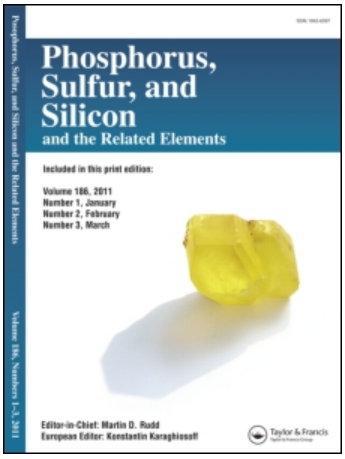

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A FACILE SYNTHESIS OF DERIVATIVES OF 4-ARYL-1,3,2-DIOXAPHOSPHORINANE-2-SULFIDE VIA LAWESSON'S REAGENT

LIANG-NIAN HE[a*], KAI LI[a], YAN-PING LUO[a], XIAO-PENG LIU[b], MING-WU DING[a], QING-CHUN ZHOU[a], TIAN-JIE WU[b] and FEI CAI[b]

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The derivatives of 4-aryl-1,3,2-dioxaphosphorinane-2-sulfide, namely, 4-aryl-5,5-dimethyl-1,3,2-dioxaphosphorinane-2-sulfides (**6**) were synthesized in moderate yields by the cyclization reaction of 1-aryl-2,2-dimethyl-1,3-propanediols(**5**) with Lawesson's reagent using acetonitrile as a solvent. 8-Membered cyclic trithiopyrophosphonates (**7**) were isolated as side-products.

Keywords: Synthesis; 4-aryl-1,3,2-dioxaphosphorinane-2-sulfides; Lawesson's reagent; trithiopyrophosphonates

INTRODUCTION

Within the rapid development of the chemistry of phosphorus heterocycles,[1] functionlized phosphorus-heterocycles and their dervatives have received considerable attention since they are of great interest as bioactive substances with various properties.[2] It was reported that the heterocyclic compounds, which incorporate phosphinothioylene moiety, are of potential interest as herbicides,insecticides,and fungicides.[3-7]

Recently, we became interested in the synthesis of phosphorus heterocycles by cyclization reactions of Lawesson's reagent (**LR**), 2,4-bis(4-meth-

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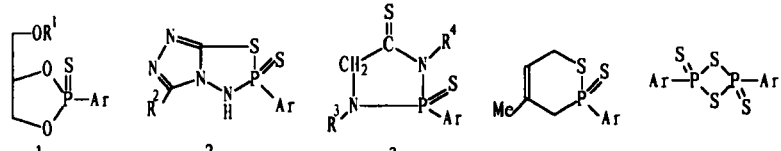
oxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide, with certain substrates.Thus, reactions[8–12] of Lawesson's reagent with long-chain -glycerin monoethers, 3-mercapto-4-amino-1,2,4-triazoles, 1,3-disubstituted glycinamides, and 2- methyl-1,3-butadiene were investigated. It was found that these reactions yield cyclic phospholipid analogues **1**, fused heterocycles **2**, 5-membered phosphorus rings **3**, and 6-membered heterocycle **4**, respectively, as shown in scheme.The preliminary biological screening tests of these rings showed that they possess significant selective herbicidal activity against rape. In this paper we describe the synthesis of substituted 1,3,2-dioxaphosphoninane-2-sulfides(**6**) via Lawesson's reagent.

1,3,2-Dioxaphosphorinane-2-sulfides can be prepared in two or three steps by initial condensation of $RCH[CH_2(OH)]_2$ with $PSCl_3$ followed by alcoholysis or by phosphorochloridate to give the corresponding phosphites which were heated with sulfur to form 1,3,2-dioxaphosphorinane-2-sulfides. Also, different methods have been used to synthesize such compounds, which are very important as pesticides[7,13] but it is clear that these methods are cumbersome and give low yields.



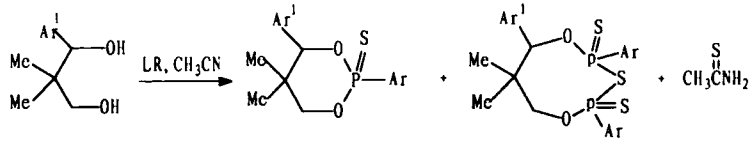
Ar= *p*-$CH_3OC_6H_4$; R^1= C_{11-13} alkyl group; R^2, R^3,R^4= H, alkyl, aryl

SCHEME 1

RESULTS AND DISCUSSION

0.5 Molar equivalents of Lawesson's reagent (LR) reacted with one mole of the corresponding 1,3-propanediols(**5a-h**)in acetonitrile at 70°C under anhydrous nitrogen for 10–12 hrs to give 4-aryl-5,5-dimethyl-1,3,2-dioxaphosphorinane-2-sulfides (**6**) as the main reaction product in moderate yields(20–38%), cyclic trithiopyrophosphonates (**7**) as side-product(3–6%), and the thioacetamide(m.p. 113°C), as depicted in Scheme 2.

When the above reaction was performed using 1:1 molar ratio of (Lawesson's reagent and 1,3-propanediol),compound (**7**) was obtained as the



5-7	Ar[1]	Ar	5-7	Ar[1]	Ar
a	Ph	4-MeOPh	e*	3-NO_2Ph	4-MeOPh
b*		4-MeOPh	f	4-NO_2Ph	4-MeOPh
c	4-ClPh	4-MeOPh	g*	4-MePh	4-MeOPh
d	2-ClPh	4-MeOPh	h*	4-FPh	4-MeOPh

*Compound **7b**, **7e**, **7g** and **7h** were not obtained

SCHEME 2

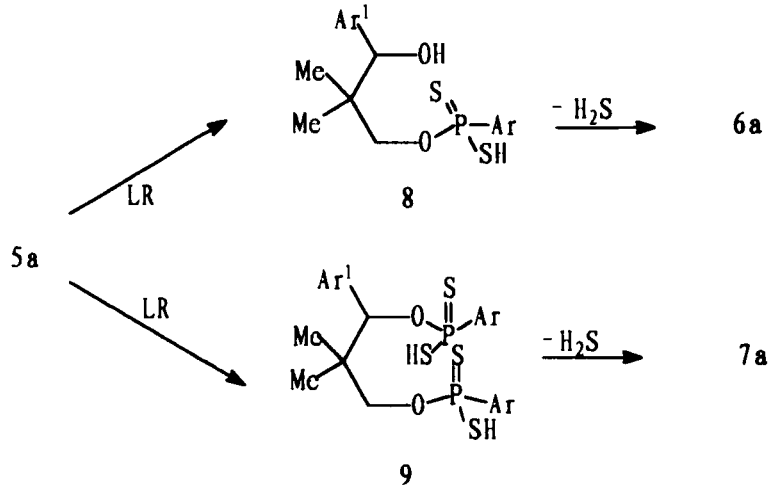
main product in yield of 10–15%, together with the minor products (**6**) in yields of 1–3%, and thioacetamide. However, when the reaction was carried out at reflux temperature in anhydrous toluene, benzene, or chloroform, respectively, very complex reaction mixtures resulted and neither (**6**) nor (**7**) could be isolated and characterized.

As to the mechanism of this reaction, it is suggested that the electrophilic attack of the phosphorus atom of the momeric species of LR on the nucleophilic oxygen of 1,3-propanediol, **5a**, will afford the intermediates **8** and **9** (Scheme 3), which in the presence of acetoitrile yield products **6a** and **7a**, together with thioacetamide.

The herbicidal activity of the title compounds (**6**) was tested. Preliminary bioasssys indicated that some of them displayed good selective herbicidal activity against rape. In conclusion, The cyclization reaction of Lawesson's reagent with propane-1,3-diols provides a facile route leading to biologically active heterocycles namely 4-aryl-5,5-dimethyl-1,3,2-dioxaphosphorinane-2-sulfides(**6**).

EXPERIMENTAL

Melting points were uncorrected, ^{1}HNMR spectra and ^{31}P NMR spectra were recorded on a Varian XL-200 MHz spectrometer. Mass spectra were



SCHEME 3

measured on a HP 5988A spectrometer and a VG-7070E spectrometer. The IR spectra were measured by using a Shimadzu-408 instrument. Elemental analyses were performed with a PE-2400 elementary analyzer. Column chromatography was performed on silica gel II (10–40 μ, Hai Yang Chemical Factory of Qingdao). All solvents and materials were reagent grade and purified as required. Lawesson's Reagent was prepared in a yield of 75% according to published procedure.[14] 1-Aryl-2,2-dimethyl-1,3-Propanediols were prepared as described in ref. 15.

General Procedure for Cyclization Reaction of Lawesson's Reagent with,3-Propanediol(5) using 1:2 molar ratio

A mixture of the appropriate propane-1,3-diol **5a-h** (2mmol), Lawesson's reagent(0.4g,1mmol), and dry acetonitrile 10mL) was stirred at 70°C for 10–12 hrs until no more of the starting material could be detected by TLC. The solvent was evaporated under reduced pressure. The residue was purified by passing through a short column with silica gel in petroleum ether / anhydrous ethyl ether (2:1) to give compounds **6** and **7**.

2-(4-Methoxylphenyl)-4-phenyl-5,5-dimethyl-1,3,2-dioxaphosphorinane-2-sulfide (**6a**): m.p. 102–103°C; yield 38%; Anal. Calcd for

$C_{18}H_{21}O_3PS$ C, 62.07; H, 6.03. Found : C, 62.31; H, 5.87. IR (KBr, cm^{-1}): 705, 1030. ^1H NMR($CDCl_3$) δ: 0.88(s, 3H, CH_3), 1.15(s, 3H, CH_3), 3.89(s, 3H, OCH_3), 4.76–4.84(dd, 2H, *J*=4.4Hz, CH_2-O), 5.73–5.75(d. H, *J*=4.4Hz, HC-O), 7.01–8.17(m, 9H, Ar). ^{31}P NMR($CDCl_3$) δ 89.52. MS *m/z* (%): 348(100, M^+), 292 (57), 187(77), 171(18).

2-(4-Methoxylphenyl)-4-furyl-5,5-dimethyl-1,3,2-dioxaphosphorinane-2-sulfide (**6b**): m.p. 52–53°C; yield 25%; Anal. Calcd for $C_{16}H_{19}O_4PS$ C, 56.80; H, 5.62. Found : C, 56.61; H, 5.78. IR (KBr, cm^{-1}): 690, 1040. ^1H NMR($CDCl_3$) δ: 0.93(s, 3H, CH_3), 1.28(s, 3H, CH_3), 3.87(s, 3H, OCH_3), 4.54–4.58(m, 2H, CH_2-O), 4.92–4.94(d, 1H, *J*=6.0Hz, HC-O), 6.28–6.54(m, 3H, H_{furyl}), 6.99–7.80(m, 4H, Ar). MS *m/z* (%):338(87, M^+), 283(25), 187(39), 112(100).

2-(4-Methoxylphenyl)-4-(4-chlorophenyl)-5,5-dimethyl-1,3,2-dioxaphosphorinane-2-sulfide (**6c**): m.p. 139–140°C: yield 28%; Anal. Calcd for $C_{18}H_{20}ClO_3PS$ C, 56.47; H, 5.23. Found : C, 56.75; H, 5.02. IR (KBr, cm^{-1}): 700, 1030. ^1H NMR($CDCl_3$) δ: 0.86(s, 3H, CH_3), 1.12(s, 3H, CH_3), 3.88(s, 3H, OCH_3), 4.74–4.84(dd, 2H, *J*=4.6Hz, CH_2-O), 5.69–5.73(d, 1H, *J*=4.6Hz, HC-O), 7.02–8.13(m, 8H, Ar). ^{31}P NMR($CDCl_3$) δ 87.84. MS *m/z* (%):382(100, M^+), 384(32, M+2), 328(25), 187(89), 171(21), 111(8).

2-(4-Methoxylphenyl)-4-(2-chlorophenyl)-5,5-dimethyl-1,3,2-dioxaphosphorinane-2-sulfide (**6d**): m.p. 145–146°C; yield 20%; Anal. Calcd for $C_{18}H_{20}ClO_3PS$ C, 56.47; H, 5.23. Found : C, 56.21; H, 5.46. IR (KBr, cm^{-1}): 698, 1025. ^1H NMR($CDCl_3$) δ: 0.92(s, 3H, CH_3), 1.24(s, 3H, CH_3), 3.87(s, 3H, OCH_3), 4.83–4.90(dd, 2H, *J*=4.4Hz, CH_2-O), 5.32–5.36(d, 1H, *J*=4.4Hz, HC-O), 6.99–8.0(m, 8H, Ar). MS *m/z* (%):382(100, M^+), 384(37, M+2), 328(21), 187(99), 171(20).

2-(4-Methoxylphenyl)-4-(3-nitrophenyl)-5,5-dimethyl-1,3,2-dioxaphosphorinane-2-sulfide (**6e**): m.p. 166–167°C: yield 30%; Anal. Calcd for $C_{18}H_{20}NO_5PS$ C, 54.96; H, 5.10; N, 3.56. Found: C, 54.75; H, 5.32; N, 3.41. IR (KBr, cm^{-1}): 705, 1035. ^{1}HNMR($CDCl_3$) δ: 0.92(s, 3H, CH_3), 1.15(s, 3H, CH_3), 3.90(s, 3H, OCH_3), 3.95–4.82(dd, 2H, *J*=4.4Hz, CH_2-O), 5.84–5.86(d, 1H, *J*=4.4Hz, HC-O), 7.03–8.21 (m, 8H, Ar). ^{31}PNMR($CDCl_3$) δ 90.27. MS *m/z* (%):393(100, M^+), 337(2), 187(42), 171(11), 123(10).

2-(4-Methoxylphenyl)-4-(4-nitrophenyl)-5,5-dimethyl-1,3,2-dioxaphosphorinane-2-sulfide (**6f**): m.p. 168–170°C; yield 27%; Anal. Calcd for $C_{18}H_{20}NO_5PS$ C, 54.96; H, 5.10; N, 3.56. Found : C, 54.83; H, 5.45; N,

3.36. IR (KBr, cm^{-1}): 710, 1030. ^1H NMR($CDCl_3$) δ: 0.90(s, 3H, CH_3), 1.11(s, 3H, CH_3), 3.88(s, 3H, OCH_3), 4.80–4.85(dd, 2H, *J*=4.4Hz, CH_2-O), 5.81–5.83(d, 1H, *J*=4.4Hz, HC-O), 7.01–8.20(m, 8H, Ar). MS *m/z* (%):393(100, M^+), 337(5), 187(97), 171(43), 123(26).

2-(4-Methoxylphenyl)-4-(4-methylphenyl)-5,5-dimethyl-1,3,2-dioxaphosphorinane-2-sulfide (**6g**): m.p. 108–109°C; yield 35%; Anal. Calcd for $C_{19}H_{23}O_5PS$ C, 62.98; H, 6.35. Found : C, 62.75; H, 6.47. IR (KBr, cm^{-1}): 702, 1035. ^1H NMR($CDCl_3$) δ : 0.86(s, 3H, CH_3), 1.15(s, 3H, CH_3), 2.34(s, 3H, CH_3), 3.88(s, 3H, OCH_3), 4.73–4.84(dd, 2H, *J*=4.4Hz, CH_2-O), 5.67–5.74(d, 1H, *J*=4.4Hz, HC-O), 7.02–8.22(m, 8H, Ar). ^{31}PNMR($CDCl_3$) δ 89.45. MS *m/z* (%): 362(90, M^+), 306(83), 187(92), 171(26), 92(63).

2-(4-Methoxylphenyl)-4-(4-flurophenyl)-5,5-dimethyl-1,3,2-dioxaphosphorinane-2-sulfide (**6h**): m.p. 148–149°C; yield 26%; Anal. Calcd for $C_{18}H_{20}FO_3PS$ C, 59.02; H, 5.46. Found : C, 59.32; H, 5.19. IR (KBr, cm^{-1}): 705, 1025. ^1H NMR($CDCl_3$) δ : 0.88(s, 3H, CH_3), 1.20(s, 3H, CH_3), 3.87(s, 3H, OCH_3), 4.72–4.86(dd, 2H, *J*=4.4Hz, CH_2-O), 5.70–5.78(d, H, *J*=4.4Hz, HC-O), 7.10–8.02(m, 8H, Ar). MS *m/z* (%): 366(25, M^+), 171(8), 139(59), 63(100).

2,4-Di-(4-methoxylphenyl)-6-phenyl-7,7-dimethyl-1,5,3,2,4-dioxathiadiphosphocane-2,4-disulfide (**7a**): m.p. 157–158°C; yield 4%; Anal. Calcd for $C_{25}H_{28}O_4P_2S_3$ C, 54.55; H, 5.09. Found : C, 54.37; H, 5.23. IR (KBr, cm^{-1}): 705, 1040. ^1H NMR($CDCl_3$) δ: 0.92(s, 3H, CH_3), 1.20(s, 3H, CH_3), 3.85 (s, 3H, OCH_3), 3.88(s, 3H, OCH_3), 4.70–4.95(dd, 2H, *J*=10.2Hz, CH_2-O), 5.92–6.01(d, 1H, *J*=17.6Hz, HC-O), 6.94–8.12(m, 13H, Ar). ^{31}P NMR($CDCl_3$) δ 88.55, 84.88. MS *m/z*(%):550 (53, M^+), 405(43), 364(100), 348(64), 202(21), 187(43), 171(13), 139(88).

2,4-Di-(4-methoxylphenyl)-6-(4-chlorophenyl)-7.7-dimethyl-1,5,3,2,4-dioxathiadiphosphocane-2,4-disulfide (**7c**): m.p. 211–213°C; yield 6%; Anal. Calcd for $C_{25}H_{27}ClO_4P_2S_3$ C, 51.33; H, 4.63. Found : C, 51.37; H, 4.43. IR (KBr, cm^{-1}): 702, 1025. ^1H NMR($CDCl_3$) δ : 0.95(s, 3H, CH_3), 1.22(s, 3H, CH_3), 3.93 (s, 3H, OCH_3), 3.95(s, 3H, OCH_3), 4.80–4.89(dd, 2H, *J*=10.8Hz, CH_2-O), 5.90–6.00(d, 1H, *J*=12.3Hz, HC-O), 7.00–8.10(m, 12H, Ar). MS *m/z* (%):584(12, M^+), 586(4, M+2), 405(36), 398(82), 382(22), 202(29), 187(67), 171(15), 139(100).

2,4-Di-(4-methoxylphenyl)-6-(2-chlorophenyl)-7,7-dimethyl-1,5,3,2,4-dioxathiadiphosphocane-2,4-disulfide (**7d**): m.p. 203–204;

yield 5%; Anal. Calcd for $C_{25}H_{27}ClO_4P_2S_3$ C, 51.33; H, 4.63. Found : C, 51.45; H, 4.39. IR (KBr, cm^{-1}): 710, 1027. ^1H NMR($CDCl_3$) δ : 1.05(s, 3H, CH_3), 1.21(s, 3H, CH_3), 3.85 (s, 3H, OCH_3), 3.89(s, 3H, OCH_3), 4.76–4.90(dd, 2H, *J*=15Hz, CH_2-O), 6.57–6.66(d, 1H, *J*=17.6Hz, HC-O), 6.93–8.15(m, 12H, Ar). ^{31}P NMR($CDCl_3$) δ 88.07, 84.86. MS *m/z*(%): 584(37, M^+), 586(12, M+2), 405(37), 398(10), 382(44), 202(20), 187(70), 171(21), 139(100).

2,4-Di-(4-methoxylphenyl)-6-(4-nitrophenyl)-7,7-dimethyl-1,5,3,2,4-dioxathiadiphosphocane-2,4-disulfide (**7f**): m.p. 241–242°C; yield 3%; Anal. Calcd for $C_{25}H_{27}NO_6P_2S_3$ C, 50.42; H, 4.54; N, 2.35. Found : C, 50.72; H, 4.34; N, 2.56. IR (KBr, cm^{-1}): 700, 1030. ^1H NMR($CDCl_3$) δ : 1.33(s, 3H, CH_3), 1.53(s, 3H, CH_3), 3.78(s, 3H, OCH_3), 3.85(s, 3H, OCH_3), 4.83–4.98(dd, 2H, *J*=10.3Hz, CH_2-O), 5.86–5.95(d, 1H, *J*=19.2Hz, HC-O), 7.10–8.20(m, 12H, Ar). ^{31}P NMR($CDCl_3$) δ 84, 65, 85, 70. MS *m/z* (%):595(21, M^+), 409(15), 405(9), 393(55), 202(20), 187(72), 171(23), 139(100).

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