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STUDIES ON ORGANOPHOSPHORUS COMPOUNDS. SYNTHESIS AND REACTIONS OF 1,2,4-TRIAZOLO(4,3-d)-1,3,4,2-BENZO-OXADIAZAPHOSPHOPINE AND TRIAZAPHOSPHOPINE DERIVATIVES

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2,4-Bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulphide (Lawesson's Reagent, LR) reacted with 4-amino-3-mercapto-5-(o-hydroxyphenyl and/or o-aminophenyl)-1,2,4-triazoles (**1a** and **2a**) in boiling acetonitrile to afford s-triazolo(4,3-d)-1,3,4,2-benzo- oxadiazaphosphopine-6-sulphide (**3a**) and triazaphosphopine-6-sulphide (**4a**) derivatives, respectively. Compounds **3a** and **4a** were alkylated with methyl iodide, benzyl chloride, ethyl chloroacetate and/or chloroacetanilide to give the corresponding s-alkylated derivatives (**3b-e** and **4b-e**, respectively). The structures of the products were proved chemically by the preparation via condensation of LR with the corresponding 3-alkylthio-4-amino-5-aryl-1,2,4-triazoles (**1b-e** and **2b-e**). Also, the structures of all new compounds were elucidated on the basis of elemental analysis, IR, ^{1}H-NMR, and MS spectra.

Keywords: 4-amino-5-(o-hydroxy- or o-aminophenyl)-3-mercapto-1,2,4-triazole 2,4-Bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulphide

INTRODUCTION

It is well known that 2,4-Bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulphide (Lawesson's Reagent, LR) is a most effective and versatile thiation reagent for different carbonyl compounds[1–7]. Lawesson's reagent undergoes also ring-closure reactions with substrates containing two functional groups[8–12]. To extend the use of LR to other classes of substrates with two functional groups its reaction with 4-amino-3-mer-

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capto-5-(o-hydroxy and/or o-amino- phenyl)-1,2,4-triazoles in boiling acetonitrile has been found to give a new ring systems, 1,2,4-triazolo(4,3-d)-1,3,4,2-benzo- oxadiazaphosphopine-6-sulphide **(3a)** and triazaphosphopine-6-sulphide **(4a)** derivatives, respectively.

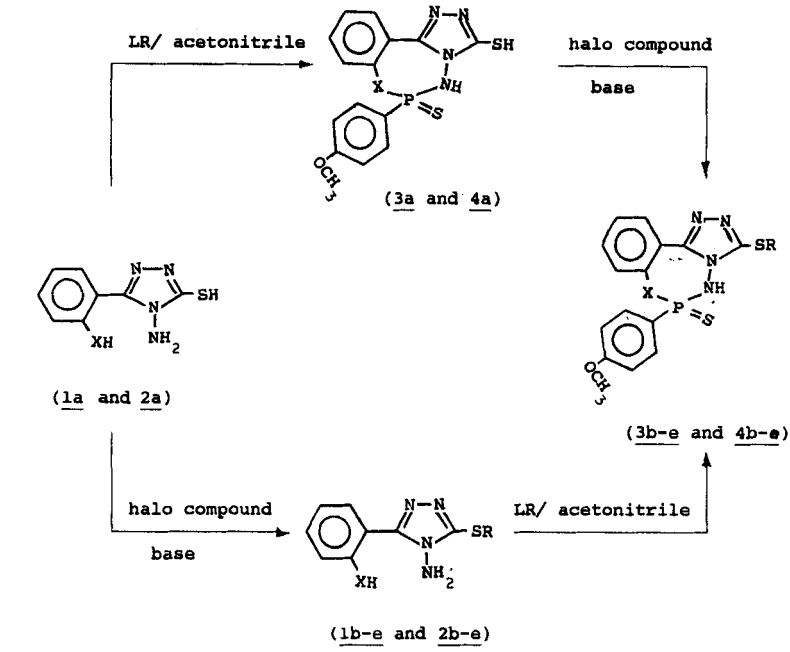
RESULTS AND DISCUSSION

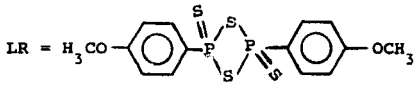
The parent compounds 4-amino-3-mercapto-5-(o-hydroxyphenyl) and/or 5-(o-aminophenyl)-1,2,4-triazoles (**1a** and **2a**) were prepared from the corresponding 1,3,4-Oxadiazole derivatives by the action of hydrazine hydrate (99 %) in boiling water in 90 and 87 % yields, respectively. The IR spectra (KBr, Cm^{-1}) of compounds **1a** and **2a** showed the absence of bands corresponding to C-O-C while exhibiting the charectaristic absorption bands at 3386–3255 corresponding to the amino groups. The ^{1}H-NMR (DMSO, δ) spectra of compounds **1a** and **2a** showed signals corresponding to N-NH_2 at 6.0–5.4 ppm. indicating the formation of the required products.

Treatment of compounds **1a** and **2a** with 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulphide (Lawesson's Reagent, LR) in boiling acetonitrile afforded s-triazolo(4,3-d)-1,3,4,2- benzo-oxadiazaphosphopine-6-sulphide (**3a**) and triazaphosphopine-6-sulphide (**4a**) derivatives, respectively (Scheme 1). The IR spectra (KBr, Cm^{-1}) of compounds **3a** and **4a** showed the absence of bands corresponding to the hydroxyl and amino groups, while exhibiting the characteristic absorption bands at 1029 for P-O-C and at 651–646 for P=S. The ^{1}H-NMR (DMSO, δ) spectra of compounds **3a** and **4a** are in agreement with the proposed structures (cf. Table I). The MS of compounds **3a** and **4a** showed the molecular ions at **m/e** (rel. int. %) 376(100) and 375(87.9) respectively, indicating the formation of the products.

Reaction of compounds **3a** and **4a** with different halo compounds namely; methyl iodide, benzyl chloride, ethyl chloroacetate and chloroacetanilide in alkaline medium afforded the corresponding sulphides **3b-e** and **4b-e,** respectively (Scheme 1). The structures of these products were proved by elemental analysis, IR and ^{1}H-NMR spectra (cf. Experimental part and Table I).

Alkylation of compounds **1a** and **2a** with the forementioned halo compounds gave s-alkylated derivatives **1b-e** and **2b-e,** respectively (Scheme 1). The IR spectra (KBr, Cm^{-1}) of compounds **1b-e** and **2b-e**





1 and 3; X=O
2 and 4; X=NH

R: b, $-CH_3$; c, $-CH_2Ph$; d, $-CH_2COOC_2H_3$;
e, $-CH_2-CONHPh$

SCHEME 1

revealed the absence of bands corresponding to C=S while exhibiting the characteristic absorption bands at 693–671 for C-S-C. The ^{1}H-NMR (DMSO, δ) spectra of compounds **1b-e** and **2b-e** are in agreement with the proposed structures (cf. Table I). The MS of compound **1b** showed the molecular ion at **m/e** (rel. int. %) 222(80.7).

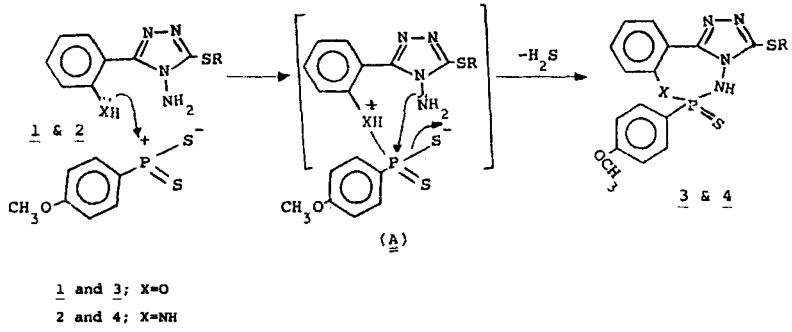
The reaction of compounds **1b-e** and **2b-e** with LR in boiling dry acetonitrile or dry benzene yielded compounds which are identical in all respects with authentic samples of compounds **3b-e** and **4b-e,** respectively (Scheme 1).

TABLE I Spectral Data of compounds **1**, **2**, **3** and **4**

Comp. No.	*IR (γ, cm^{-1}), ^{1}H-NMR (δ, ppm) and MS Spectra*
1a	IR: 3549 (OH) ; 3305, 3255 (NH_2) ; 3151(NH); 3076(CH,arom.); 1625(C=N)
	^{1}H-NMR: (DMSO) 14.0–13.7(br, 1H, NH);8.4–8.2(br,lH,OH);7.7–6.8(m,4H, arom.);5.9–5.4(br, 2H, NH_2).
1b	IR: 3472 (OH) ; 3327, 3258 (NH_2) ; 3087 (CH, arom.) ; 2922,2892(CH,aliph.) 1625(C=N).
	^{1}H-NMR: (DMSO) 8.2–8.0(br, 1H, OH);7.8–6.9(m,4H,arom.);6.2–5.9(br,2H, NH_2) ; 2.7 (s, 3H, CH_3).
	MS m/e (rel.Int. %): 222 (M^+, 80.7) ; 206(100); 120(38.7); 91(20.2); 74(18.9)
1c	IR: 3412 (OH) ; 3362, 3311 (NH_2) ; 3031(CH,arom.); 2986(CH,aliph.); 1631(C=N)
	^{1}H-NMR: (DMSO) 8.6–8.3(br,lH,OH);7.8–6.7(m,9H,arom.);6.2–5.8(br,2H, NH_2); 4.2 (s, 2H, CH_2).
1d	IR: 3388 (OH) ; 3300, 3264, 3189 (NH_2) ; 3046(CH,arom.); 2984, 2955, 2933 (CH,aliph.); 1728 (C=O) ; 1613(C=N).
	^{1}H-NMR: ($CDCl_3$) 8.5–8.3(br,lH,OH);7.7–6.9(m,4H,arom.);5.9–5.5(br,2H, NH_2);4.45–4.00(q,2H,O-CH_2);4.0(s,2H,S-CH_2) ; 1.4–1.1(t, 3H, CH_3)
1e	IR: 3549 (OH) ; 3475, 3416 (NH_2) ; 3239(NH); 3051(CH,arom.); 2977,2930, (CH,aliph.); 1682 (C=O) ; 1616(C=N).
	^{1}H-NMR : (DMSO) 10.7–10.5(br, 1H, NH);9.7–9.3(br,lH,OH);8.0–6.8(m,9H, arom.); 5.6–5.1(br, 2H, NH_2);4.1(s, 2H, CH_2).
2a	IR: 3386, 3342, 3291 ($2NH_2$); 3191(NH); 3039(CH,arom.); 1619(C=N).
	^{1}H-NMR: (DMSO) 14.2–13.8(br,lH,NH);7.9–6.6(m,4H,arom.);6.0–5.5 (br, 4H, $2NH_2$).
2b	IR: 3379, 3331 ($2NH_2$) ; 3041 (CH, arom.) ; 2976,2911(CH,aliph.);1621(C=N)
	^{1}H-NMR: (DMSO) 8.0–6.6(m,4H,arom.);5.8–4.9(br, 4H, $2NH_2$);2.7(s, 3H, CH_3)
2c	IR: 3356,3319,3289(2NH) ; 3032(CH,arom.); 2993(CH,aliph.);1612(C=N)
	^{1}H-NMR: (DMSO) 8.2–6.8(m,9H,arom.);6.5–5.9(br, 4H, $2NH_2$);4.3(s, 2H, CH_2)
2d	IR: 3373,3322,3251(2NH) ; 3056(CH,arom.); 2969, 2919 (CH, aliph.) ; 1723 (C=O) ; 1616 (C=N).
	^{1}H-NMR: ($CDCl_3$) 7.7–6.7(m,4H,arom.);5.9–5.4(br, 4H, $2NH_2$);4.4–4.0(q, 2H,O-CH_2);3.95(s,2H,S-CH_2);1.35–1.10(t, 3H, CH_3).
2e	IR: 3391,3454,3282($2NH_2$, NH); 3036(CH,arom.); 2991,2962(CH,aliph.); 1689 (C=O) ; 1613(C=N).
	^{1}H-NMR: (DMSO) 9.9–9.7(br, 1H, NH);7.9–6.8(m,9H, arom.); 5.9–5.3 (br, 4H, $2NH_2$);4.0(s, 2H, CH_2).
3a	IR: 3319,3125(2NH); 3050(CH,arom.); 2933(CH,aliph.); 1612 (C=N) ; 1029 (P-O-C) ; 651(P=S).

Comp. No.	*IR (γ, cm^{-1}), ^{1}H-NMR (δ, ppm) and MS Spectra*
	^{1}H-NMR: (DMSO) 14.3–14.1(br, 1H, NH);9.7–9.5(br,lH,NH);8.3–7.0(m,8H, arom.); 3.9 (s, 3H, CH_3).
	MS m/e (rel.Int. %): 376 (M^+, 100) ; 313(37); 312(34.5); 225(36.4); 222(29); 194(11.9); 170(31.5); 155(18.9); 108(10.6); 92(11.9); 64(24.4); 63(44.4); 46(21.9).
3b	IR: 3211(NH); 3061(CH,arom.); 2979,2937(CH,aliph.); 1629(C=N). ^{1}H-NMR: (DMSO) 9.9–9.7(br,1H,NH);8.1–7.0 (m, 8H, arom.);3.9(s,3H, OCH_3) ; 2.6 (s, 3H, SCH_3).
3c	IR: 3226,3192(NH); 3083 (CH, arom.) ; 2982,2960(CH,aliph.); 1631(C=N).
	^{1}H-NMR: (DMSO) 8.3–6.7(m,14H,arom.+NH);4.2(s, 2H, CH_2);3.9(s, 3H, OCH_3).
3d	IR: 3211(NH);3019(CH,arom.);2979,2931(CH, aliph.) ; 1719 (C=O) ; 1631 (C=N)
	^{1}H-NMR: (DMSO) 9.9–9.7(br,lH,NH) ; 8.1–6.8(m,8H,arom.) ; 4.5–4.1 (q, 2H, O-CH_2);4.1(s,2H,S-CH2);3.9(s, 3H, OCH_3) ; 1.45–1.15 (t, 3H, C-CH_3).
3e	IR: 3247,3207,3140(2NH); 3076(CH,arom.); 2968(CH,aliph.); 1680 (C=O) ; 1607(C=N)
	^{1}H-NMR : (DMSO) 10.9–10.7(br, 1H, NH);9.0–8.7(br, 1H, NH);8.3–6.7(m,13H, arom.); 4.2(s, 2H, CH_2);3.9(s, 3H, OCH_3).
4a	IR: 3349,3237,3129(3NH); 3072(CH,arom.); 2912(CH,aliph.); 1622 (C=N); 649 (P=S).
	^{1}H-NMR: (DMSO) 14.2–14.0(br, 1H, NH) ; 10.2–10.0(br, 1H, NH);9.8–9.7(br, 1H, NH);8.0–6.8(m,8H,arom.); 3.9 (s, 3H, CH_3).
	MS m/e (rel.Int. %): 375 (M^+, 89.7) ; 310(47); 224(66.9); 192(16.9); 169 (36.5) ; 168(10.9); 153(11.6); 107(13.9); 63(34.4); 45(21).
4b	IR: 3223,3289(2NH); 3039 (CH, arom.) ; 2991,2952(CH,aliph.); 1616(C=N)
	^{1}H-NMR: (DMSO) 10.2–10.0(br, 1H, NH);9.9–9.7(br, 1H, NH) ; 8.2–7.1 (m, 8H, arom.) ; 3.9 (s, 3H, OCH_3) ; 2.6 (s, 3H, SCH_3).
4c	IR: 3271,3201,3186(NH); 3036(CH,arom.); 2981,2932(CH,aliph.); 1611(C=N)
	^{1}H-NMR: (DMSO) 9.9–9.6(br, 1H, NH);8.2–6.8(m,14H,arom.+NH);4.2(s,2H, CH_2) ; 3.9 (s, 3H, OCH_3).
4d	IR: 3316,3226(NH); 3032 (CH, arom.) ; 2986,2942,2906(CH,aliph.); 1721 (C=O) ; 1619 (C=N).
	^{1}H-NMR: (DMSO) 10.15–10.00(br, 1H, NH);9.9–9.7(br, 1H, NH);8.1–7.0(m, 8H, arom.) ; 4.3–4.0 (q, 2H, O-CH_2);4.0(s,2H,s-CH_2);3.9(s,3H, OCH_3) ; 1.4–1.1 (t, 3H, C-CH_3).
4e	IR: 3316,3272,3189(3NH); 3042 (CH, arom.) ; 2961(CH,aliph.); 1681 (C=O) ; 1609(C=N).
	^{1}H-NMR: (DMSO) 11.8–11.5(br,1H,NH) ; 10.6–10.3(br, 1H, NH) ; 9.1–8.8 (br, 1H,NH);8.2–6.7(m,13H,arom.); 4.15(s, 2H, CH_2);3.9(s, 3H, OCH_3).

As to the mechanism for the formation of P-heterocycles **3** & **4,** it is suggested that a nucleophilic attack on LR gives the intermediate **A** which at elevated temperature looses H_2S to give **3** & **4,** respectively (scheme 2). The structures of these products were based on spectroscopic data and elemental analyses (cf. Experimental part and Table I).



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. The chemical shifts are expressed in δ values (ppm). TMS was used as 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 by Microanalytical Laboratory, Cairo university, Giza, Egypt. All compounds were checked for their purity on TLC plates.

1- Syntheses of 4-amino-5-(o-hydroxyphenyl) and/or 5-(o-aminophenyl)-1,2,4-triazole-3-thione (1a and 2a) respectively

To a suspension of 5-(o-hydroxyphenyl and/or o-aminophenyl)-1,3,4-oxadiazole-3-thione (0.02 mole) in water (50 ml) hydrazine hydrate (8 ml of 99% hydrazine) was added. The reaction mixture was refluxed for 5 hrs., and was diluted with 100 ml of cold water, was acidified by dropwise

addition of concentrated hydrochloric acid, and filtered. The solid was washed with cold water and was crystallized from 1:1 ethanol/water.

Compound **1a** m.p. 218 °C, yield 90 %

Analysis:

Found		C, 46.01;	H,3.81;	N,26.83
$C_8H_8N_4OS$	Calcd.	C,46.14;	H,3.87;	N,26.91

Compound **2a** m.p. 192 °c, yield 87 %

Analysis:

Found		C,46.19;	H,4.29;	N,33.87
$C_8H_9N_5S$	Calcd.	C,46.36;	H,4.38;	N, 33.79

2- Reaction of 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphtane-2,4-disulphide (Lawesson's Reagent, LR) with compounds 1a and 2a

4-Bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphtane-2,4-disulphide (LR) (2.02 g; 0.005 mole) and 5-(o-hydroxyphenyl)-4-amino-3-mercapto-1,2,4-triazole **(1a)** (2.08 g; 0.01 mole) and/or 5-(o-aminophenyl)-4-amino-3-mercapto-1,2,4-triazole **(2a)** (2.07 g; 0.01 mole) were dissolved in acetonitrile (100 ml). The reaction mixture was refluxed for 5 hrs., concentrated and cooled, the precipitate was filtered off, dried and recrystallized from ethanol to give compounds 3-mercapto-6-(p-methoxyphenyl)-s-triazolo(4,3-d)-1,3,4,2-benzo- oxadiazaphosphopine-6-sulphide **(3a)** and triazaphosphopine-6-sulphide **(4a),** respectively.

Compound **3a** m.p. 260 °c, yield 85 %

Analysis:

Found		C,47.63;	H,3.40;	N,14.69
$C_{15}H_{13}N_4O_2S_2P$	Calcd.	C,47.86;	H,3.48;	N,14.86

Compound **4a** m.p. 217 °c, yield 82 %

Analysis:

Found		C,47.73;	H,3.79;	N,18.47
$C_{15}H_{14}N_5OS_2P$	Calcd.	C,47.99;	H,3.76;	N,18.66

3- Reaction of compounds 3a and 4a with methyl iodide and/or benzyl chloride

The appropriate halo compound (methyl iodide and benzyl chloride) (0.01 mole) was added to an alcoholic solution of compound **3a** and/or **4a** (0.01 mole) and sodium hydroxide (0.01 mole). The reaction mixture was refluxed for 1 hr., concentrated and cooled, the precipitate was filtered off washed with water and crystallized from ethanol to give the corresponding sulphide; 3-methylthio and/or 3-benzylthio-6-(p-methoxyphenyl)-s-triazolo(4,3-d) 1,3,4,2-benzo- oxadiazaphosphopine-6-sulphide **(3b,c)** and triazaphosphopine-6-sulphide **(4b,c)**, respectively.

Comp. No.	*m.p. °C*	*Yield %*	*Formula*	*Analysis Calc./found*		
				C	*H*	*N %*
3b	239	84	$C_{16}H_{15}N_4O_2S_2P$	49.22 49.09	3.87 3.81	14.35 14.22
3c	235	72	$C_{22}H_{19}N_4O_2S_2P$	56.64 56.51	4.11 4.05	12.01 11.91
4b	199	82	$C_{16}H_{16}N_5OS_2P$	49.34 49.23	4.14 4.08	17.98 17.83
4c	219	74	$C_{22}H_{20}N_5OS_2P$	56.76 56.59	4.33 4.27	15.04 15.00

4- Reaction of ethyl chloroacetate with compounds 3a and 4a

To a solution of compound **3a** (3.76 g; 0.01 mole) and/or compound **4a** (3.75 g; 0.01 mole) in dry pyridine (30 ml), ethyl chloroacetate (1.23 g; 0.01 mole) was added. The reaction mixture was refluxed for 4 hrs. After cooling, the reaction mixture was poured into ice/cold water. The formed precipitate was filtered off and recrystallized from ethanol to give 3-carbethoxymethylthio-6-(p-methoxyphenyl)-s-triazolo(4,3-d)-1,3,4,2-benzo-oxadiazaphosphopine-6-sulphide **(3d)** and triazaphosphopine-6-sulphide **(4d)**, respectively.

Compound **3d** m.p. 181 °c, yield 86 %

Analysis:

Found		C,49.19;	H,4.09;	N,12.03
$C_{19}H_{19}N_4O_4S_2P$	Calcd.	C,49.34;	H,4.14;	N,12.11

Compound **4d** m.p. 173 °c, yield 82 %

Analysis:

Found		C,49.29;	H,4.31;	N,15.05
$C_{19}H_{20}N_5O_3S_2P$	Calcd.	C,49.45;	H,4.37;	N,15.18

5- Reaction of chloroacetanilide with compounds 3a and 4a

A mixture of compound **3a** and/or **4a** (0.01 mole), chloroacetanilide (0.01 mole) and anhydrous potassium carbonate (0.01 mole) in dry acetone (70 ml) was refluxed for 5 hrs. The reaction mixture was filtered while hot, concentrated and cooled. The formed precipitate was filtered off and recrystallized from ethanol to give 3-[(N-Phenyl)carboxamidomethylthio]-6-(p-methoxyphenyl)-s-triazolo(4,3-d)-1,3,4,2-benzo- oxadiazaphosphopine-6-sulphide **(3e)** and triazaphosphopine-6-sulphide **(4e)**, respectively.

Compound **3e** m.p. 270 °C, yield 76 %

Analysis:

Found		C,53.83;	H,4.27;	N,13.58
$C_{23}H_{22}N_5O_3S_2P$	Calcd.	C,54.00;	H,4.34;	N,13.69

Compound **4e** m.p. 241 °C, yield 74 %

Analysis:

Found		C,54.23;	H,4.51;	N,16.55
$C_{23}H_{23}N_6O_2S_2P$	Calcd.	C, 54.10 ;	H,4.54;	N,16.46

6- Reaction of compounds 1a and 2a with methyl iodide and/or benzyl chloride

A mixture of compound **1a** and/or **2a** (0.01 mole), sodium hydroxide (0.01 mole) and a proper halo compound (methyl iodide and/or benzyl chloride) (0.01 mole) in ethanol (70 ml) was refluxed for 1 hr., concentrated the precipitate was filtered off, washed with water and crystallized from ethanol to give the corresponding sulphide 4-amino-3-metylthio-5-(o-hydroxy and/or o-amino- phenyl)-1,2,4-tria-

zole (**1b** and **2b**) and 4-amino-3-benzylthio-5-(o-hydroxy- and/or o-amino-phenyl)-1,2,4-triazole (**1c** and **2c**), respectively

Comp. No.	*m.p. °C*	*Yield %*	*Formula*	*Analysis Calc./found*		
				C	*H*	*N %*
1b	208	92	$C_9H_{10}N_4OS$	48.63 48.41	4.53 4.45	25.21 25.11
1c	221	83	$C_{15}H_{14}N_4OS$	60.38 60.52	4.73 4.67	18.78 18.71
2b	156	86	$C_9H_{11}N_5S$	48.85 48.63	5.01 4.93	31.65 31.51
2c	202	78	$C_{15}H_{15}N_5S$	60.58 50.33	5.08 5.00	23.55 23.41

7- Reaction of ethyl chloroacetate with compounds 1a and 2a

A mixture of 4-amino-3-mercapto-5-(o-hydroxyphenyl) and/or 5-(o-aminophenyl)-1,2,4-triazole **1a** and/or **2a** (0.01 mole), ethyl chloroacetate (0.01 mole) and anhydrous potassium carbonate (0.01 mole) in dry acetone (60 ml) was refluxed for 4 hrs. The reaction mixture was filtered while hot, concentrated and cooled. The formed precipitate was filtered off and recrystallized from ethanol to give 4-amino-3-carbethoxymethylthio-5- (o-hydroxyphenyl) and/or 5-(o-aminophenyl)-s-triazole (**1d** and **2d**), respectively.

Compound **1d** m.p. 143 °C, yield 89 %

Analysis:

Found		C,48.73;	H,4.71;	N,18.87
$C_{12}H_{14}N_4O_3S$	Calcd.	C,48.97;	H,4.79;	N,19.04

Compound **2d** m.p. 138 °C, yield 87 %

Analysis:

Found		C,49.00;	H,5.01 ;	N,23.71
$C_{12}H_{15}N_5O_2S$	Calcd.	C,49.13;	H,5.15;	N,23.87

8- Reaction of chloroacetanilide with compounds 1a and 2a

A mixture of compound **1a** and/or **2a** (0.01 mole), chloroacetanilide (0.01 mole) and anhydrous potassium carbonate (0.01 mole) in dry ace-

tone (60 ml) was refluxed for 5 hrs. The reaction mixture was filtered while hot, concentrated and cooled. The formed precipitate was filtered off and recrystallized from ethanol to give 4-amino-3-[(N-Phenyl)carboxamidomethylthio]-5-(o-hydroxyphenyl and/or o-aminophenyl)-s-triazole (**1e**, **2e**), respectively.

Compound **1e** m.p. 231 °C, yield 76 %

Analysis:

Found		C,56.52;	H,4.31;	N,20.71
$C_{16}H_{15}N_5O_2S$	Calcd.	C,56.29;	H,4.43;	N,20.52

Compound **2e** m.p. 211 °C, yield 73 %

Analysis:

Found		C,56.32;	H,4.65;	N,24.53
$C_{16}H_{16}N_6OS$	Calcd.	C,56.45;	H,4.74;	N,24.69

9- Reaction of 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulphide (Lawesson's Reagent, LR) with s-alkylated compounds 1b-e and 2b-e (general procedure).

A mixture of the proper sulphide (**1b-e** and/or **2b-e**) (0.01 mole) and 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulphide (LR) in dry acetonitrile (80 ml) (dry benzene is used in case of compounds **1d** and **2d**) was refluxed for 5 hrs., concentrated and cooled. The formed precipitate was filtered off and recrystallized from ethanol to give compounds which are identical in all respects with authentic samples of **3b-e** and **4b-e,** respectively.

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