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Reaction of Lawesson's reagent with Mannich base hydrochlorides: synthesis of novel 4H-1,3,2-oxathiaphosphorine-2-sulfide derivatives

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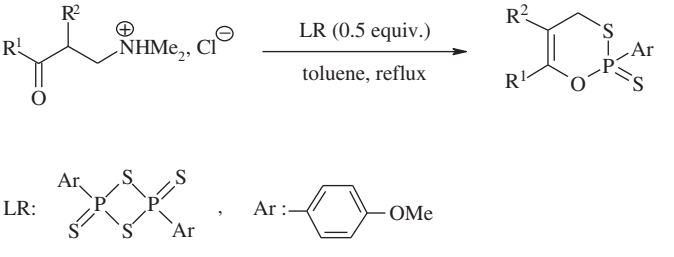
In a simple and general protocol, the treatment of Mannich base hydrochlorides, derived from acyclic and cyclic ketones, with Lawesson's reagent, leads to novel 4H-1,3,2-oxathiaphosphorine derivatives in good yields. A possible reaction mechanism, involving a [4 + 2] cycloaddition, is proposed.



Keywords: Lawesson's reagent; Mannich base hydrochlorides; oxathiaphosphorines; heterocycles; cycloaddition

1. Introduction

The use of 2,4-bis(p-methoxyphenyl)-1,3,2,4-dithiaphosphetane-2,4-disulfide (Lawesson's reagent (LR)) in heterocyclic synthesis has been well documented.[1–4] One of its important applications involves [3 + 2] and [4 + 2] cycloadditions with 1,3- and 1,4-dipolar reagents, giving rise to a wide range of five- and six-membered heterocyclic rings incorporating sulfur and phosphorus atoms introduced by LR itself.[5–11] These heterocycles are an important class of compounds in the medicinal chemistry with interesting biological properties including antimicrobial, antifungal and antitumor activities.[12–14]

In the last few years, it was shown that the reaction of LR with α, β-unsaturated carbonyl compounds [12,15–17] or phenolic Mannich bases [18,19] can lead to 4H-1,3,2-oxathiaphosphorine derivatives. The scope of these reactions is, however, limited and only a

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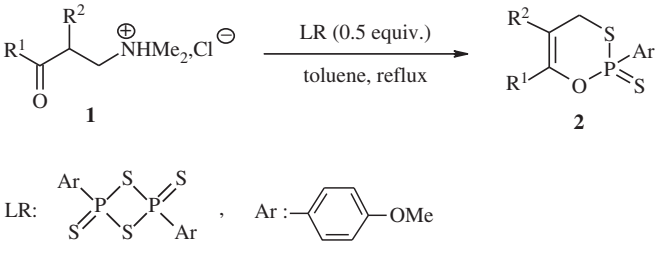
few 1,3,2-oxathiaphosphorine derivatives have been synthesized from these strategies. Therefore, additional synthetic methods are required to obtain a wider variety of compounds belonging to this class, for biological screening.

With this in mind, and in continuation of our research on the use of LR for the synthesis of novel heterocyclic scaffolds with possible biological properties,[20–23] we have investigated the reaction of LR with Mannich base hydrochlorides derived from acyclic and cyclic ketones, which could represent an easy and general method to access novel types of 4H-1,3,2-oxathiaphosphorine derivatives.

2. Results and discussion

The starting Mannich base hydrochlorides **1** were easily prepared according to the reported Mannich synthetic procedure.[24] It was found that the reaction of compounds **1** with a stoichiometric amount of LR (0.5 equiv.), performed in refluxing toluene, for 8–48 h, led to 4H-1,3,2-oxathiaphosphorine-2-sulfides **2** in 60–90% yield (Scheme 1).



Scheme 1. Synthesis of 4H-1,3,2-oxathiaphosphorine-2-sulfides **2**.

The scope of the reaction was assessed with a range of substrates including acyclic and cyclic Mannich base hydrochlorides (Table 1). All the substrates reacted in good to high yields. A plausible mechanism for the formation of compounds **2** is depicted in Scheme 2. The transformation is believed to proceed via the deamination of the Mannich base hydrochloride **1**, by heating, giving rise to the enone intermediate **I**. The interception of this last one by the monomer of LR leads, after cycloaddition, to the 4H-1,3,2-oxathiaphosphorine derivative **2** as final product.

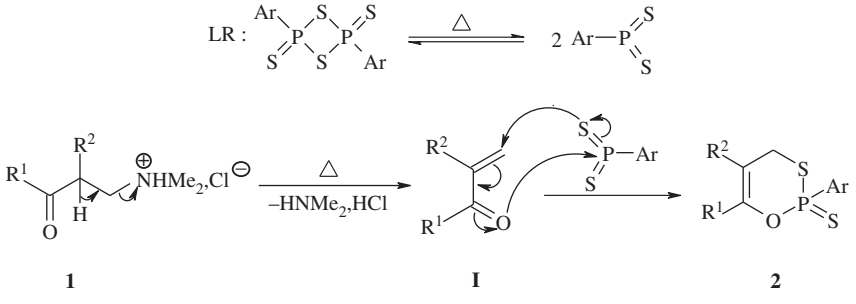
The formation of compounds **2** was confirmed by IR, NMR (^{1}H, ^{31}P, ^{13}C) and mass spectral data. The IR spectra revealed the presence of absorption bands near 700 cm^{-1} corresponding to the P=S stretching frequency. The ^{1}H NMR spectrum of each compound **2** showed, in particular, a singlet at 3.7 ppm, ascribable to the OCH_3 protons. When $R^2 \neq H$, the CH_2-S protons in the heterocyclic ring resonate between 3 and 4 ppm as the AB part of an ABX spin system. This coupling pattern can be rationalized taking into account that the methylene protons are diastereotopic due to the neighboring asymmetric phosphorus atom. The ^{31}P NMR shifts recorded for compounds **2** were $d = 64$–87 ppm which is consistent with the thiophosphoryl chemical shift values. The ^{13}C NMR spectra display the characteristic signals of all carbons and particularly those corresponding to the oxathiaphosphorine ring. Of particular note is the CH_2-S carbon that resonates as a doublet ($^{2}J_{CP} = 4$–6 Hz) around 40 ppm. The structures of compounds **2** were further supported by their mass spectra that showed the correct molecular ion peaks.

In summary, we have successfully developed an efficient and straightforward synthesis of novel 4H-1,3,2-oxathiaphosphorine derivatives, via the reaction of Mannich base hydrochlorides, derived from acyclic and cyclic ketones, with LR. By comparison with the existing strategies,[12,15–19] our method offers significant advantages such as generality, efficiency and

Table 1. Substrate scope studies.

Entry	R^1	R^2	Product	Yield (%)[a]	Time (h)[b]
1	Ph	Me	**2a**	90	12
2	CH_2−Ph	Ph	**2b**	76	16
3	Ph	H	**2c**	85	8
4		H	**2d**	78	12
5	Me	H	**2e**	65	24
6	Et	H	**2f**	71	36
7	Et	Me	**2g**	60	36
8	$(CH_2)_3$		**2h**	74	36
9	$(CH_2)_4$		**2i**	78	48

[a]Isolated yield.
[b]The progress of the reactions was monitored by TLC.



Scheme 2. Reaction mechanism for the synthesis of compounds **2**.

high yields. Furthermore, the use of Mannich base hydrochlorides, instead of enones, as starting materials is very beneficial since they are synthetically equivalent to enones but in general more stable and easier to obtain.

3. Experimental

^{1}H, ^{31}P and ^{13}C NMR spectra were recorded with $CDCl_3$ as the solvent, on a Bruker AC-300 spectrometer operating at 300.1 MHz for ^{1}H, 121.5 MHz for ^{31}P and 75.5 MHz for ^{13}C. The chemical shifts are reported in ppm relative to TMS (internal reference) for ^{1}H and ^{13}C NMR and relative to 85% H_3PO_4 (external reference) for ^{31}P NMR. The coupling constants are reported in Hz. For the ^{1}H NMR, the multiplicities of signals are indicated by the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Mass spectra were determined on an Agilent 5975B spectrometer, under electronic impact (EI) conditions. IR spectra were recorded on a Nicolet IR200 spectrometer. The progress of the reactions was monitored by TLC. Purification of products was performed by column chromatography using silica gel 60 (Fluka).

3.1. *Synthesis of Mannich base hydrochlorides 1*

The starting Mannich base hydrochlorides **1** were prepared according to the reported procedure.[24]

3.2. *Synthesis of 4H-1,3,2-oxathiaphosphorine-2-sulfides 2*

A mixture of the Mannich base hydrochloride **1** (0.01 mol), LR (0.005 mol) and dry toluene (30 mL) was heated under reflux with stirring for 8–48 h (Table 1). After cooling, the mixture was extracted with water (2 × 30 mL). The organic phase was dried over Na_2SO_4 and concentrated under vacuum. The obtained residue was chromatographed on a silica gel column using a mixture of ether and petroleum ether (1:1) as eluent.

2-(4-Methoxyphenyl)-5-methyl-6-phenyl-4H-1,3,2-oxathiaphosphorine-2-sulfide (2a). Brown oil; ^{31}P NMR: $\delta = 85.4$; ^{1}H NMR: $\delta = 2.06$ (d, 3H, $^{5}J_{PH} = 6.0$, $CH_3-C{=}C$); 3.75 (AB part of an ABX system, 2H, $^{2}J_{HH} = 12.6$, $^{3}J_{PHa} = 20.7$, $^{3}J_{PHb} = 21.9$, CH_2-S); 3.76 (s, 3H, CH_3-O); 6.87–7.98 (m, 9H, arom-H); ^{13}C NMR: $\delta = 20.6$ (s, $\underline{C}H_3-C{=}C$); 40.3 (d, $^{2}J_{CP} = 5.2$, CH_2-S); 55.5 (s, CH_3-O); 114.2 (d, $^{3}J_{CP} = 15.0$, $\underline{C}{=}C-O-P$); 142.4 (d, $^{2}J_{CP} = 10.5$, $C{=}\underline{C}-O-P$); 163.0 (d, $^{4}J_{CP} = 3.7$, $CH_3-O-\underline{C}{=}C$); phenyl carbons: $\delta = 127.5$, 128.1, 128.2, 128.6, 129.5, 133.7, 133.9, 134.0, 134.2, 134.3, 134.6; IR (neat): $\nu_{P=S} = 703\,cm^{-1}$; EI–HRMS: calculated for $C_{17}H_{17}O_2PS_2$: 348.0408 (M^+); found: 348.0406.

6-Benzyl-2-(4-methoxyphenyl)-5-phenyl-4H-1,3,2-oxathiaphosphorine-2-sulfide (2b). Brown oil; ^{31}P NMR: $\delta = 86.1$; ^{1}H NMR: $\delta = 2.41$ (s, 2H, $C\underline{H}_2-Ph$); 3.76 (AB part of an ABX system, 2H, $^{2}J_{HH} = 15.0$, $^{3}J_{PHa} = 20.0$, $^{3}J_{PHb} = 22.1$, CH_2-S); 3.78 (s, 3H, CH_3-O); 6.90–7.84 (m, 14H, arom-H); ^{13}C NMR: $\delta = 32.5$ (s, $\underline{C}H_2-Ph$); 38.8 (d, $^{2}J_{CP} = 4.5$, CH_2-S); 55.6 (s, CH_3-O); 117.7 (d, $^{3}J_{CP} = 12.0$, $\underline{C}{=}C-O-P$); 150.4 (d, $^{2}J_{CP} = 13.5$, $C{=}\underline{C}-O-P$); 163.3 (d, $^{4}J_{CP} = 3.0$, $CH_3-O-\underline{C}{=}C$); phenyl carbons: $\delta = 124.8$, 126.4, 126.7, 128.0, 128.6, 128.8, 128.9, 129.0, 129.1, 129.6, 133.0, 133.2, 137.2, 139.1; IR (neat): $\nu_{P=S} = 704\,cm^{-1}$; EI–HRMS: calculated for $C_{23}H_{21}O_2PS_2$: 424.0721 (M^+); found: 424.0717.

2-(4-Methoxyphenyl)-6-phenyl-4H-1,3,2-oxathiaphosphorine-2-sulfide (2c). Brown oil; ^{31}P NMR: $\delta = 86.4$; ^{1}H NMR: $\delta = 3.57$–3.65 (m, 2H, CH_2-S); 3.67 (s, 3H, CH_3-O); 6.62–6.69 (m, 1H, $CH_2-C\underline{H}{=}C$); 6.90–7.71 (m, 9H, arom-H); ^{13}C NMR: $\delta = 44.7$ (d, $^{2}J_{CP} = 5.4$, CH_2-S); 55.5 (s, CH_3-O); 113.8 (d, $^{3}J_{CP} = 18.0$, $\underline{C}{=}C-O-P$); 141.3 (d, $^{2}J_{CP} = 12.7$, $C{=}\underline{C}-O-P$); 164.2 (d, $^{4}J_{CP} = 3.0$, $CH_3-O-\underline{C}{=}C$); phenyl carbons: $\delta = 127.3$, 128.2, 128.5, 128.6, 128.7, 129.0, 133.9, 134.1, 134.2, 134.4, 134.6; IR (neat): $\nu_{P=S} = 695\,cm^{-1}$; EI–HRMS: calculated for $C_{16}H_{15}O_2PS_2$: 334.0251 (M^+); found: 334.0252.

2-(4-Methoxyphenyl)-6-(thiophen-2-yl)-4H-1,3,2-oxathiaphosphorine-2-sulfide (2d). Brown oil; ^{31}P NMR: $\delta = 80.5$; ^{1}H NMR: $\delta = 3.52$–3.69 (m, 2H, CH_2-S); 3.61 (s, 3H, CH_3-O); 6.68–6.72 (m, 1H, $CH_2-C\underline{H}{=}C$); 6.90–7.77 (m, 7H, arom-H); ^{13}C NMR: $\delta = 40.7$ (d, $^{2}J_{CP} = 5.1$, CH_2-S); 55.3 (s, CH_3-O); 113.4 (d, $^{3}J_{CP} = 13.5$, $\underline{C}{=}C-O-P$); 147.7 (d, $^{2}J_{CP} = 13.1$, $C{=}\underline{C}-O-P$); 162.5 (d, $^{4}J_{CP} = 3.0$, $CH_3-O-\underline{C}{=}C$); phenyl carbons: $\delta = 125.2$, 125.3, 125.6, 126.7, 128.2, 132.2, 132.4, 132.6, 132.8, 133.5, 137.8; IR (neat): $\nu_{P=S} = 699\,cm^{-1}$; EI–HRMS: calculated for $C_{14}H_{13}O_2PS_3$: 339.9815 (M^+); found: 339.9811.

2-(4-Methoxyphenyl)-6-methyl-4H-1,3,2-oxathiaphosphorine-2-sulfide (2e). Brown oil; ^{31}P NMR: $\delta = 75.5$; ^{1}H NMR: $\delta = 2.38$ (s, 3H, $CH_3-C{=}C$); 3.78–3.86 (m, 2H, CH_2-S); 3.84 (s, 3H, CH_3-O); 6.84–6.9.95 (m, 1H, $CH_2-C\underline{H}{=}C$); 7.16–8.18 (m, 4H, arom-H); ^{13}C NMR: $\delta = 25.8$ (s, $\underline{C}H_3-C{=}C$); 37.5 (d, $^{2}J_{CP} = 4.5$, CH_2-S); 55.6 (s, CH_3-O); 114.2 (d, $^{3}J_{CP} = 12.7$, $\underline{C}{=}C-O-P$); 144.3 (d, $^{2}J_{CP} = 13.1$, $C{=}\underline{C}-O-P$); 164.3 (d, $^{4}J_{CP} = 3.0$, $CH_3-O-\underline{C}{=}C$); phenyl carbons: $\delta = 128.1$, 129.5, 133.9, 134.0, 134.3, 134.5; IR (neat): $\nu_{P=S} = 703\,cm^{-1}$; EI–HRMS: calculated for $C_{11}H_{13}O_2PS_2$: 272.0095 (M^+); found: 272.0092.

6-Ethyl-2-(4-methoxyphenyl)-4H-1,3,2-oxathiaphosphorine-2-sulfide (2f). Brown oil; ^{31}P NMR: $\delta = 85.7$; ^{1}H NMR: $\delta = 1.42$ (t, 3H, $^{3}J_{HH} = 6.0$, $C\underline{H}_3-CH_2$); 2.02 (q, 2H, $^{3}J_{HH} = 6.0$, $CH_3-C\underline{H}_2$); 3.29–3.59 (m, 2H, CH_2-S); 3.67 (s, 3H, CH_3-O); 6.66–6.90 (m, 1H, $CH_2-C\underline{H}{=}C$); 7.56–8.17 (m, 4H, arom-H); ^{13}C NMR: $\delta = 20.3$ (s, $\underline{C}H_3-CH_2$); 31.5 (s, $CH_3-\underline{C}H_2$); 40.4 (d, $^{2}J_{CP} = 5.25$, CH_2-S); 55.4 (s, CH_3-O); 113.8 (d, $^{3}J_{CP} = 11.2$, $\underline{C}{=}C-O-P$); 141.0 (d, $^{2}J_{CP} = 12.0$, $C{=}\underline{C}-O-P$); 164.3 (d, $^{4}J_{CP} = 3.0$, $CH_3-O-\underline{C}{=}C$); phenyl carbons: $\delta = 123.3$, 125.2,

128.4, 128.5, 133.6, 133.8; IR (neat): $\nu_{P=S} = 705\,cm^{-1}$; EI–HRMS: calculated for $C_{12}H_{15}O_2PS_2$: 286.0251 (M^+); found: 286.0258.

6-Ethyl-2-(4-methoxyphenyl)-5-methyl-4H-1,3,2-oxathiaphosphorine-2-sulfide (2g). Brown oil; ^{31}P NMR: $\delta = 80.9$; ^1H NMR: $\delta = 1.48$ (t, 3H, $^3J_{HH} = 6.0$, $C\underline{H}_3-CH_2$); 2.06 (s, $CH_3-C=C$); 2.25 (q, 2H, $^3J_{HH} = 6.0$, $CH_3-C\underline{H}_2$); 3.71 (AB part of an ABX system, 2H, $^2J_{HH} = 12.0$, $^3J_{PHa} = 21.0$, $^3J_{PHb} = 21.7$, CH_2-S); 3.74 (s, 3H, CH_3-O); 6.89–7.74 (m, 4H, arom-H); ^{13}C NMR: $\delta = 20.4$ (s, $\underline{C}H_3-CH_2$); 27.4 (s, $\underline{C}H_3-C=C$); 30.1 (s, $CH_3-\underline{C}H_2$); 40.8 (d, $^2J_{CP} = 5.5$, CH_2-S); 54.3 (s, CH_3-O); 112.5 (d, $^3J_{CP} = 13.0$, $\underline{C}=C-O-P$); 142.2 (d, $^2J_{CP} = 12.5$, $C=\underline{C}-O-P$); 161.5 (d, $^4J_{CP} = 3.0$, $CH_3-O-\underline{C}=C$); phenyl carbons: $\delta = 127.2$, 128.4, 131.2, 131.3, 132.9, 133.1; IR (neat): $\nu_{P=S} = 700\,cm^{-1}$; EI–HRMS: calculated for $C_{13}H_{17}O_2PS_2$: 300.0408 (M^+); found: 300.0403.

2-(4-Methoxyphenyl)-5,6-trimethylene-4H-1,3,2-oxathiaphosphorine-2-sulfide (2h). Brown oil; ^{31}P NMR: $\delta = 64.4$; ^1H NMR: $\delta = 1.36$–2.52 (m, 6H, $(CH_2)_3$); 3.72 (AB part of an ABX system, 2H, $^2J_{HH} = 12.0$, $^3J_{PHa} = 20.4$, $^3J_{PHb} = 20.9$, CH_2-S); 3.78 (s, 3H, CH_3-O); 7.86–8.01 (m, 4H, arom-H); ^{13}C NMR: $\delta = 20.8$ (s, $CH_2-\underline{C}H_2-CH_2$); 28.0 (s, $O-C=C-\underline{C}H_2$); 32.6 (s, $O-C-\underline{C}H_2$); 37.3 (d, $^2J_{CP} = 6.0$, CH_2-S); 55.3 (s, CH_3-O); 114.3 (d, $^3J_{CP} = 15.0$, $\underline{C}=C-O-P$); 147.6 (d, $^2J_{CP} = 12.0$, $C=\underline{C}-O-P$); 163.5 (d, $^4J_{CP} = 3.0$, $CH_3-O-\underline{C}=C$); phenyl carbons: $\delta = 128.2$, 129.5, 132.8, 133.0, 133.3, 133.4; IR (neat): $\nu_{P=S} = 682\,cm^{-1}$; EI–HRMS: calculated for $C_{13}H_{15}O_2PS_2$: 298.0251 (M^+); found: 298.0245.

2-(4-Methoxyphenyl)-5,6-tetramethylene-4H-1,3,2-oxathiaphosphorine-2-sulfide (2i). Brown oil; ^{31}P NMR: $\delta = 84.5$; ^1H NMR: $\delta = 1.11$–2.35 (m, 6H, $(CH_2)_4$); 3.78 (AB part of an ABX system, 2H, $^2J_{HH} = 12.3$, $^3J_{PHa} = 18.0$, $^3J_{PHb} = 20.1$, CH_2-S); 3.79 (s, 3H, CH_3-O); 6.90–7.88 (m, 4H, arom-H); ^{13}C NMR: $\delta = 21.4$ (s, $O-C=C-CH_2-\underline{C}H_2$); 24.9 (s, $O-C-CH_2-\underline{C}H_2$); 29.1 (s, $O-C=C-\underline{C}H_2$); 31.6 (s, $O-C-\underline{C}H_2$); 37.3 (d, $^2J_{CP} = 6.0$, CH_2-S); 55.5 (s, CH_3-O); 113.7 (d, $^3J_{CP} = 15.0$, $\underline{C}=C-O-P$); 142.2 (d, $^2J_{CP} = 12.0$, $C=\underline{C}-O-P$); 162.7 (d, $^4J_{CP} = 3.0$, $CH_3-O-\underline{C}=C$); phenyl carbons: $\delta = 128.0$, 129.3, 133.3, 133.5, 133.9, 134.0; IR (neat): $\nu_{P=S} = 694\,cm^{-1}$; EI–HRMS: calculated for $C_{14}H_{17}O_2PS_2$: 312.0408 (M^+); found: 312.0405.

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