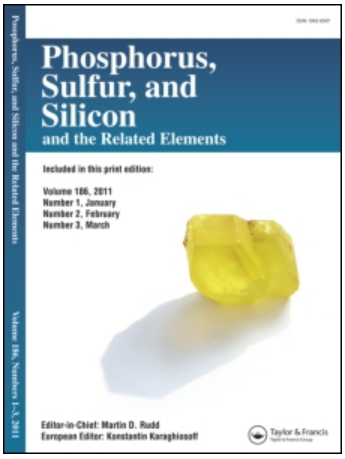


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

THE REACTION OF 2,4=BIS(4-METHOXYPHENYL)- 1,3,2,4-DITHIADIPHOSPHETANE-2,4- DISULPHIDE (LAWESSON'S REAGENT, LR)WITH SOME S-TRIAZOLE DERIVATIVES. SYNTHESIS OF S-TRIAZOLE-FUSED P-HETEROCYCLES

H. M. Moustafa[a]
[a] Chemistry Department, Faculty of Science, Sohag, Egypt

To cite this Article Moustafa, H. M.(2000) 'THE REACTION OF 2,4=BIS(4-METHOXYPHENYL)- 1,3,2,4-DITHIADIPHOSPHETANE-2,4- DISULPHIDE (LAWESSON'S REAGENT, LR)WITH SOME S-TRIAZOLE DERIVATIVES. SYNTHESIS OF S-TRIAZOLE-FUSED P-HETEROCYCLES', Phosphorus, Sulfur, and Silicon and the Related Elements, 164: 1, 11 — 22
To link to this Article: DOI: 10.1080/10426500008045229
URL: http://dx.doi.org/10.1080/10426500008045229

Phosphorus, Sulfur and Silicon, 2000, Vol. 164, pp. 11-22
Reprints available directly from the publisher
Photocopying permitted by license only

THE REACTION OF 2,4-BIS(4-METHOXYPHENYL)-1,3,2,4-DITHIADIPHOSPHETANE-2,4-DISULPHIDE (LAWESSON'S REAGENT, LR) WITH SOME S-TRIAZOLE DERIVATIVES. SYNTHESIS OF S-TRIAZOLE-FUSED P-HETEROCYCLES

H.M. MOUSTAFA*

Chemistry Department, Faculty of Science, Sohag, Egypt

(Received November 13, 1998; In final form November 14, 1999)

Lawesson's reagent (LR, **1**) reacted with 3-(o-hydroxy-, o-amino- and o-methylamino-substituted)phenyl-4-hydroxy(phenylamino)-5-mercapto(methylthio)-1,2,4-triazoles $\mathbf{2_{a-f}}$ and $\mathbf{4_{a-f}}$ to afford the fused systems $\mathbf{3_{a-f}}$ and $\mathbf{5_{a-f}}$, respectively. A similar treatment of **1** with 3-(o-hydroxy-, o-amino- and o-methylamino- substituted)phenyl-5-mercapto(benzylthio)-1,2,4-triazoles $\mathbf{6_{a-c}}$ and $\mathbf{8_{a-c}}$ gave the condensed systems $\mathbf{7_{a-c}}$ and $\mathbf{9_{a-c}}$, respectively.

Keywords: 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulphide; 5-aryl-4-hydroxy –3-mercapto-1,2,4-triazoles

INTRODUCTION

The chemistry of Lawesson's reagent, (LR) as a thiation reagent has been studied for many years,[1–4] and several papers[5–13] describe its ring-closure reactions with substrates containing two functional groups. In connection with our continuing interest[14] in this respect, we wish to report herein the reaction of LR with some s-triazoles containing two nucleophilic functional groups to obtain new s-triazole-fused P-heterocycles.

* Corresponding Author.

RESULTS AND DISCUSSION

The parent compounds, 3-(o-hydroxy-, o-amino- and o-methylamino- substituted)phenyl-4-hydroxy-5-mercapto-1,2,4-triazoles **2**$_{a-c}$ were prepared in good yields from the corresponding 1,3,4-oxadiazole derivatives by the action of hydroxylamine hydrochloride in boiling pyridine, whereas 3-(o-hydroxy-, o-amino- and o-methylamino-substituted)phenyl-4-phenylamino-5-mercapto-1,2,4-triazoles **2**$_{d-f}$ were prepared in good yields via the reaction of the corresponding 1,3,4-oxadiazole derivatives with phenylhydrazine in boiling isopropyl alcohol. Also, 3-(o-hydroxy-, o-amino- and o-methylamino- substituted)phenyl-5-mercapto-1,2,4-triazoles **6**$_{a-c}$ were prepared in good yields by the reaction of the corresponding acid hydrazide derivatives with ammonium thiocyanate in ethanol in presence of sodium ethoxide. It has been reported[15]that compound **6**$_a$ was prepared by another method. The reaction of 3-(o-hydroxy-, o-amino- and o-methylamino- substituted)phenyl-4-hydroxy-5-mercapto-1,2,4-triazoles **2**$_{a-c}$ with 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulphide (LR, **1**) in boiling acetonitrile afforded 3-mercapto-6-(4-methoxyphenyl)-s-triazolo[4,3-b]-1,6,2,7-benzodioxaazaphosphopine-6-sulphide (**3**$_a$), 3-mercapto-6-(4-methoxyphenyl)(7H)-s-triazolo-[4,3-d]-1,2,6,7-benzooxadiazaphosphopine-6-sulphide (**3**$_b$), and 3-mercapto-6-(4-methoxyphenyl)-7-methyl-s-triazolo[4,3-b]-1,2,6,7-benzooxadiazaphosphopine-6-sulphide (**3**$_c$), respectively (Scheme 1). The IR spectra of compounds **3**$_{a,c}$showed the absence of bands corresponding to hydroxyl groups, while exhibiting the characteristic absorption bands at 653, 650 & 645 cm^{-1} for P=S, respectively. The ^{1}H-NMR (DMSO, δ) spectra of compounds **3**$_{a,c}$ exhibited a singlet at 3.9 ppm corresponding to OCH_3. The mass spectrum of compound **3**$_a$showed the molecular ion at m/e (rel. int.%) 377 (93), indicating the formation of the product. Treatment of compounds **2**$_{d-f}$ with Lawesson's reagent (**1**) afforded 3-mercapto-5-phenyl-6-(4-methoxyphenyl)-s-triazolo[4,3-d]-1,3,4,2-benzooxadiazaphosphopine-6-sulphide (**3**$_d$), 3-mercapto-5-phenyl-6-(4-methoxyphenyl)(7H)-s-triazolo[4,3-b]-1,2,6,7-benzotriazaphosphopine-6-sulphide (**3**$_e$) and 3-mercapto-5-phenyl-6-(4-methoxyphenyl)-7-methyl-s-triazolo[4,3-b]-1,2,6,7-benzotriazaphosphopine-6-sulphide (**3**$_f$), respectively (Scheme 1). The IR spectrum of compound **3**$_d$ revealed the absence of absorption bands corresponding to the amino and hydroxyl groups while the IR spectra of compound **3**$_{e,f}$ revealed the absence of absorption bands corresponding to the amino

group. The ^{1}H-NMR spectra of compounds $\mathbf{3_{d-f}}$, are in Table II. The mass spectrum of compound $\mathbf{3_d}$ showed the molecular ion at m/e (rel. int.%) 352.3 (71) indicating the formation of the product.

When compounds $\mathbf{2_{a-f}}$ were allowed to react with methyl iodide in presence of sodium hydroxide, the corresponding S-methyl derivatives $\mathbf{4_{a-f}}$ were obtained in good yields. The structure of compounds $\mathbf{4_{a-f}}$ have been confirmed by elemental and spectral analyses (cf. Tables I and II). The reaction of compounds $\mathbf{4_{a-f}}$with Lawesson's reagent afforded 3-methylthio-6-(4-methoxyphenyl)-s-triazolo[4,3-b]-1,6,2,7-benzodioxazaphosphopine-6-sulphide ($\mathbf{5_a}$), 3-methylthio-6-(4-methoxyphenyl)(7H)-s-triazolo[4,3-b]-1,2,6,7-benzooxadiazaphosphopine-6-sulphide ($\mathbf{5_b}$), 3-methylthio-6-(4-methoxyphenyl)-7-methyl-s-triazolo[4,3-b]-1,2,6,7-benzooxadiazaphosphopine-6-sulphide ($\mathbf{5_c}$), 3-methylthio-5-phenyl-6-(4-methoxyphenyl)-s-triazolo[4,3-d]-1,3,4,2-benzotriazaphosphopine-6- sulphide ($\mathbf{5_d}$), 3-methylthio-5-phenyl-6-(4-methoxyphenyl)(7H)-s-triazolo[4,3-b]-1,2,6,7-benzotriazaphosphopine-6-sulphide ($\mathbf{5_e}$), and 3-methylthio-5-phenyl-6-(4-methoxyphenyl)-7-methyl-s-triazolo[4,3-b]-1,2,6,7-benzotriazaphosphopine-6-sulphide ($\mathbf{5_f}$), respectively (Scheme 1). The IR and ^{1}H-NMR spectra of these compounds confirm the proposed structures (cf. Table II). Alkylation of compounds $\mathbf{3_{a-f}}$ with methyl iodide yielded compounds which are identical in all respects with authentic samples of compounds $\mathbf{5_{a-f}}$, respectively (Scheme 1).

TABLE I Physical and Analytical Data of The New Compounds

Product No	*M.P (°C) Cryst. Solvent*	*Yield (%)*	*Mol. Form. (Mol. Wt)*	*Analytical Data (Cal./ Found)*		
				C	*H*	*N*
$\mathbf{2_a}$	189	89	$C_8H_7N_3O_2S$	45.92	3.37	20.08
	(EtOH)		(209.221)	45.65	3.19	20.00
$\mathbf{2_b}$	171	87	$C_8H_8N_4OS$	46.14	3.87	26.91
	(EtOH)		(208.236)	45.91	3.71	26.69
$\mathbf{2_c}$	147	76	$C_9H_{10}N_4OS$	48.63	4.53	25.21
	(EtOH)		(222.262)	48.47	4.39	25.00
$\mathbf{2_d}$	227	77	$C_{14}H_{12}N_4OS$	59.13	4.25	19.70
	(EtOH)		(284.328)	59.26	4.11	19.56
$\mathbf{2_e}$	203	75	$C_{14}H_{13}N_5S$	59.34	4.62	24.72
	(EtOH)		(283.343)	59.20	4.49	24.53

Product No	M.P (°C) Cryst. Solvent	Yield (%)	Mol. Form. (Mol. Wt)	Analytical Data (Cal./ Found)		
				C	H	N
$\mathbf{2_f}$	169	70	$C_{15}H_{15}N_5S$	60.58	5.08	23.55
	(EtOH)		(297.369)	60.34	4.89	23.38
$\mathbf{3_a}$	221	83	$C_{15}H_{12}N_3O_3PS_2$	47.74	3.21	11.14
	(EtOH)		(377.369)	47.51	3.01	10.95
$\mathbf{3_b}$	231	81	$C_{15}H_{13}N_4O_2PS_2$	47.86	3.48	14.89
	(EtOH)		(376.384)	47.53	3.33	13.67
$\mathbf{3_c}$	199	79	$C_{16}H_{15}N_4O_2PS_2$	49.22	3.87	14.35
	(EtOH)		(390 410)	49.49	3.96	14.42
$\mathbf{3_d}$	281	77	$C_{21}H_{17}N_4O_2PS_2$	55.74	3.79	12.38
	(Dioxan)		(452 476)	55.53	3.59	12.19
$\mathbf{3_e}$	236	72	$C_{21}H_{18}N_5OPS_2$	55.83	4.02	15.50
	(Dioxan)		(451 776)	55.66	3.86	15.31
$\mathbf{3_f}$	191	74	$C_{22}H_{20}N_5OPS_2$	56.76	4.33	15.04
	(EtOH)		(465 517)	56.57	4.09	15.00
$\mathbf{4_a}$	171	81	$C_9H_9N_3O_2S$	48.42	4.06	18.82
	(EtOH)		(223 247)	48.71	4.11	18.80
$\mathbf{4_b}$	153	83	$C_9H_{10}N_4OS$	48.63	4.53	25.21
	(EtOH)		(222 262)	48.41	4.33	25.03
$\mathbf{4_c}$	125	76	$C_{10}H_{12}N_4OS$	50.83	5.12	23.71
	(EtOH)		(236 288)	50.54	5.21	23.50
$\mathbf{4_d}$	193	75	$C_{15}H_{14}N_4OS$	60.38	4.73	18.78
	(EtOH)		(298 354)	60.17	4.47	18.55
$\mathbf{4_e}$	177	77	$C_{15}H_{15}N_5S$	60.58	5.08	23.55
	(Dioxan)		(297 369)	60.29	5.19	23.29
$\mathbf{4_f}$	133	67	$C_{16}H_{17}N_5S$	61.71	5.50	22.49
	(EtOH)		(311 395)	61.43	5.28	22.23
$\mathbf{5_a}$	203	80	$C_{16}H_{14}N_3O_3PS_2$	49.10	3.61	10.74
	(EtOH)		(391.395)	48.83	3.45	10.67
$\mathbf{5_b}$	217	87	$C_{16}H_{15}N_4O_2PS_2$	49.22	3.87	14.35
	(EtOH)		(390.410)	49.01	3.59	14.09
$\mathbf{5_c}$	172	76	$C_{17}H_{17}N_4O_2PS_2$	50.48	4.24	13.85

Product No	M.P (°C) Cryst. Solvent	Yield (%)	Mol. Form. (Mol. Wt)	Analytical Data (Cal./ Found)		
				C	H	N
	(EtOH)		(404.436)	50.19	4.10	13.59
5d	222	77	$C_{22}H_{19}N_4O_2PS_2$	56.64	4.11	12.01
	(EtOH)		(466.502)	56.36	3.93	11.82
5e	193	75	$C_{22}H_{20}N_5OPS_2$	56.76	4.33	15.04
	(EtOH)		(465.517)	56.53	4.11	14.85
5f	177	70	$C_{23}H_{22}N_5\ OPS_2$	67.60	4.62	14.60
	(EtOH)		(479 543)	67.54	4.53	14.51
6b	212	81	$C_8H_8N_4S$	49.98	4.19	29.15
	(EtOH)		(192.236)	49.71	4.00	28.96
6c	181	79	$C_9H_{10}N_4S$	52.40	4.89	27.16
	(EtOH)		(206 292)	52.15	4.68	26.99
7a	251	77	$C_{15}H_{12}N_3O_2PS_2$	49.85	3.35	11.63
	(EtOH)		(361 369)	49.63	3.19	11.39
7b	230	72	$C_{15}H_{13}N_4OPS_2$	49.99	3.64	15.55
	(Dioxan)		(360.384)	49.70	3.46	15.33
7c	198	74	$C_{16}H_{15}N_4OPS_2$	51.32	4.04	14.96
	(EtOH)		(374 410)	51.03	3.83	14.72
8a	178	89	$C_{15}H_{13}N_3OS$	63.58	4.62	14.83
	(EtOH)		(283 339)	63.28	4.51	14.63
8b	163	83	$C_{15}H_{14}N_4S$	63.80	4.99	19.84
	(EtOH)		(282 354)	63.51	4.83	19.61
8c	143	76	$C_{16}H_{16}N_4S$	64.84	5.44	18.90
	(EtOH)		(296 380)	64.66	5.31	18.77
9a	219	76	$C_{22}H_{18}N_3O_2PS_2$	58.52	4.02	9.31
	(EtOH)		(451.487)	58.33	3.88	9.10
9b	201	67	$C_{22}H_{19}N_4OPS_2$	58.65	4.25	12.44
	(EtOH)		(450 502)	58.43	4.06	12.27
9c	183	70	$C_{23}H_{21}N_4OPS_2$	59.46	4.56	12.06
	(EtOH)		(464 528)	59.23	4.39	11.89

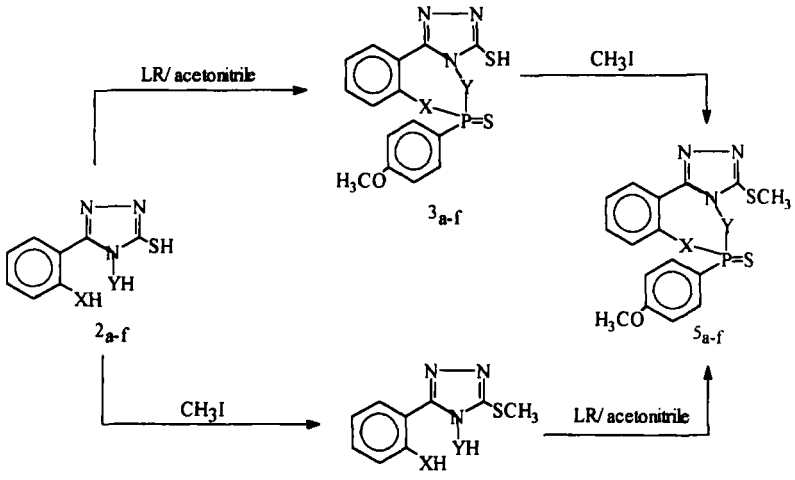
TABLE II Spectral Data of The New Compounds

IR (Cm^{-1})	*^{1}H-NMR (δ ppm)*
421,3373(2 OH); 3236(NH); 3056(CH,arom.).	10.6–10.4 (br, 1 H,NH); 9.1–8.9 (br, 1 H,OH); 8.7–8.5 (br, 1 H,OH); (m, 4 H,arom.).
410(OH); 3346,3260,3210(NH_2 +NH); 3080(CH,arom.).	10.9–10.7 (br, 1 H,NH); 9.9 9.7 (br, 1 H, OH); 7.7–7.0 (m, 4 H,arom.) 4.6 (br, 2 H, NH_2).
21(OH); 3370, 3286(2 NH); 3019(CH,arom.); 930(CH,aliph.).	12.0–11.8 (br, 1 H,NH); 11.6–11.4 (br, 1 H, NH); 9.4–9.2 (br, 1 H,OH 6.8 (m, 4 H, arom.); 2.9 (s, 3 H,CH_3).
42(OH); 3340,3281(2 NH); 3071(CH,arom.)	11.0–10.8 (br, 1 H,NH); 10.2–10.0 (br, 1 H, NH); 9.0–8.8 (br, 1 H,OH 7.0 (m, 9 H, arom.)
39,3290,3207,3193(NH_2+2NH) 3062(CH,arom.).	11.8–11.6 (br, 1 H,NH); 10.4–10.2 (br, 1 H, NH); 7.8–6.9 (m, 9 H,aro 5.0–4.7 (br, 2 H, NH_2).
61,3336,3301(3NH); 3020(CH, arom.); 2940(CH,aliph.).	12.0–11.8 (br, 1 H,NH); 11.3–11.1 (br, 1 H, NH); 10.9–10.7 (br, 1 H,N 7.8–6.8 (m, 9 H, arom.); 2.85 (s, 3 H,CH_3).
81(NH); 3061(CH,arom.); 2927, 2883(CH,aliph.); 653(P=S).	12.6–12.4 (br, 1 H,NH); 7.9–7.0 (m, 8 H, arom.); 3.9 (s, 3 H,CH_3).
	MS m/e(rel.Int.%): 377(93); 314(41); 307(12); 226(42); 195(29); 156(99(16); 64(49).
22,3226(2NH); 3052(CH,arom.); 2930(CH.aliph.); 650(P=S).	13.1–12.9 (br, 1 H,NH); 10.3–10.1 (br, 1 H, NH); 7.9–6.9 (m, 8 H,aro 3.9(s, 3 H,CH_3).
12(NH); 3060(CH,arom.); 2916 (CH,aliph.); 649(P=S).	10.9–10.7 (br, 1 H,NH), 8.0–6.9 (m, 8 H,arom.); 3.9 (s, 3 H,OCH_3); 2. H,NCH_3).
01(NH); 3039(CH, arom.); 2912(CH, aliph.); 651(P=S).	11.9–11.7 (br, 1 H,NH), 8.0–6.8 (m, 13 H, arom.); 3.9 (s, 3H,CH_3).
	MS m/e(rel.Int.%): 352.3(71); 335(52); 312(60); 304(23); 216(33); 18 132(19); 84(20).

IR (Cm^{-1})	*^{1}H-NMR (δ ppm)*
319,3205(2NH); 3081(CH,arom.); 2952(CH,aliph.); 650(P=S).	13.6–13.4 (br, 1 H,NH); 10.0–9.8 (br, 1 H,NH); 8.0–6.8 (m, 13 H, aror (s, 3 H,CH_3).
330(NH); 3090(CH,arom.); 2930 (CH,aliph.); 651(P=S).	11.0–10.8 (br, 1 H,NH); 8.0–6.9 (m, 13 H, arom.); 3.9 (s, 3 H,OCH_3); 3 H,NCH_3).
428,3356(2OH); 3032(CH,arom.); 2992, 2932(CH, aliph.);	9.9 –9.7 (br, 1 H,OH); 8.9–8.7 (br, 1 H, OH): 8.1–7.0 (m, 4 H,arom.); 3 H,CH_3).
936(OH); 3360,3310(NH_2); 3036 (CH,arom.); 2946,2864(CH, iph.).	9.8–9.6 (br, 1 H,OH), 7.7–6.8 (m, 4 H,arom.); 5.0–4.7 (br, 2 H,NH_2); 3 H,CH_3).
89(OH); 3290(NH); 3050(CH, arom.); 2970,2893(CH,aliph.).	10.9–10.7 (br, 1 H,NH); 8.9–8.7 (br, 1 H,OH): 7.7–6.8 (m, 4 H,arom.); 3 H,NCH_3); 2.7 (s, 3 H, SCH_3).
08(OH); 3288(NH); 3070(CH, arom.); 2959, 2894(CH, ph.).	10.9–10.7 (br, 1 H,NH), 8.9–8.7 (br, 1 H,OH); 8.0–6.8 (m, 9 H,arom.); 3 H,CH_3)
58,3290,3207(NH_2+NH); 3080 (CH,arom.); 2939(CH,aliph.).	11.1–10.9 (br, 1 H,NH); 7.9–6.8 (m, 9 H, arom.); 5.0–4.7 (br, 2 H,NH_2 2.7(s, 3 H,CH_3).
30,3278(2NH); 3068(CH,arom.); 2970,2861(CH,aliph.).	12.1–11.9 (br, 1 H,NH); 10.8–10.6 (br, 1 H, NH); 7.8–6.8 (m, 9 H,arom (s, 3 H, NCH_3); 2.7 (s, 3 H, SCH_3).
79(CH,arom.); 2942,2883(CH, aliph.); 649(P-S).	8.1–6.9 (m, 8 H,arom.); 3.9 (s, 3 H,OCH_3); 2.7 (s, 3 H, SCH_3).
46(NH); 3046(CH,arom.); 2936, 2882(CH.aliph.); 642(P=S).	10.6–10.4 (br, 1 H,NH); 8.0–6.9 (m, 8 H,arom.); 3.9 (s, 3 H,OCH_3); 2. H,SCH_3).
39(CH,arom.); 2963,2891(CH, aliph.); 655(P-S).	8.0–6.9 (m, 8 H,arom.); 3.9 (s, 3 H,OCH_3); 2.9 (s, 3 H,NCH_3); 2.7 (s, H,SCH_3).
92(CH,arom.); 2961,2913(CH, aliph.); 651 (P=S).	8.1–6.8 (m, 13 H,arom.); 3.9 (s, 3 H,OCH_3); 2.7 (s, 3 H, SCH_3).
19(NH); 3053(CH,arom.); 2919, 2891(CH,aliph.); 651(P=S).	11.1–10.9 (br, 1 H,NH); 8.0–6.9 (m, 13 H, arom.); 3.9(s, 3 H,OCH_3); 2. H,SCH_3).

IR (Cm^{-1})	*^{1}H-NMR (δ ppm)*
042(CH,arom.); 2980,2903(CH, aliph.); 640(P=S).	8.0–6.8 (m, 13 H,arom.); 3.9(s, 3 H,OCH_3); 2.85 (s, 3 H,NCH_3); 2.7 (H,SCH_3).
379,3310,3257,3199(NH_2+2NH) 3050(CH,arom.).	11.9–11.7 (br, 1 H,NH); 10.8–10.6 (br, 1 H, NH); 7.7–6.8 (m, 4 H,aro 5.1–4.8 (br, 2 H, NH_2).
300,3247,3203(3NH); 3077(CH, arom.); 969,2898(CH,aliph.).	12.8–12.6 (br, 1 H,NH); 11.7–11.5 (br, 1 H, NH); 10.3–10.1 (br, 1 H,N 7.8–6.9 (m, 4 H, arom.). 2.85 (s, 3 H, NCH_3).
320(NH); 3061(CH,arom.); 2927, 2883(CH,aliph.); 655(P=S).	12.2–12.0 (br, 1 H,NH); 7.9–7.0 (m, 8 H, arom.); 3.9(s, 3 H,CH_3).
333,3276(2NH); 3052(CH,arom.); 2930(CH.aliph.); 650(P=S).	12.9–12.7 (br, 1 H,NH); 10.6–10.4 (br, 1 H, NH); 7.9–6.9 (m, 8 H,aro (s, 3 H,CH_3).
	MS m/e(rel.Int.%): 360.1(69); 325(52); 302(45); 279(33); 217(23); 1 112(15); 94(22).
299(NH); 3060(CH,arom.); 2916 (CH, aliph.); 649(P=S).	10.7–10.5 (br, 1 H,NH), 7.9–6.9 (m, 8 H,arom.); 3.9 (s, 3 H,OCH_3); 2.8 H,NCH_3).
3380(OH); 3299(NH), 3050(CH, arom.); 2932(CH,aliph.);	11.1–10.9 (br, 1 H,NH); 9.9 –9.7 (br, 1 H, OH); 8.1–7.0 (m, 9 H,arom (s, 2 H,CH_2).
3360,3310,3246(NF_2+NH); 3036 (CH,arom.); 2946,2864(CH,aliph.).	10.8–10.6 (br, 1 H,NH), 7.7–6.8 (m, 9 H, arom.); 5.0–4.7 (br, 2 H,NH_2 (s, 2 H,CH_2).
3299,3237(2NH); 3067(CH,arom.); 2953, 2881(CH, aliph.).	10.7–10.5 (br, 1 H,NH), 10.2–10.0 (br, 1 H, NH), 8.0–6.9 (m, 9 H,aro 4.1(s, 2 H,CH_2); 2.85(s, 3 H,CH_3).
3066(CH,arom.); 2936,2888(CH, aliph.); 642(P=S).	8.1–6.9 (m, 13 H,arom.); 4.1(s, 2 H,CH_2); 3.9 (s, 3 H,CH_3).
3289(NH); 3089(CH,arom.); 2941 (CH,aliph.); 655(P=S).	10.9–10.7 (br, 1 H,NH), 8.1–6.9 (m, 13 H, arom.); 4.1(s, 2 H,CH_2); 3.9 H,CH_3).
3042(CH,arom.); 2971,2923(CH, aliph.); 657(P=S).	7.9–6.8 (m, 13 H,arom.); 4.1 (s, 2 H, CH_2); 3.9(s, 3 H,OCH_3); 2.85 (s, H,NCH_3).

The reaction of 3-(o-hydroxy-, o-amino- and o-methylamino- substituted)phenyl-5-mercapto-1,2,4-triazoles $\mathbf{6_{a-c}}$ with LR (**1**) in boiling acetonitrile afforded 3-mercapto-5-(4-methoxyphenyl)-s-triazolo[4,3-c]-1,3,2-benzooxazaphosphoxine-5-sulphide ($\mathbf{7_a}$), 3-mercapto-5-(4-methoxyphenyl)(6H)-s-triazolo[4,3-c]-1,3,2-benzodiazaphosphoxine-5-sulphide ($\mathbf{7_b}$), and 3-mercapto-5-(4-methoxyphenyl)-6-methyl-s-triazolo[4,3-c]-1,3,2-benzodiazaphosphoxine-5-sulphide ($\mathbf{7_c}$), respectively (Scheme 2). The structure of compounds $\mathbf{7_{a-c}}$ have been elucidated via analytical results and spectroscopic data (cf. Tables I and II). The mass spectrum of compound $\mathbf{7_b}$ (taken as representative example) showed the molecular ion at m/e (rel. int.%) 360.1 (69) indicating the formation of the product.

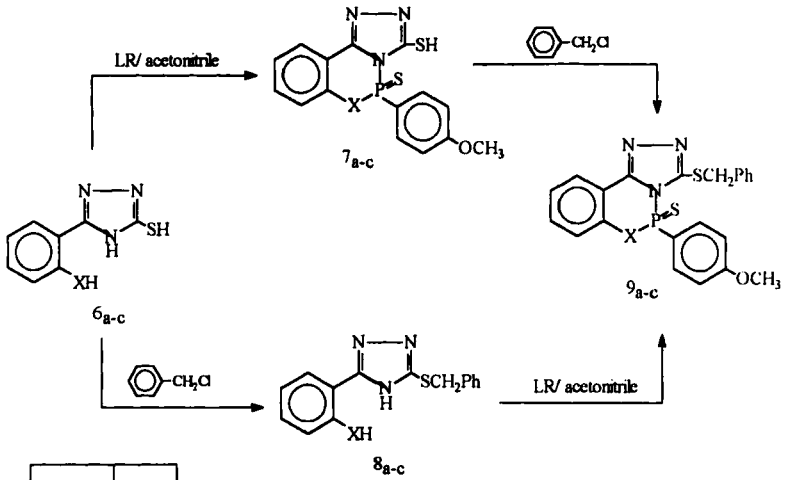


Comp.No.	X	Y
2,3,4,5a	O	O
b	NH	O
c	NCH_3	O
d	O	NPh
e	NH	NPh
f	NCH_3	NPh

1

SCHEME 1

When compounds $\mathbf{6_{a-c}}$ were allowed to react with benzyl chloride in presence of potassium carbonate, the corresponding S-alkyl derivatives $\mathbf{8_{a-c}}$ were obtained in good yields. The IR and ^{1}H-NMR spectra of these



Comp.No.	X
6,7,8,9a	O
b	NH
c	NCH_3

SCHEME 2

compounds confirm the proposed structures (cf. Table II). The reaction of compounds $\mathbf{8_{a-c}}$with LR (**1**) afforded 3-benzylthio-5-(4-methoxyphenyl)-s-triazolo[4,3-c]-1,3,2-benzooxaazaphosphoxine-5-sulphide ($\mathbf{9_a}$), 3-benzylthio-5-(4-methoxyphenyl)(6H)-s-triazolo[4,3-c]-1,3,2-benzodiazaphosphoxine-5-sulphide ($\mathbf{9_b}$), and 3-benzylthio-5-(4-methoxyphenyl)-6-methyl-s-triazolo[4,3-c]-1,3,2-benzodiazaphosphoxine-5-sulphide ($\mathbf{9_c}$), respectively (Scheme 2). The IR and ^{1}H-NMR spectra of these compounds confirm the proposed structures (cf. Table II). Alkylation of compounds $\mathbf{7_{a-c}}$ with benzyl chloride in presence of potassium carbonate yielded compounds which are identical in all respects with authentic samples of compounds $\mathbf{9_{a-c}}$ respectively (Scheme 2).

Experimental

All melting points are uncorrected. IR spectra (cm^{-1}) were recorded on a Nicolet, 710 FT-IR Spectrophotometer in KBr, ^{1}H-NMR spectra were

recorded at 60 MHz on a Varian A-60 Spectrophotometer using TMS as an internal reference standard. The mass spectra were recorded on a CEC 21–104 single focusing mass Spectrometer operating at 70 ev using direct inlet. Elemental analyses were carried out on an elemental analyzer, model 240 C. All compounds were checked for purity on TLC plates.

Preparation of Compounds 2_{a-c}. (General procedure)

A mixture of the appropriate 1,3,4-oxadiazole derivatives (0.01 mol) and hydroxylamine hydrochloride (0.01 mol) in pyridine (30 ml.) was refluxed for 6 h. On cooling, the mixture was poured into 100 ml of dilute hydrochloric acid, and the separated solid was crystallized from the appropriate solvent (cf. Table I).

Preparation of Compounds 2_{d-f}. (General procedure)

Phenylhydrazine (0.01 mol) was added to a solution of the appropriate 1,3,4- oxadiazole derivatives (0.01 mol) in isopropyl alcohol (60 ml.). The reaction mixture was refluxed for 8 h. The precipitate was washed with ethanol and crystallized from the appropriate solvent (cf Table I).

Preparation of Compounds 6_{a-c}. (General procedure)

A mixture of the proper benzoic acid hydrazide derivative (0.01 mol) and ammonium thiocyanate (0.01 mol) in ethanol (70 ml) was refluxed for 8 h. Then sodium ethoxide (0.23 g. of Na in 8 ml of ethanol) was added, and the mixture was refluxed for 5 h, concentrated and, cooled. The precipitate was filtered, washed with water and crystallized from the appropriate solvent to give compounds $\mathbf{6_{a-c}}$ (cf Table I).

Reaction of 2,4-bis(4-Methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulphide (1) with compounds 2_{a-f}, 4_{a-f}, 6_{a-c} and 8_{a-c}. (General procedure)

A mixture of the proper triazole ($\mathbf{2_{a-f}}$, $\mathbf{4_{a-f}}$, $\mathbf{6_{a-c}}$ and/or $\mathbf{8_{a-c}}$) (0.01 mol.) and compound **1** (0.005 mol.) in dry acetonitrile (80 ml) was refluxed for 6 h., concentrated, and cooled. The precipitate formed was filtered off and crystallized from the appropriate solvent to give compounds $\mathbf{3_{a-f}}$, $\mathbf{5_{a-f}}$, $\mathbf{7_{a-c}}$and $\mathbf{9_{a-c}}$, respectively (cf. Table I).

Reaction of Compounds 2_{a-f} and 3_{a-f} with Methyl Iodide (General procedure)

A mixture of the proper sulphide derivative ($2_{a-f}$and/or 3_{a-f}) (0.01 mol), sodium hydroxide (0.01 mol) and methyl iodide (0.012 mol) in ethanol (80 ml) was refluxed for 2 h, concentrated and cooled. The precipitate formed was filtered off, washed with water, and crystallized from the appropriate solvent to give compounds $\mathbf{4_{a-f}}$ and $\mathbf{5_{a-f}}$, respectively (cf. Table I).

Reaction of Benzyl Chloride with Compounds 6_{a-c} and 7_{a-c} (General procedure)

A mixture of the proper sulphide derivative ($6_{a-c}$and/or 7_{a-c}) (0.01 mol), benzyl chloride (0.01 mol) and anhydrous potassium carbonate (0.01 mol) in dry acetone (60 ml) was refluxed for 5 h. The reaction mixture was filtered while hot, concentrated, and cooled. The precipitate was filtered off and crystallized from the appropriate solvent to give compounds $\mathbf{8_{a-c}}$ and $\mathbf{9_{a-c}}$, respectively (cf. Table I).

Acknowledgements

Thanks are due to Prof. Dr. A.-B. Ghattas, Chemistry Department, Faculty of Science, South Valley University, Sohag, Egypt, for his invaluable help.

References

[1] B.S. Pedersen, S. Scheibye, N.H. Nilsson and S.-O. Lawesson, Bull. Soc. Chim. Belg. **87**, 223(1978).
[2] S. Scheibye, B.S. Pedersen and S.-O. Lawesson, Bull. Soc. Chim. Belg. **87**, 299(1978).
[3] K. Clausen, B.S. Pedersen, S. Scheibye, S.-O. Lawesson and J.H. Bowie, Int. J. Mass Spectrum Ion Phys. **29**, 223(1979).
[4] K. Clausen and S.-O. Lawesson, Bull. Soc. Chim. Belg. **88**, 305(1979).
[5] K. Clausen and S.-O. Lawesson, Nouv. J. Chim. **4**, 43(1980).
[6] R. Shabana, S. Scheibye, K. Clausen, S.O. Olesen and S.-O. Lawesson, Nouv. J. Chim. **4**, 87(1980).
[7] A.A. El-Barbary, K. Clausen and S.-O. Lawesson, Tetrahedron, **36**, 3309(1980).
[8] A.A. El-Barbary and S.-O. Lawesson, Tetrahedron, **37**, 2647(1981).
[9] A.A. El-Barbary and S.-O. Lawesson, Tetrahedron, **37**, 2641(1981).
[10] R. Shabana, F.H. Osman and S.S. Atrees, Tetrahedron, **49**, 1271(1993).
[11] R. Shabana, F.H. Osman and S.S. Atrees, Tetrahedron, **50**, 6975(1994).
[12] A.-B. A.G. Ghattas, E.-E. A.M. El-Khrisy and S.-O. Lawesson, Sulfur Lett., 69 (1982).
[13] T.P. Andersen, A.-B. A.G. Ghattas and S.-O. Lawesson, Tetrahedron, **39**, 3419 (1983).
[14] H.M. Moustafa, Phosphorous, Sulfur and Silicon, **148**, 131(1999).
[15] W. Guenther, L. Siegfried, Z. Chem. **12**(5), 175(1972).