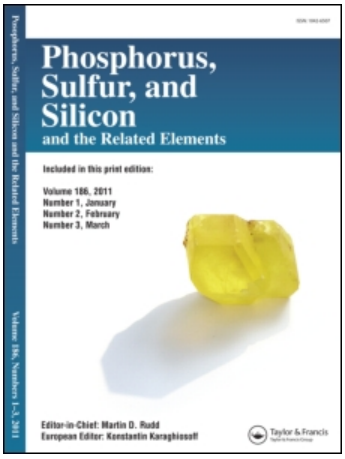

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REACTION OF AMIDOXIMES WITH 1,3-DITHIA-2,4-DIPHOSPHETANE-2,4-DISULFIDES

N. M. Yousif[a]
[a] National Research Centre, Cairo, Egypt

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REACTION OF AMIDOXIMES WITH 1,3-DITHIA-2,4-DIPHOSPHETANE-2,4-DISULFIDES

N. M. YOUSIF
National Research Centre, Dokki, Cairo, Egypt

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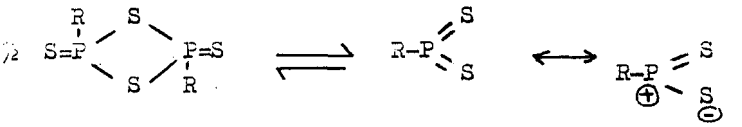
Amidoximes 9a–d react with 1,3-dithia-2,4-diphosphetane-2,4-disulfides 1a–c at 110°C to give the corresponding 1,2,4-thiadiazaphosphol derivatives 10a–f. The sodium salt of benzamidoxime reacts with compound 1a to form the phosphonothiolothionate derivative 12, which reacts with alkyl iodide to yield *S*-alkyl derivatives 13a,b.

Key words: dithiadiphosphetanes; amidoximes; NMR; IR.

INTRODUCTION

1,3-Dithia-2,4-diphosphetane-2,4-disulfide 1a–c are useful as thiation reagents. It has been considered that at elevated temperature, compounds 1 exist in equilibrium with the monomer species 2 and or 3.[1–3]



1 2 3

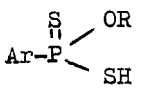
a, R= H_3C–O–C$_6$H$_5$

b, R= H_5C_6–O–C$_6$H$_5$

c, R= H_5C_6–S–C$_6$H$_5$

d, R= H_3C–S–

Compound 1a reacts with alcohols[4] or with amines[5] to give compound 4 and compound 5.



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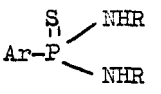

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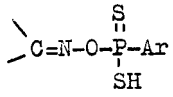
Compound 1a reacts with ketoximes[6] benzhydroxamic chlorides, or with aminoketone[7] to give phosphonodithioate 6, oxathiazaphospholes 7 or thiazophosphole 8.



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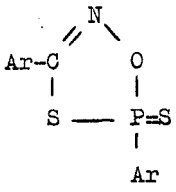

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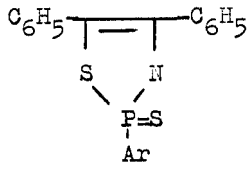

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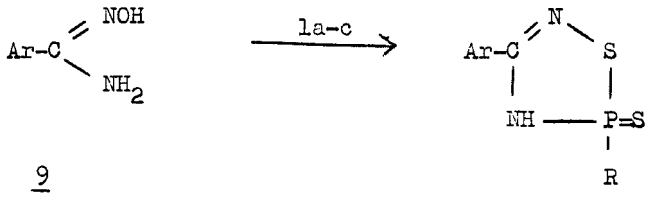
The present paper reports the reaction of amidoximes with 1,3-dithia-2,4-diphosphetane-2,4-disulfides.

RESULTS AND DISCUSSION

Amidoximes Ar—C=NOH(NH_2) 9 (Ar=C_6H_5—CH_2—, C_6H_5, $C_6H_4.CH_3O$, and $C_6H_4.CH_3p$) react with 1,3-dithia-2,4-diphosphetane-2,4-disulfides 1a–c in toluene at 110°C to give the corresponding 1,2,4-thiadiazaphosphole derivatives 10a–f. The structure of compounds 10a–f are deduced from microanalysis, IR, ^1H NMR and MS (Tables I and II).



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10a, Ar= C_6H_5-CH_2 , R= CH_3-O-C_6H_4-

b, = C_6H_5-CH_2 , = C_6H_5-O-C_6H_4-

c, = C_6H_5-CH_2 , = C_6H_5-S-C_6H_4-

d, = C_6H_5 , = CH_3-O-C_6H_4-

e, = $C_6H_4.CH_3o$, = CH_3-O-C_6H_4-

f, = $C_6H_4.CH_3p$, = CH_3-O-C_6H_4-

TABLE I

Experimental data and ^1H NMR for the reaction of amidoximes with 1a–d

Product	M.P. °C	Time, h	Yield, %	^1H NMR δ (ppm)
10a	67–68	2	62	3.5(2H, s, CH_2), 3.7(3H, s, OCH_3), 6.9–7(9H, br, aromatic), 9.2–9.4(1H, br, NH)
b	90–91	3	53	3.6(2H, s, CH_2), 6.7–8(14H, br, aromatic) 8.9–9.3(1H, br, NH)
c	79–80	3	50	3.5(2H, s, CH_2), 6.8–7.7(14H, br, aromatic) 8.9–9.2(1H, br, NH)
d	94–95	3	72	3.8(3H, s, OCH_3), 6.8–8(9H, br, aromatic) 9.1–9.4(1H, br, NH)
e	60–61	4	47	2.2(3H, s, CH_3), 3.7(3H, s, OCH_3), 6.6–7(8H, br, aromatic), 8.5–9.2(1H, br, NH)
f	62–63	3	50	2.2(3H, s, CH_3), 3.7(3H, s, OCH_3), 6.6–8.3(8H, br, aromatic), 9–9.2(1H, br, NH)
12	48–49	3	95	3.8(3H, s, OCH_3), 5.1–5.4(2H, br, NH_2), 6.7–8(9H, br, aromatic)
13a	—	6	53	2.3–2.6(3H, d, CH_3, $^3J_{PH}$ = 15 Hz), 3.7(3H, s, OCH_3), 5–5.3(2H, br, NH_2), 6.8–8.1(9H, br, aromatic)
b	—	6	60	1.4(3H, t, CH_3), 2.3–3(2H, m, SCH_2), 3.7 (3H, s, OCH_3), 5–5.3(2H, br, NH_2), 6.8–8(9H, br, aromatic)
14	—	0.5	65	1.3(1H, d, SH), 3.7(3H, s, OCH_3), 4–4.4(2H, br, NH_2), 6.6–8(9H, br, aromatic)
15	127–128	1.5	60	1.4(3H, t, CH_3), 4.2(2H, q, CH_2), 7–7.7(5H br, aromatic), 8.4(2H, br, NH_2)

1. The reaction condition for the preparation of the products 10a–f is toluene at 110°C, and for the products 12, 13 is CH_2Cl_2 at 20°C.
2. The products 10a–f, 13, 14, and 15 give M^+ in MS.
3. For all the products the solvent used in ^1H NMR spectra is $CDCl_3$, except for compounds 10b and c it is DMSO.

TABLE II

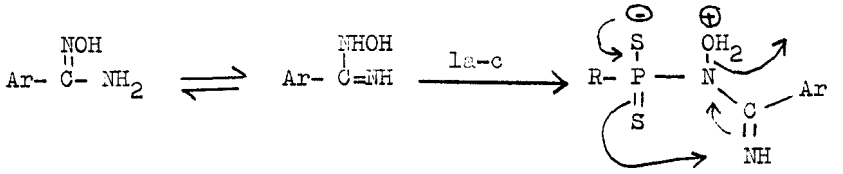
Analytical data for the products 10a–f, 13a,b, 14 and 15[a]

Compound	Formula mol. wt.	Analysis Calc./Found C	H	S
10a	$C_{15}H_{15}N_2OPS_2$	53.87	4.52	19.18
	334.4	53.6	4.5	19.3
b	$C_{20}H_{17}N_2OPS_2$	60.71	4.33	16.21
	395.7	60.5	4.2	16.4
c	$C_{20}H_{17}N_2PS_3$	58.34	4.16	23.36
	411.7	58.1	4.0	23.5
d	$C_{14}H_{13}N_2OPS_2$	52.48	4.09	20.02
	320.4	52.3	3.9	20.2
e	$C_{15}H_{15}N_2OPS_2$	53.87	4.52	19.18
	334.4	53.6	4.4	19.3
f	$C_{15}H_{15}N_2OPS_2$	53.87	4.52	19.18
	334.4	54.0	4.6	19.0
13a	$C_{15}H_{17}N_2O_2PS_2$	51.12	4.86	18.20
	352.4	51.0	4.7	18.4
b	$C_{16}H_{19}N_2O_2PS_2$	52.44	5.23	17.50
	366.4	52.3	5.1	17.7
14	$C_{14}H_{15}N_2O_2PS_2$	49.69	4.47	18.95
	338.4	49.4	4.3	19.0
15	$C_{10}H_{12}N_2O_2S$	53.55	5.40	14.29
	224.3	53.8	5.4	14.0

[a]Compound 12 is hydroscopic, so a satisfactory microanalysis could not be obtained.

The IR spectra (KBr) of compounds 10a–f shows NH absorption in the region 3300–3400 cm^{-1}. In the MS of 10a–f peaks are always observed at M^+.

As to the formation of compounds 10a–f it is suggested that nucleophilic attack of the more potent α-effect nucleophile on the phosphorus of compound 1a–c to



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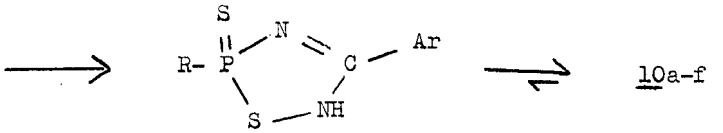
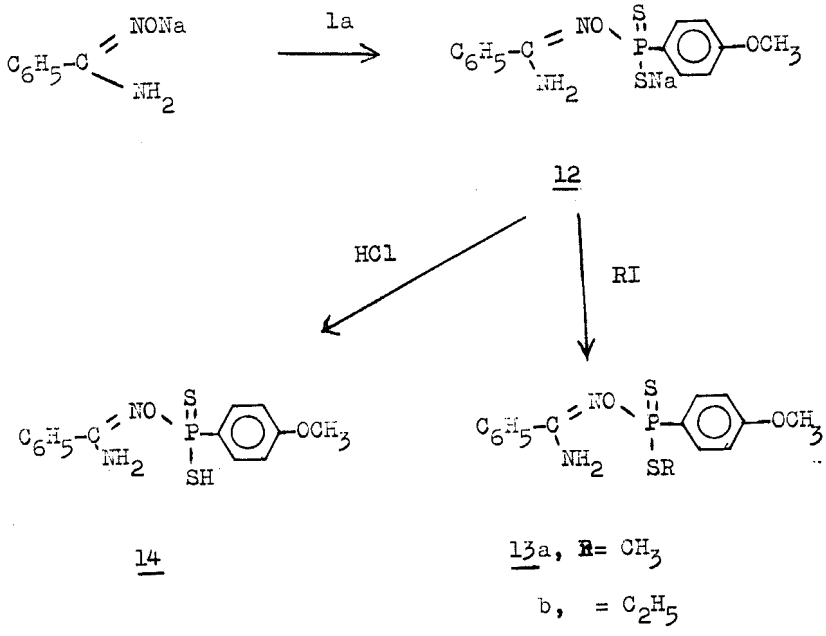


give the intermediate 11, which is supposed to loose water to form the products 10a–f. Mass spectra of the reaction mixture were in some cases recorded and a fragment with the mass M + 18 was present, which is due to structure 11.

The sodium salt of benzamidoxime reacts with compound 1a to form S-sodium-O-benzamidodoxime(4-methoxyphenyl)phosphonothiolothionate 12, which reacts with alkyl iodide to produce the more stable S-alkyl derivatives 13a and b. Compound 12 is acidified to produce O-benzamidoxime(4-methoxyphenyl)phosphonothiolothionate 14.



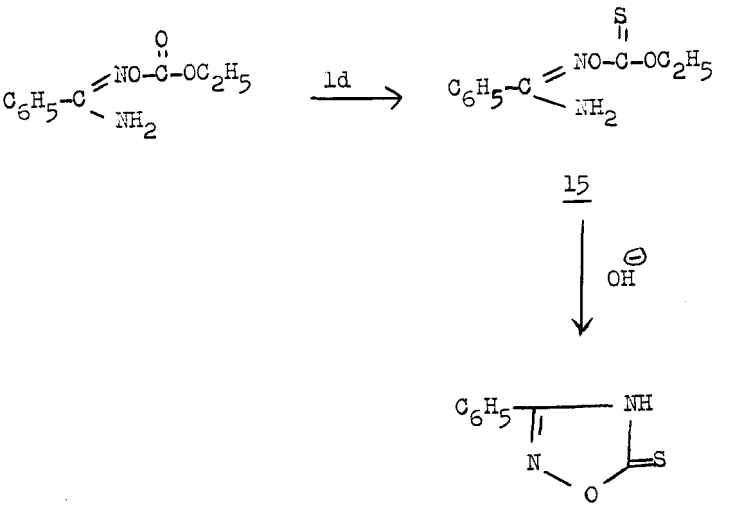
14

13a, R= CH_3

b, = C_2H_5

The structure of compounds 13 and 14 were deduced from IR, ^{1}H NMR and MS (Table I).

Benzamidoxime O-ethylcarboxylate reacts with 1d to produce thionoester 15, which cyclises in alkaline medium to give 3-phenyl-1,2,4-oxadiazol-5-thion.[8] The structure of compound 15 was confirmed from microanalysis, ^{1}H NMR and mass spectra.



EXPERIMENTAL

^{1}H NMR spectra were recorded at 60 MHz on a Varian A-60 spectrometer. TMS is used as internal standard and chemical shifts are expressed in δ-values. IR spectra were recorded on a Beckmann IR-18 spectrometer. Mass spectra were recorded on a micromass 7070 E spectrometer operating at 70 ev using direct inlet.

General procedure for the preparation of 1,2,4-thiadiazaphosphole derivatives 10a–f. The starting amidoximes 9[9] (0.02 mol) and 1a–d (0.01 mol) in 20 ml anhydrous toluene are heated at 110°C with stirring for X hours (Table I) until the starting amidoxime is consumed (TLC). The solvent is concentrated under reduced pressure and subsequent crystallization from toluene-PE to give the products 10a–f.

Reaction of sodium benzamidoxime with 1a *and alkyl iodide.* (0.79 g, 0.005 mol) of sodium benzamidoxime and 2.02 g, 0.005 mol of compound 1a are added to 10 ml CH_2Cl_2 with stirring at 20°C for 3 hours. The reaction mixture is concentrated and crystallized from CH_2Cl_2—PE to give compound 12. 0.005 mol of compound 12 and 0.005 mol alkyl iodide are mixed in 10 ml CH_2Cl_2 with stirring at 20°C for 6 hours. The reaction mixture is placed on a silica gel column and the products 13a,b are eluted with CH_2Cl_2—PE, 50%. The IR spectra ($CHCl_3$) of compounds 12, 13a and b show NH_2 absorption in the region 3300–3500 cm^{-1}.

Formation of compound 14. HCl gas is passed in 20 ml CH_2Cl_2 contain 1.8 g (0.005 mol) of compound 12, for ½ hour with stirring at 20°C. Then the reaction mixture is heated under reflux for 1 hour. The reaction mixture is placed on a silica gel column and the product 14 is eluted with CH_2Cl_2—PE, 80%.

Reaction of benzamidoxime O-ethylcarboxylate with 1d. 1 g (0.005 mol) of benzamidoxime O-ethylcarboxylate[10] and 1.4 g (0.005 mol) of 1d in 15 ml toluene was heated at 80°C for 1.5 hour, until the starting ester is consumed (TLC). The solvent is stripped off and the residue is placed on a silica gel column. Compound 15 is eluted with ether PE, 25%. The IR spectrum (KBr) for compound 15 shows NH_2 absorption at 3300 cm^{-1}.

Formation of 3-phenyl-1,2,4-oxadiazole-5-thion. 1 g (0.005 mol) of thiono ester 15 in 30 ml sodium hydroxide solution 3% is heated at 60–80°C for ½ hour. At room temp. the reaction mixture is acidified

using cold HCl, the solid formed is filtered and purified by crystallization from methanol, m.p. = 134°C, m.p. and mixed m.p. with authentic[8] sample not depressed.

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