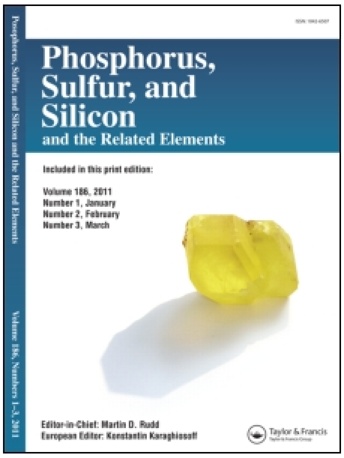

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SIMPLE NEW ROUTES TO OXIMINOPHOSPHONODITHIOATES, 1,3,5,2-OXATHIAZAPHOSPHOLES AND 1,3,2-THIAZAPHOSPHOLINES FROM OXIMES AND THEIR DERIVATIVES

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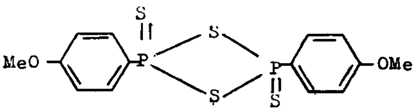
2,4-Bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide, **1**, reacted with ketoximes at 25° followed by alkylation with methyl iodide to give oximino-4-methoxyphenyl-S-methyl-phosphonodithioate, **4**. *p*-Tolualdehyde oxime when treated with **1** gave 2,4,6-tri-p-tolyl-1,3,5-trithiolidine, **6**. The reaction of benzohydroxamoyl chlorides with **1** yielded 1,3,5,2-oxathiazaphospholes, **8**, whereas *p*-nitrobenzohydroxamoyl chloride gave 3,6-di(4-nitrophenyl)-1,4,2,5-dioxadiazine, **11**. Diarylketoximes with **1** produced **13** and **14**. 9-Benzanthrone oxime with **1** afforded 9-benzanthrone thione, **16**. The reaction of oximes of phenyl phenylmethylketoximes or 1,3-diphenyl-2-propanone with **1** at 80° afforded 1,3,2-thiazaphospholines, **18**.

INTRODUCTION

For some time we have been occupied in studying the reaction of 2,4-bis-(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide, **1**, with different substrates.[1-5]

In an investigation of the reaction of ketoximes with **1**, it was found that oximinophosphonodithioates were formed.[6-8] Because of this fact and the potential interest in these products as acaricides and insecticides,[6-8] we felt prompted to make further investigations on the reaction of **1** with ket- and aldoximes and their chloro derivatives under different conditions. Our results are reported in this paper.



1

RESULTS AND DISCUSSION

2,4-Bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4 disulfide, **1**, reacts with ketoximes, **2**, in anhydrous benzene at 25° to give the intermediate **3**, which on alkylation using methyl iodide gave oximino-p-methoxyphenyl-S-methylphosphonodithioate, **4**, in high yields (Scheme 1).

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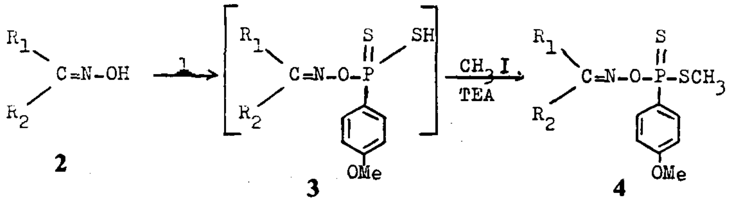


	R_1	R_2		R_1	R_2
a	CH_3	CH_3	c	$-(CH_2)_5-$	
b	CH_3	C_6H_5	d	$-(CH_2)_4-$	
			e	C_6H_5	$C_6H_5CH_2$

SCHEME 1

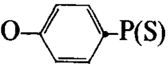
TABLE I

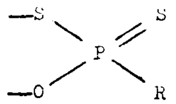
Reaction conditions, physical and analytical data of the products

Starting compd	Product	% yield	Reaction time (*h*)	Reation temp (°C)	M.P. (°C)	Analyses (Calcd/Found)% C	H	P	S
2a	**4a**	(81)	$1\frac{1}{2}$	25	51	45.67	5.54	10.73	22.15
						45.51	5.62	10.33	22.00
2b	**4b**	(83)	2	25	90	Precise MS 351.0531 (351.0515)			
2c	**4c**	(70)	$1\frac{3}{4}$	25	83	51.06	6.92	10.73	19.45
						50.89	7.03	10.60	19.53
2d	**4d**	(76)	2	25	65	53.98	5.71	9.84	20.32
						54.04	5.59	9.70	20.60
2e	**4e**	(85)	4	25	110	Precise MS 427.0825 (427. 0821)			
5	**6**	(15)	1	25	150	ref. 11			
7a	**8a**	(52)	4	25	105	52.33	3.74	9.66	19.93
						52.30	3.71	9.59	19.66
7b	**8b**	(53)	6	25	88	55.38	4.18	9.25	19.10
						55.29	4.28	9.40	19.29
7c	**8c**	(56)	$4\frac{1}{2}$	25	93	Precise MS 335.0204 (335.0201)			
7d[a]	**8d**	(78)	4	25	99	Precise MS 335.0204 (335.0213)			
10	**11**	(30)	10	25	220	ref. 12			
12a[b]	**13a**	(51)	$3\frac{1}{2}$	80	162	—	—	—	—
	14a	(24)			100	ref. 15, 16			
12b[b]	**13b**	(49)	5	80	145	ref. 13, 14			
	14b	(33)			97[d]	60.27	4.11	—	29.22
						60.18	4.20	—	29.40
12a[c]	**14a**	(79)	2	80		—	—	—	—
12b[c]	**14b**	(82)	$2\frac{1}{2}$	80	—	—	—	—	—
15	**16**	(36)	$\frac{1}{2}$	80	134	ref. 17			
2e	**18a**	(21)	3	80	178	63.80	4.56	7.85	16.20
						63.93	4.48	7.62	15.83
	19	(15)			90	ref. 16			
17	**18b**	(27)	1	80	99	64.55	4.89	7.58	15.65
						64.49	4.90	7.49	15.30

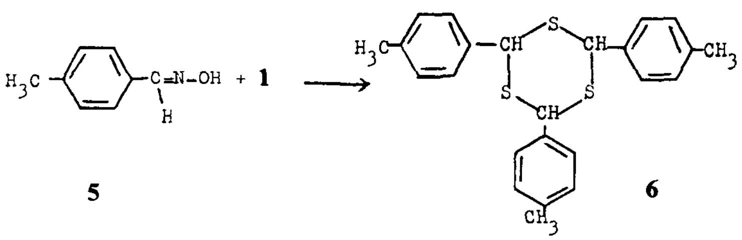
[a] Pure material of **7d** was used (**7a**, **b**, **c**, Crude materials were used)
[b] **12a**, **b** (1 mole) + **1** (1 mole)
[c] (1 mole **12a**, **b** : 2 mole **1**)
[d] (N; Calcd 6.39, Found 6.20%)

Reaction times, yields, m.p.s, precise mass spectral measurements and analytical data are given in the Experimental and Table I.

The products **4** were identified by ^{1}H, ^{13}C and ^{31}P NMR and precise MS measurements and elemental analyses. In the ^{1}H NMR spectra the SCH_3 protons appear as a doublet at 2.3–2.7 ppm (3 H, $^{3}J_{PH}$ 15–16 Hz, coupling to P) and the OCH_3 protons (3H) appear as a singlet at 3.8–3.9 ppm. In the ^{13}C NMR spectra of **4**, the $\underline{C}{=}N$ absorbs at 162.8–176.2 ppm ($^{3}J_{CP}$ = 12.8–15.6 Hz), the $\underline{S}CH_3$[9] absorbs at 13.8–15.0 ppm ($^{2}J_{CP}$= 3.5–3.7 Hz), and the  carbon absorbs in the region 124.0–124.6 ppm ($^{1}J_{CP}$ = 121.0–121.7 Hz). The mass spectra of **4** all showed the molecular ions (M^+) and in many cases M^+—47 (M^+—SCH_3) was the base peak. M^+—15 (M^+—CH_3) and m/e 217[$MeO.C_6H_4.P(S)SCH_3$] and M^+—$R_1R_2.CNO$ was abundant for most compounds. Also m/e 202 ($MeO.C_6H_4.PS_2$), 187 ($MeO.C_6H_4.PO_2SH$) and 139 ($OMe.C_6H_4PH$) were always observed. In the ^{31}P NMR spectra of **4** there is one singlet in the region 101.1–108.3 ppm also in accordance with literature data for the following structure:[10a]



The reaction of *p*-tolualdehyde oxime, **5**, with **1** in anhydrous benzene at 25° gave only 2,4,6-tri-*p*-tolyl-1,3,5-trithiolidine, **6**.

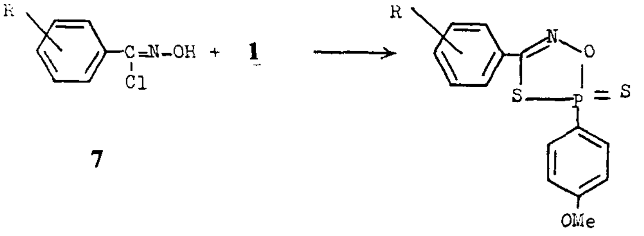


5 **6**

The structure of **6** is known[11] and was also confirmed by MS and ^{1}H-NMR.

The reaction of aldoximes with **1** followed by alkylation with methyl iodide under different conditions gave a complex reaction mixture.

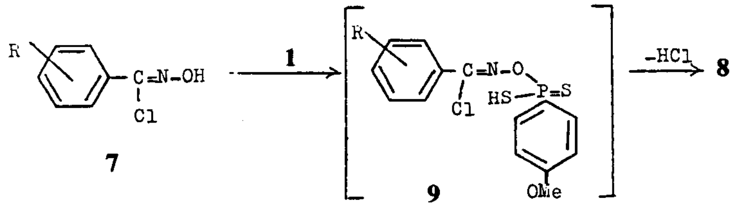
On the other hand, the reaction of benzohydroxamoyl chlorides, **7**, with **1** at 25° in anhydrous benzene yielded 1,3,5,2-oxathiazaphospholes, **8**, in high yields.



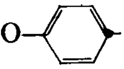
7 **8**

7,8: a,R = H ; b,R = o-CH_3

c,R = m-CH_3 ; d,R = p-CH_3

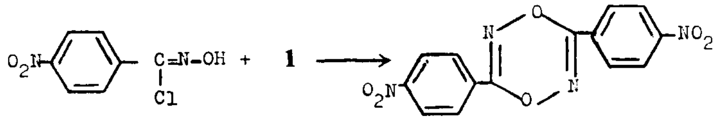


SCHEME 2

The best yields of **8** (78%) were found when using a pure sample of **7**. The structural proofs of **8** are based on ^{1}H, ^{13}C, and ^{31}P NMR spectra and MS and elemental analyses. In the ^{1}H-NMR spectra there is a singlet at 3.8 ppm (3 H, OCH_3). In **8b–8d** the CH_3 protons (3 H) appear as a singlet in the region 2.3–2.4 ppm. In the ^{13}C NMR spectra the $\underline{C}$=N absorbs in the region 161.3–162.0 ppm ($^2J_{CP}$ = 9.1–9.7 Hz) and in compounds **8b–8d** the $\underline{C}H_3$ appears as a singlet in the region 21.3–21.8 ppm. The $O\underline{C}H_3$ appears as a singlet at 55.3–55.6 ppm, while the MeOP(S) carbon at 123.4–123.7 ppm ($^1J_{CP}$ = 116.0–116.5 Hz). The mass spectra of **8** all showed molecular ions (M^+) and M^+—33 (M^+—SH). Also, M^+—15 (M^+—CH_3), m/e 149 ($CH_3.C_6H_4.CNS$) and 117 ($CH_3.C_6H_4.CN$) were observed in the spectra of **8b–8d**. The ^{31}P NMR spectra of **8** showed a signal in the region 117.0–118.4 ppm which is in accordance with literature data.[10a]

As to the mechanism for the formation of **8**, it is suggested (Scheme 2) that a nucleophilic attack on **1** gives the intermediate **9**, followed by ring closure and expulsion of HCl to produce **8**.

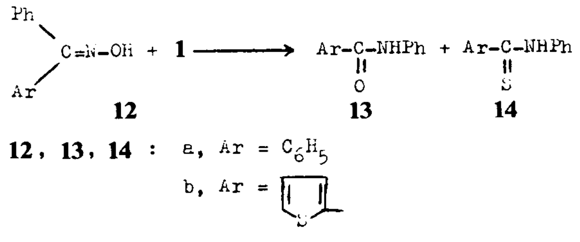
On the other hand, *p*-nitrobenzohydroxamoyl chloride, **10**, unable to give a phosphorus heterocycle, reacted with **1** in anhydrous benzene at 25° or at 80° to give 3,6-di(4-nitrophenyl)-1,4,2,5-dioxadiazine, **11**.



10 **11**

The structure of **11** is known[12] and also was confirmed by MS and ^{1}H-NMR. The formation of **11** is probably due to the dimerization which occurs by double nucleophilic displacement of chlorine by hydroxyl group, then loss of H^+.

The reaction of equimolecular amounts of diphenylketoxime, **12a** with **1** in anhydrous benzene at 80° gave benzanilide, **13a**, and thiobenzanilide, **14a**. Similarly thiophene-2-ketoxime, **12b**, with **1** gave thiophene-2-carboxanilide, **13b**, besides its thioanalogue, **14b**.

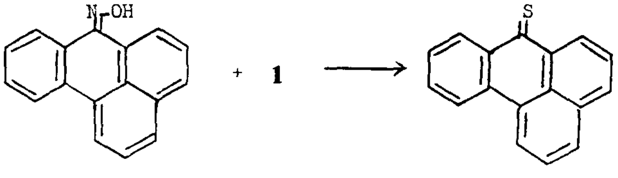


In the reaction of **12** (1 mole) with excess of **1** (2 moles) in anhydrous benzene at 80°, **13** was not isolated but the yield of **14** increased (due to thiation of **13**).

The structures of **13a**, **13b**,[13,14] and **14a**[15,16] are known and also were confirmed by ^1H NMR, MS and mixed m.p. with authentic samples. The structural proof of **14b** is based on IR, ^1H and ^{13}C NMR and mass spectral data and elemental analysis. Its IR showed a band at 1255 cm^{-1} (C=S). In the ^1H NMR spectrum the NH proton (1 H) appeared as a singlet at 9.2 ppm and the aromatic protons (Ph and thiopheno, 8H) appeared as a multiplet at 6.8–7.7 ppm. Its mass spectrum exhibited the molecular ion peak (M^+) at m/e 219. Peaks at m/e 186 (M^+—SH), 126 (M^+—$PhNH_2$) and 136 ($M^+C_4H_3S$) were also observed. In the ^{13}C NMR spectrum of **14b** the thiocarbonyl carbon appeared at 187.4 ppm.

The formation of **14** can be attributed to Beckmann rearrangement[14] for **12** catalyzed by **1** to give the anilide **13** which on thiation by **1** gave **14**.

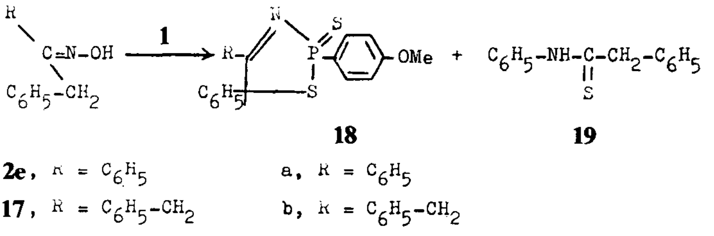
The reaction of 9-benzanthrone oxime, **15**, with **1** in anhydrous benzene at 80°, gave 9-benzanthrone thione, **16**, as the sole product in addition to polymeric substances.



15 **16**

The structure of **16** is known[17] and confirmed by mixed m.p. with authentic sample, ^1H NMR and MS.

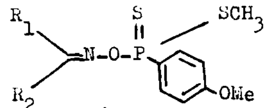
The reaction of oximes of 1,3-diphenyl-2-propanone, **17** and phenyl phenylmethyl ketoxime, **2e**, with **1** at 80° in anhydrous benzene afforded 1,3,2-thiazaphospholines, **18**,. In one case (**2e**, R = Ph), 1-phenylthioacetanilide, **19**,[16] was isolated.



The structural proof for **18** is based on ^1H, ^{13}C and ^{31}P NMR spectra and MS and elemental analyses. In the ^1H NMR spectra of **18a** and **18b**, the CH proton appears as a multiplet at 5.2 and 5.0 ppm, respectively. In **18b** the CH_2 protons (2H) absorb at 3.65 ppm. In the ^{13}C NMR spectrum of **18a**, the $\underline{C}H$ absorbs at 70.4 ppm ($^2J_{CP}$ = 11.2 Hz) and that for **18b** absorbs at 72.3 ppm ($^2J_{CP}$ = 10.6 Hz), but the $\underline{C}H_2$—Ph carbon in **18b** absorbs at 35.0 ppm ($^3J_{CP}$ = 9.1 Hz). The MS of **18a** and **18b** showed m/e at 395 (M^+) and 409 (M^+), respectively. Peaks at m/e 362 and 376 (M^+—SH) and m/e 292 (M^+—PhCN) and (M^+—$PhCH_2CN$) are observed in the spectra of **18a** and **18b**, respectively. The ^{31}P NMR spectra of **18a** and **18b** showed

TABLE II

^{13}C and ^{31}P NMR data of oximino-*S*-methylphosphonodithioates

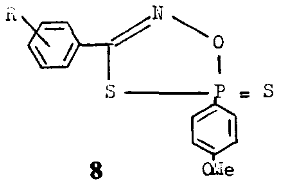


4

R_1	R_2	$\delta_{\underline{C}=N}$ (ppm)	$^3J_{^{32}P-^{13}C}$ (Hz)	$\delta_{S\underline{C}H_3}$ (ppm)	$^2J_{^{31}P-^{13}C}$ (Hz)	$\delta_{^{31}P}$ (ppm)
CH_3	CH_3	163.8	13.5	13.8	3.7	101.4
CH_3	Ph	162.8	15.6	14.2	3.7	108.3
$—(CH_2)_5—$		170.0	12.8	15.0	3.5	101.2
$—(CH_2)_4—$		176.2	13.5	14.5	3.5	101.1
Ph	$PhCH_2$	164.3	14.0	14.7	3.7	103.9

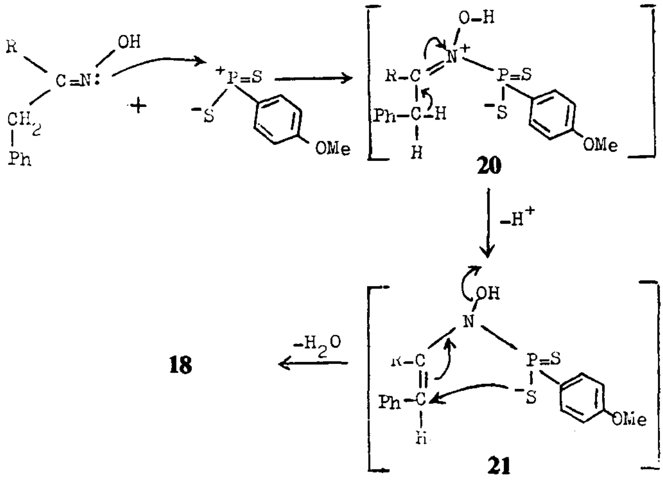
TABLE III:

^{13}C and ^{31}P data of 2,4,1,3-oxathiazaphospholes



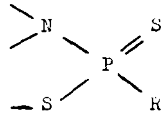
8

R	δ CH_3 (ppm)	$\delta_{\underline{C}=N}$ (ppm)	$^2J_{^{31}P-^{13}C}$ (Hz)	$\delta_{^{31}P}$ (ppm)
H	—	162.0	9.7	117.0
o-CH_3	21.5	161.5	9.6	118.1
m-CH_3	21.3	161.7	9.1	118.5
p-CH_3	21.8	161.3	9.5	118.4



SCHEME 3

signals at 80.8 and 83.1 ppm, respectively, which is in accordance with other compounds containing the following structure:[10b]



As to the mechanism for the formation of **18**, it is suggested (Scheme 3) that a nucleophilic attack on **1** by the oxime gives the intermediates **20** and **21** followed by ring closure (and removal of H_2O) to produce **18**.

EXPERIMENTAL

IR spectra were recorded on a Beckman IR-18A spectrophotometer. ^1H NMR spectra were recorded at 60 MHz on a Varian spectrometer. ^{13}C and ^{31}P NMR spectra were obtained on a Varian CFT-20 instrument at 20.4 and 32.19 MHz, respectively, $CDCl_3$ was used as a solvent and TMS as internal reference standard. Chemical shifts are expressed as δ-Values. Also ^{31}P chemical shifts are reported positive low field to (external) H_3PO_4. Mass spectra were recorded on a Micromass 7070 F mass spectrometer operating at 70 eV using direct inlet. Elementary analyses were carried out by Novo Microanalytical laboratory, Novo Industri A/S, Novo Allé, DK-2880 Bagsvaerd, Denmark. Silica gel 60 (Merck) was used for column chromatography. The light petroleum ether used boiled below 45°C. M.p.'s are uncorrected.

Starting materials. Compound **1** (now available from Fluka AG, Merck-Schuchardt AG, Hoechst AG, and Aldrich Chemical CO.) was prepared as described earlier. Compounds **2a**,[18] **2b**,[19] **2c**,[20] **2d**,[21] **2e**,[22] **5**,[23] **7a**,[24] **7b, c, d**,[25] **10**,[24] **12a**,[22] **12b**,[26] **15**,[27] **17**[28] were prepared by known methods.

General procedure for the reaction of **2** *and* **1**. A mixture of **2** (0.01 mole) and **1** (0.01 mole) was stirred in 10 ml of anhydrous benzene at room temperature until no more of the starting material could be detected (TLC). The solution was cooled in an ice bath to 10° and 0.01 mole of methyl iodide was added followed by 0.12 mole of triethylamine over a period of 10–15 min. The resulting mixture was stirred at room temperature for 1–4 hr. Then the solvent was evaporated under reduced pressure and the residue chromatographed over a silica gel column using an ethyl ether-pet. ether mixture as eluant. The reaction conditions and the physical data are summarized in Table I.

General procedure for the reaction of **2e**, **5**, **7**, **10**, **12**, **15**, **17**, *and* **1**.
A mixture of **1** (0.01 mole) and the appropriate compound (0.01 mole) was refluxed in 10 ml of anhydrous benzene with stirring until no more of the starting material could be detected (TLC). After cooling the reaction mixture to room temperature, the solvent was removed under reduced pressure and the residue chromatographed over a silica gel column using an ethyl ether-pet. ether mixture as eluant. The reaction conditions and characterization data of the products are given in Table I.

A molar ratio of (1 : 2) of **12** : **1**, when allowed to react under identical conditions as above, gave results with varying yield and different compounds.

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