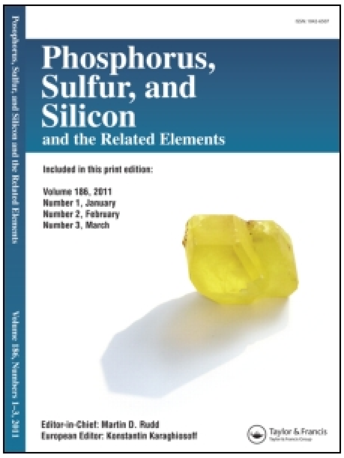

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SIMPLE NEW ROUTES TO PHOSPHORINS FROM 2- MERCAPTO-1,3,4-OXA- AND THIADIAZOLE AND 3- MERCAPTO-1,2,4-TRIAZOLE

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SIMPLE NEW ROUTES TO PHOSPHORINS FROM 2-MERCAPTO-1,3,4-OXA- AND THIADIAZOLE AND 3-MERCAPTO-1,2,4-TRIAZOLE

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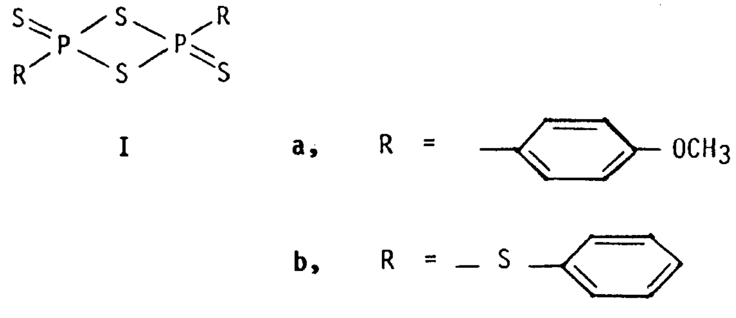
1,3,2,4-Dithiadiphosphetane-2,4-disulfides $\mathbf{I}_a$ and $\mathbf{I}_b$ react with $\mathbf{II}_{a,b}$ and **III** to give cyclic compounds $\mathbf{IV}_{a,b,c,d}$ and $\mathbf{V}_{a,b}$, respectively. The given structures were based upon analytical, chemical and spectroscopic results.

Key words: Oxadiazole; thiadiazole; triazole; Lawesson and Japanese reagents.

The antitubercular,[1] antiviral,[2] antifungal,[3] carcinostatic,[4] hypoglycemic[5] properties exhibited by oxa- and thiadiazole derivatives have made them important chemotherapeutic agents. Also 1,2,4-triazole derivatives are known as biologically active materials[6,7] besides having many other uses and applications.[8,9] In our present investigation we synthesized new derivatives of these compounds which might be expected to possess high biological activities.

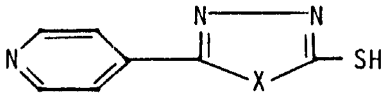
It has been found that 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide, LR (Lawesson reagent) $\mathbf{I}_a$ and 2,4-bis(phenyl thio)-1,3,2,4-dithiadiphosphetane, 2,4-disulfide JR (Japanese reagent) $\mathbf{I}_b$ are potent thiating agents for diverse carbonyl compounds e.g., ketones,[10] esters[11] and lactans.[12]



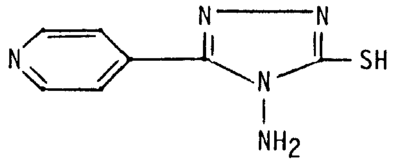
I

The reagents $\mathbf{I}_a$ and $\mathbf{I}_b$ are easily available and undergo also ring-closure reactions with substrates containing two functional groups.[13-16]

To extent the use of $\mathbf{I}_{a,b}$ to other bifunctional substrates, its reactions with 2-mercapto-5(4-pyridyl)-1,3,4-oxidiazole $\mathbf{II}_a$, 2-mercapto-5(4-pyridyl)-1,3,4-thiadiazole $\mathbf{II}_b$ and 3-mercapto-4-amino-5(4-pyridyl)-1,2,4-triazole **III**, have been investigated and found to give new phosphorus heterocycles. Our results are reportred in this paper.

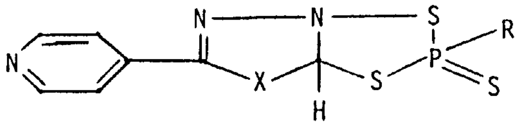


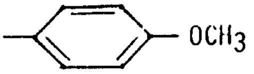
II a, X = O
b, X = S

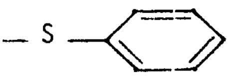


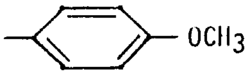
III

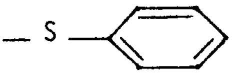
The reaction of I_a (or I_b) with II_a and II_b proceed in anhydrous toluene (or in dry tetrahydrofuran, THF) to yield cyclic structures IV_a, IV_b, IV_c and IV_d, respectively,[11-15] which were confirmed by elemental analyses, molecular weight determination MS, IR, ^{1}H-NMR and ^{31}P-NMR spectra (Tables I and II).



IV a, X = O , R = 

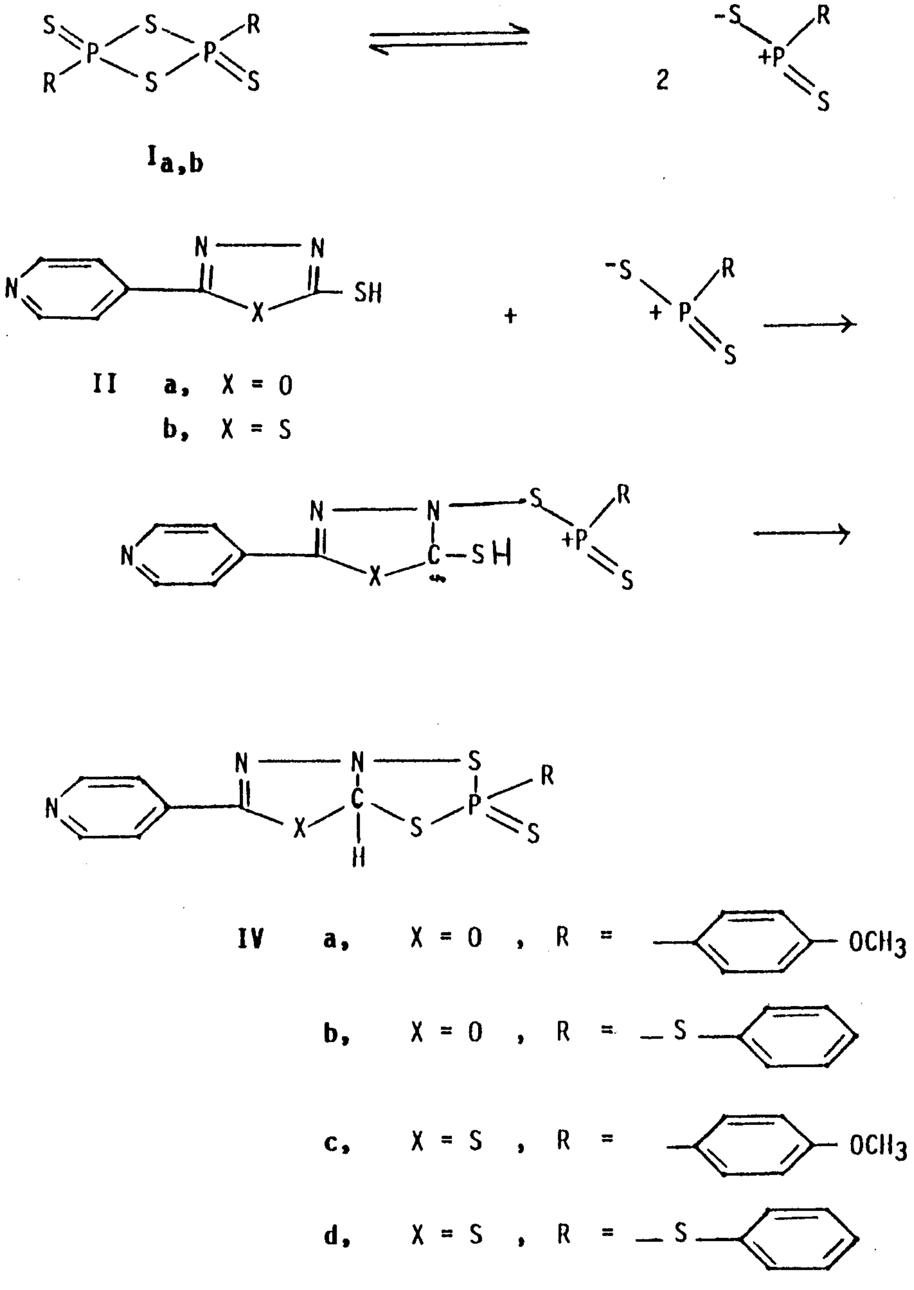
b, X = O , R = 

c, X = S , R = 

d, X = S , R = 

A possible explanation of the reaction $I_{a,b}$ with $II_{a,b}$ is illustrated in "Scheme A".

Taking IV_d as example, its elemental analyses corresponded to $C_{13}H_{10}N_3S_5P$, the IR spectrum showed absorption bands at 650 cm^{-1} due to $\overset{S}{\diagdown}$P=S, at 1640-1560 cm^{-1} due to C=N vibration, at 710 cm^{-1} due to C—S—C and the spectrum however showed strong absorption bands in the region 1600-1500 cm^{-1} due to aromatic C=C stretching vibrations. The NMR spectrum of IV_d showed signals at δ 2.7 ppm (1H, CH) and the aromatic protons gave multiplet at δ 7.7-8.8 ppm region (9H, multiplet). In ^{31}P-NMR spectrum there is a singlet at δ 80 ppm, the MS spectrum showed m/e 399 (M^+).



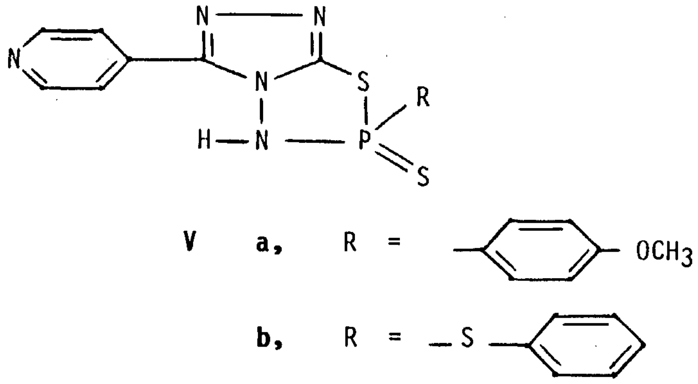
▪ Scheme A ▪

TABLE I

Physical constants of analytical data of new compounds

Compound	Reaction time (hrs)	Solvent of crystallization	Yield %	M.P. °C	Formula mol. wt.	Analysis calc. / found C	H	N	S	P
IV$_a$	3	Ethanol	70	171	$C_{14}H_{12}N_3S_3PO_2$	44.10	3.15	11.02	25.20	8.14
					381	43.95	3.09	10.97	25.00	8.03
IV$_b$	3	Ethanol	65	190	$C_{13}H_{10}N_3S_4PO$	40.73	2.61	10.97	33.42	8.09
					383	40.67	2.60	10.92	33.50	8.12
IV$_c$	1	Ethanol	75	298	$C_{14}H_{12}N_3S_4PO$	42.32	3.02	10.58	32.25	7.81
					397	42.43	3.26	10.52	32.19	7.79
IV$_d$	1	Ethanol	70	292	$C_{13}H_{10}N_3S_5P$	39.10	2.50	10.53	40.10	7.77
					399	38.83	2.41	10.26	39.90	7.60
V$_a$	3½	Toluene	75	172	$C_{14}H_{12}N_5S_2PO$	46.54	3.32	19.39	17.73	8.59
					361	46.58	3.34	19.40	17.69	8.52
V$_b$	1½	Toluene	70	125	$C_{13}H_{10}N_5S_3P$	42.98	2.76	19.28	26.45	8.54
					363	43.00	2.77	19.26	26.38	8.50

Also, I$_{a,b}$ reacted with **III** proceed in anhydrous toluene or dry THF to give the adducts V$_{a,b}$.[17]



A possible explanation of the reaction of I$_{a,b}$ with **III** is illustrated in "Scheme B".

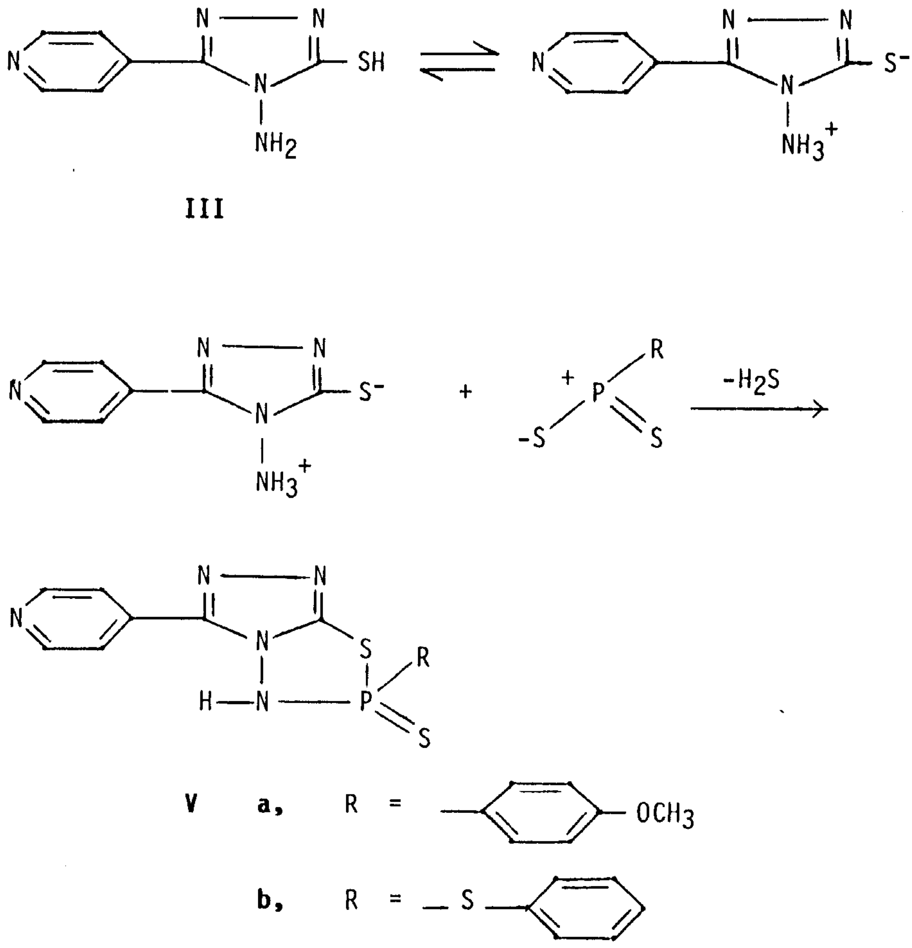
The structures V$_a$ and V$_b$ were confirmed by elemental analyses (Table I) molecular weight determination (MS), IR and ^{1}H-NMR. Taking V$_a$ as example, its

TABLE II

Spectra data of the new compounds

Compound	**I.R. (cm^{-1})**	**^{1}H-NMR (ppm)**
IV$_a$	640 ($^{S}\diagdown P{=}S$) 1050 (C-O-C) 1540 (C=N) 1605 (C=C)	2.8 (1H, CH, s) 7.7-8.5 (8H, aromatic protons) 3.7 (3, OCH$_3$, S)
IV$_b$	650 ($^{S}\diagdown P{=}S$) 1080 (C-O-C) 1550 (C=N) 1595 (C=C)	2.7 (1H, CH, s) 7.9-8.7 (9H, aromatic protons)
IV$_c$	645 ($^{S}\diagdown P{=}S$) 710 (C-S-C) 1540 (C=N) 1610 (C=C)	3.8 (1H, CH, s) 2.75 (1H, CH) 8.1-8.7 (8H, aromatic protons)
IV$_d$	650 ($^{S}\diagdown P{=}S$) 710 (C-S-C) 1560 (C=N) 1600 (C=C)	2.7 (1H, CH) 7.7-8.8 (9H, aromatic protons)
V$_a$	650 ($^{S}\diagdown P{=}S$) 1560 (C=N) 1600 (C=C) 3100 (NH)	3.9 (3H, OCH$_3$, S) 9.5 (1H, NH, exchangeable with D$_2$O) 7.9-8.8 (8H, aromatic protons)
V$_b$	645 ($^{S}\diagdown P{=}S$) 1550 (C=N) 1610 (C=C) 3120 (NH)	9.3 (1H, NH, s, exchangeable with D$_2$O) 8.1-8.7 (9H, aromatic protons)

elemental analyses corresponded to $C_{14}H_{12}N_5S_2PO$, IR spectrum lacked to SH group absorption which is recorded in the spectrum of **III**, it however showed strong absorption bands in the region 1600-1500 cm^{-1} due to the aromatic C=C stretching vibrations and showed absorption bands at 650 cm^{-1} due to $^{S}\diagdown P{=}S$, at 1640-1560 cm^{-1} due to C=N vibration and at 3100 cm^{-1} due to NH. The NMR spectrum of V$_a$ (in DMSO) showed signals at δ 3.9 ppm (3H, OCH$_3$, s), at δ 9.5 ppm (1H, NH, s) which disappeared when deuterated and showed multiplet at δ 7.9-8.8 ppm region (8H) due to the aromatic protons. The MS spectrum showed m/e 361 (M$^+$).



III

" Scheme B "

EXPERIMENTAL

All melting points were uncorrected. Tetrahydrofuran THF and toluene dried over sodium. The reagents $\mathbf{I}_a$ and $\mathbf{I}_b$ were prepared according to established procedure.[10,15,17,18] The IR spectrum (run in KBr and expressed in cm^{-1}) were recorded with Beckman infrared Model 4220 and ^{1}H-NMR spectra were measured in DMSO-d_6 and expressed in δ scale at 60 or 90 MHz on a varian instrument using TMS as an internal standard. The MS spectra were performed at 70 eV using a varian MAT 112 Mass Spectrometer.

General procedure for the reaction of $\mathbf{II}_{a,b}$ *and* **III** *with* $\mathbf{I}_a$. 0.01 mole of the starting compound and 0.01 mole of $\mathbf{I}_a$ was refluxed in 10 ml of anhydrous toluene at 110°C with stirring until no more of the starting material could be detected (TLC). After cooling to room temperature the excess of $\mathbf{I}_a$ was filtered off. Then the reaction mixture was evaporated on silica gel column arising ether/light petroleum as eluant. The physical data are summarized in Table I.

General Procedure for the Reaction of $\mathbf{II}_{a,b}$ *and* **III** *with* $\mathbf{I}_b$. 0.01 mole of the starting compound and 0.01 mole of $\mathbf{I}_b$ was heated in 10 ml of anhydrous THF at 35°C with stirring until no more of the starting material could be detected (TLC). After cooling to room temperature the excess of $\mathbf{I}_b$ was filtered off.

Then the reaction mixture was evaporated on silica gel column using benzene/hexane ($\frac{1}{1}$) as eluant. The physical data are summarized in Table I.

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