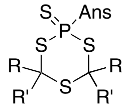

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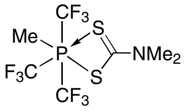

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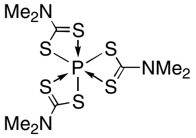

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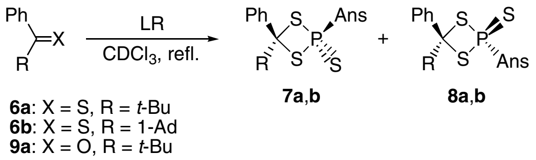
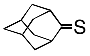


6a: X = S, R = *t*-Bu
6b: X = S, R = 1-Ad
9a: X = O, R = *t*-Bu

(1)



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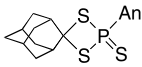

11

tert-Butyl phenyl thioketone **6a** was treated with 1.5 M amounts of LR in refluxing CDCl$_3$ for 14 h to give two diastereomeric 1,3,2-dithiaphosphetane 2-sulfides **7a** and **8a** in 85% and 5% yields, respectively. Similar treatment of **6b** with LR afforded **7b** and **8b** in 86% and

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Keywords: Thioketone; Lawesson's reagent; 1,3,2-Dithiaphosphetane 2-sulfide; X-ray analysis; Thermolysis.

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Table 1. Yields of products of the reactions of thioketones **6a**, **b**, and **10** and of ketone **9a** with LR

Entry	Substrate	LR (M equiv)	Time (h)	Products (%)			δ_P[c]
				7 or **11**	**8**	**6**	**7/8** or **11**
1	**6a** (X = S, R = *t*-Bu)	1.5	14	58[a] (85)[b]	4[a] (5)[b]	(9)[b]	37.5/38.2
2	**6b** (X = S, R = 1-Ad)	1.5	14	68[a] (86)[b]	4[a] (6)[b]	(8)[b]	40.9/42.9
3	**9a** (X = O, R = *t*-Bu)	3.0	48	(89)[b]	(4)[b]	(Trace)[b]	—
4	**10**	1.5	3	87[a]	—	—	39.0

[a] Isolated yields.

[b] ^{1}H NMR yields.

[c] ^{31}P NMR chemical shifts.

6% yields, respectively (Eq. 1, Table 1; entries 1 and 2). These diastereomers were separated by silica-gel column chromatography, whereby partial decomposition to the corresponding thioketone **6** took place. The structures of **7** and **8** were elucidated based on their spectroscopic data and elemental analyses,[5] and the stereochemistry of **7b** was determined by X-ray crystallography.[6] The X-ray analysis of the major isomer **7b** indicated the *trans* configuration of the phenyl group to the *P*-sulfide sulfur atom (Fig. 1). The four-membered ring puckers shallowly and the pucker angle between the plane S1–C1–S2 and the plane S1–P1–S2 is 8.08° with the P–Ans group inside. The S1–P1 and S2–P1 bond lengths are 2.0886(7) and 2.0927(7) Å, respectively, and the S1–P1–S2 and S1–C1–S2 ring angles are 86.14(3)° and 99.60(7)°, respectively. Incidentally, the structure of tris(dithiocarbamato) complex **5** is quite different from the structure of **7b**: the mean values of two types of S–P bonds of **5** are 2.178 ± 0.009 and 2.966 ± 0.031 Å, and those of the S–P–S and S–C–S ring angles are 68.7 ± 0.6° and 120.2 ± 0.3°, respectively.[4] The structure of **8** was assigned to be the diastereomer of **7**, in which the phenyl group and the *P*-sulfide sulfur atom are *cis*, based on the similarity of the ^{31}P and ^{13}C NMR data of **8** to those of **7**. The formation of dithiaphosphetane 2-sulfides **7a** and **8a** was also observed in the reaction of ketone **9a** with large excess amounts of LR (3 M equivalent) under similar conditions (entry 3).

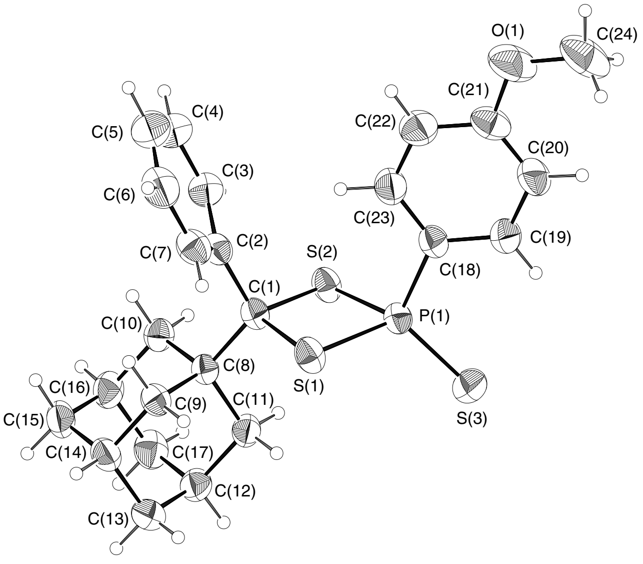


Figure 1. ORTEP drawing of **7b** (50% ellipsoids). Relevant bond length (Å), bond angle (°), and torsion angle (°) data: S1–P1 2.0886(7), P1–S2 2.0927(7), S2–C1 1.8727(15), C1–S1 1.8655(16),C1–C2 1.525(2), C1–C8 1.561(2), P1–S3 1.9303(7); S1–P1–S2 86.14(3), P1–S2–C1 86.71(5), S2–C1–S1 99.60(7), C1–S1–P1 87.01(5), C2–C1–C8 114.39(12); S1–P1–S2–C1 5.20(5).

The reaction of an aliphatic thioketone, 2-adamantanethione **10** with LR completed in a shorter reaction time to yield spiro-1,3,2-dithiaphosphetane 2-sulfide **11**[5,6] in good isolated yield (87%) (entry 4). Figure 2 shows an ORTEP drawing of **11**. The pucker angle between the plane S1–C1–S2 and the plane S1–P1–S2 is 9.43° with the P=S group inside, being opposite to the case of **7b**. In the solid state, the plane containing the 4-methoxyphenyl group of **11** bisects the 1,3,2-dithiaphosphetane ring through P1 and C1 atoms. This is true of **7b**. No formation of dithiaphosphetanes was observed in reactions of thiobenzophenone, 1-adamantyl *tert*-butyl thioketone, or 1,1,3,3-tetramethyl-2-indanethione with LR.

Dithiaphosphetane 2-sulfides **7**, **8**, and **11** turned from colorless to purple when heated over their melting points, indicating the decomposition to the corresponding thioketones. A solution of dithiaphosphetane **8a** in toluene-d_8 was heated at 80 °C, and thermal behavior of **8a** was monitored by ^{1}H NMR spectroscopy at this temperature. It was observed that the decomposition of **8a** to **6a** and the isomerization of **8a** to **7a** took place, and the ratio of **6a**/**7a**/**8a** (64/34/2) remained unchanged on prolonged heating beyond 4 h (Eq. 2). LR is known to dissociate thermally into its monomeric

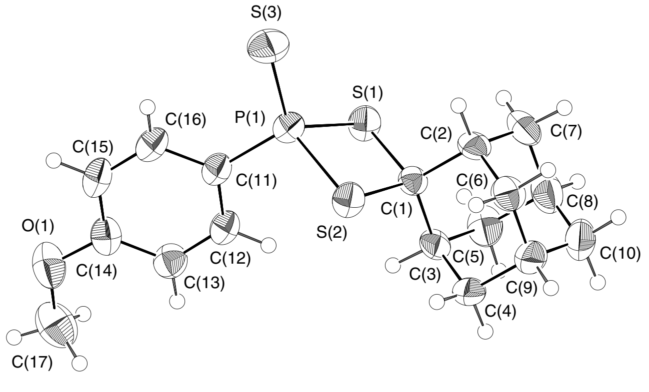
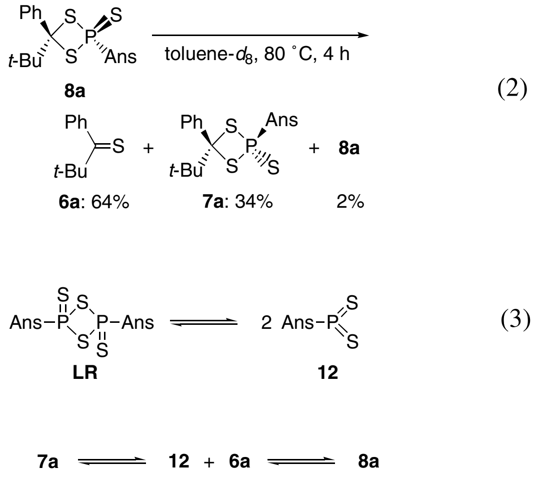


Figure 2. ORTEP drawing of **11** (50% ellipsoids). Relevant bond length (Å), bond angle (°), and torsion angle (°) data: S1–P1 2.0999(8), P1–S2 2.0914(8), S2–C1 1.8609(19), C1–S1 1.8576(18),C1–C2 1.531(2), C1–C3 1.526(2), P1–S3 1.9297(8); S1–P1–S2 86.11(3), P1–S2–C1 86.36(6), S2–C1–S1 100.62(9), C1–S1–P1 86.19(6), C2–C1–C3 109.67(15); S1–P1–S2–C1-6.02(6).



Scheme 1.

thionophosphine sulfide **12** (Eq. 3), which acts as the reactive species of sulfurization.[1] The above thermal behavior of **8a** indicates that interconversion between dithiaphosphetanes **7a** and **8a** takes place through dissociation into **12** and thioketone **6a** in solution as shown in Scheme 1, where the equilibrium lies to the side of **12** and **6a**.[7] Thus, to shift the equilibrium to the side of dithiaphosphetanes, a large excess amount of LR is necessary.[8]

Acknowledgements

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5. Compound **7a**: colorless crystals, mp 165–168 °C decomp (CH_2Cl_2/hexane). ^1H NMR (400 MHz, $CDCl_3$): δ 1.26 (s, 9H), 3.78 (s, 3H), 6.73–6.80 (m, 2H), 7.31–7.42 (m, 3H), 7.51 (d, $J = 7.5$ Hz, 2H), 7.76–7.86 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 25.6 (CH_3), 41.7 (d, $^3J_{CP} = 3.0$ Hz, C), 55.4 (CH_3), 56.5 (d, $^2J_{CP} = 3.1$ Hz, C), 113.6 (d, $^3J_{CP} = 16.8$ Hz, CH), 126.7 (CH), 127.0 (CH), 128.9 (CH), 131.0 (d, $^1J_{CP} = 89.3$ Hz, C), 134.1 (d, $^2J_{CP} = 16.0$ Hz, CH), 142.7 (d, $^3J_{CP} = 3.0$ Hz, C of Ph), 162.9 (d, $^4J_{CP} = 3.8$ Hz, C); ^{31}P NMR (162 MHz, $CDCl_3$): δ 37.5 (s); MS (FAB) *m/z* 381 (M^++1); Anal. Calcd for $C_{18}H_{21}OPS_3$: C, 56.81; H, 5.56. Found: C, 56.73; H, 5.52. Compound **8a**: colorless crystals, mp 126–128 °C decomp (CH_2Cl_2/hexane). ^1H NMR (400 MHz, $CDCl_3$): δ 1.15 (s, 9H), 3.88 (s, 3H), 6.98–7.06 (m, 2H), 7.31 (t, $J = 7.3$ Hz, 1H), 7.40 (t, $J = 7.7$ Hz, 2H), 7.75 (d, $J = 7.8$ Hz, 2H), 8.22–8.33 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 26.2 (CH_3), 41.7 (d, $^3J_{CP} = 6.6$ Hz, C), 55.6 (CH_3), 59.8 (d, $^2J_{CP} = 2.2$ Hz, C), 113.8 (d, $^3J_{CP} = 16.6$ Hz, CH), 126.5 (CH), 126.9 (CH), 130.0 (CH), 130.6 (d, $^1J_{CP} = 91.3$ Hz, C), 134.0 (d, $^2J_{CP} = 15.4$ Hz, CH), 142.6 (C), 163.1 (d, $^4J_{CP} = 3.2$ Hz, C); ^{31}P NMR (162 MHz, $CDCl_3$): δ 38.2 (s); Anal. Calcd for $C_{18}H_{21}OPS_3$: C, 56.81; H, 5.56. Found: C, 56.93; H, 5.51. Compound **7b**: colorless needles, mp 173–175 °C decomp (CH_2Cl_2/hexane). ^1H NMR (400 MHz, $CDCl_3$): δ 1.49–1.68 (m, 6H), 1.89 (br s, 6H), 2.10 (br s, 3H), 3.78 (s, 3H), 6.71–6.79 (m, 2H), 7.30–7.42 (m, 3H), 7.45 (d, $J = 7.0$ Hz, 2H), 7.74–7.85 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 28.3 (CH), 35.7 (CH_2), 36.0 (CH_2), 41.6 (d, $^3J_{CP} = 3.0$ Hz, C), 55.4 (CH_3), 57.4 (d, $^2J_{CP} = 3.0$ Hz, C), 113.5 (d, $^3J_{CP} = 17.5$ Hz, CH), 126.5 (CH), 126.9 (CH), 129.5 (CH), 131.3 (d, $^1J_{CP} = 90.0$ Hz, C), 134.1 (d, $^2J_{CP} = 16.8$ Hz, CH), 141.5 (d, $^3J_{CP} = 3.1$ Hz, C of Ph), 162.9 (d, $^4J_{CP} = 3.0$ Hz, C); ^{31}P NMR (162 MHz, $CDCl_3$): δ 40.9 (s); Anal. Calcd for $C_{24}H_{27}OPS_3$: C, 62.85; H, 5.93. Found: C, 63.00; H, 5.90. Compound **8b**: colorless crystals, mp 120–123 °C decomp (CH_2Cl_2/hexane). ^1H NMR (400 MHz, $CDCl_3$): δ 1.45–1.66 (m, 6H), 1.76 (br s, 6H), 2.05 (br s, 3H), 3.89 (s, 3H), 7.00–7.06 (m, 2H), 7.31 (t, $J = 7.5$ Hz, 1H), 7.40 (t, $J = 7.8$ Hz, 2H), 7.70 (d, $J = 7.5$ Hz, 2H), 8.24–8.33 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 28.2 (CH), 35.9 (CH_2), 36.7 (CH_2), 41.6 (d, $^3J_{CP} = 6.2$ Hz, C), 55.6 (CH_3), 60.9 (d, $^2J_{CP} = 2.2$ Hz, C), 113.8 (d, $^3J_{CP} = 16.9$ Hz, CH), 126.4 (CH), 126.8 (CH), 130.6 (CH), 130.7 (d, $^1J_{CP} = 90.6$ Hz, C), 134.2 (d, $^2J_{CP} = 15.4$ Hz, CH), 141.5 (C), 163.1 (d, $^4J_{CP} = 3.1$ Hz, C); ^{31}P NMR (162 MHz, $CDCl_3$): δ 42.9 (s); MS (FAB) *m/z* 459 (M^++1). Compound **11**: Colorless plates, mp 163–165 °C decomp (CH_2Cl_2/hexane). ^1H NMR (400 MHz, $CDCl_3$): δ 1.69–1.91 (m, 8H), 1.93–2.03 (m, 2H), 2.14–2.25 (m, 2H), 2.56 (br s, 1H), 2.83 (br s, 1H), 3.88 (s, 3H), 6.96–7.05 (m, 2H), 8.20–8.31 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 25.6 (CH), 32.7 (CH_2), 33.3 (CH_2), 36.1 (CH_2), 43.8 (d, $^3J_{CP} = 5.0$ Hz, CH), 44.9 (CH), 55.2 (d, $^2J_{CP} = 1.7$ Hz, C), 55.5 (CH_3), 113.7 (d, $^3J_{CP} = 16.5$ Hz, CH), 130.6 (d, $^1J_{CP} = 88.5$ Hz, C), 134.2 (d, $^2J_{CP} = 15.6$ Hz, CH), 163.0 (d, $^4J_{CP} = 3.2$ Hz, C); ^{31}P NMR (162 MHz, $CDCl_3$): δ 39.0 (s); Anal. Calcd for $C_{17}H_{21}OPS_3$: C, 55.41; H, 5.74. Found: C, 55.34; H, 5.68.
6. Crystal data for **7b**: $C_{24}H_{27}OPS_3$, M_w 458.645, colorless needles, $0.34\times0.26\times0.24$ mm^3, monoclinic, space group $P2_1/c$, $a = 10.240(2)$, $b = 11.377(2)$, $c = 19.486(3)$ Å, $\beta = 100.74(2)°$, $V = 2230.3(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.366$ g cm^{-3}, μ(Cu–Kα) = 3.814 mm^{-1}. 4190 independent reflections, 371 parameters; $R_1 = 0.0295$ ($I > 2\sigma I$, 4125 reflections), $wR_2 = 0.0759$ (for all), GOF = 1.097; max/min residual density = 0.252/−0.292 e Å^{-3}. Crystal data for **11**: $C_{17}H_{21}OPS_3$, M_w 368.52, colorless plates, $0.30\times0.20\times0.18$ mm^3, monoclinic, space group $P2_1/c$, $a = 6.8327(11)$, $b = 23.309(3)$, $c = 12.684(3)$ Å, $\beta = 121.69(3)°$, $V = 1718.9(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.424$ g cm^{-3}, μ(Cu–Kα) = 4.802 mm^{-1}. 3229 independent reflections, 284 parameters; $R_1 = 0.0337$ ($I > 2\sigma I$, 3166 reflections), $wR_2 = 0.0915$ (for all), GOF = 1.099; max/min residual density = 0.389/−0.321 e Å^{-3}. General crystallographic information: Mac Science MXC3KHF diffractometer with a graphite-monochromated Cu–Kα radiation ($\lambda = 1.54178$Å), solved with a

direct method (SIR97[9]) and refined with full-matrix least-squares (SHELXL-97[10]) using all independent reflections. Absorption corrections were done by the psi-scan method.[11] CCDC-224014 (**7b**) and CCDC-224015 (**11**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving. html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [fax: (internat.) +44-1223 336-033; e-mail: deposit@ccdc.cam.ac.uk].

7. The ratio of **6a/7a/8a** after cooling the solution to room temperature was substantially equal to that measured at 80 °C. In the NMR experiments, several signals due to compounds derived from **12** were observed, but they were not completely consistent with signals appearing in the ^{1}H NMR spectrum of LR measured at 80 °C. The present thermal reaction was carried out with toluene-d_8 as purchased in an NMR tube after purging air by bubbling argon gas. The possibility of partial decomposition of **12** by remaining moisture cannot be excluded.
8. In the reaction of **6** with 1.5 M amounts of LR in refluxing $CDCl_3$, the color of **6** faded out gradually at the temperatures.
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