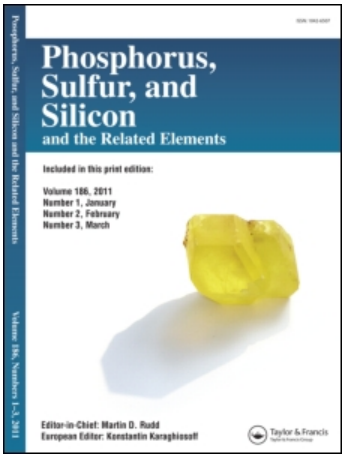

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

ADDITION REACTIONS OF PYRIDINIUM-AND RELATED N-YLIDES WITH 1,3,2,4-DITHIADIPHOSPHETANE-2,4-DISULFIDES

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To cite this Article Yousif, N. M.(1989) 'ADDITION REACTIONS OF PYRIDINIUM-AND RELATED N-YLIDES WITH 1,3,2,4-DITHIADIPHOSPHETANE-2,4-DISULFIDES', Phosphorus, Sulfur, and Silicon and the Related Elements, 44: 3, 249 — 254
To link to this Article: DOI: 10.1080/10426508908040615
URL: http://dx.doi.org/10.1080/10426508908040615

Phosphorus, Sulfur, and Silicon, 1989, Vol. 44, pp. 249–254
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ADDITION REACTIONS OF PYRIDINIUM- AND RELATED N-YLIDES WITH 1,3,2,4-DITHIADIPHOSPHETANE-2,4-DISULFIDES

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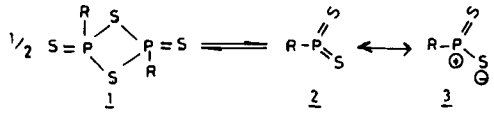
(Received November 17, 1988; in final form November 18, 1988)

Pyridinium phenacylides react with 2,4-Bis-(4-Methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide **1a** to give a mixture of 1,4,2-thiazaphosphole derivatives **8a–c** and 1,3,2-oxathiaphosphole derivatives **9a–c** in the ratio 2:1, respectively; while with compounds **1b–d** give only 1,4,2-thiazaphosphole derivatives **13a–c**. Compounds **12a–d** are obtained from the reaction of compounds **9a–c** with the corresponding alcohol. In the same way compounds **14** and **15** are produced from the reaction quinolinium- and iso-quinolinium phenacylides with **1a** respectively. Mechanistic considerations on the formation of the products are discussed.

Key words: Study the reaction of dithiadiphosphetanes with pyridinium, quinolinium, and iso-quinolinum phenacylides.

INTRODUCTION

1,3,2,4-Dithiadiphosphetane 2,4-disulfides **1a–d** are effective thiation reagents,[1–3] compounds of type 1 exists in equilibrium with the monomer species **2** or **3**.[4–6]



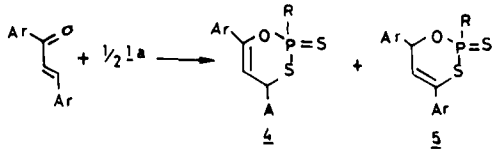
a, R = H_3C-O-

b, R = H_5C_6-O-

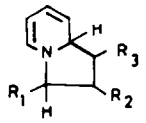
c, R = H_5C_6-S-

d, R = CH_3-S-

[2 + 4] Cycloaddition of **1a** to acyclic α,β-unsaturated ketones is known to give different products.[7,8]



Olefinic and acetylenic dipolarphiles react with pyridinium ylide to give tetrahydroindolizine derivatives.[9–11]



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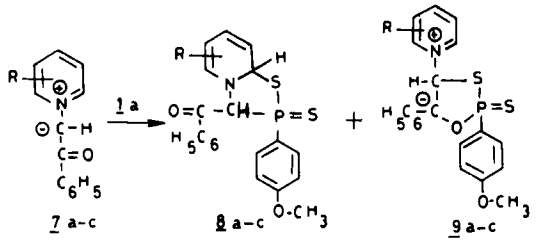
The present paper reports on another type of addition reaction between pyridinium ylides and 1,3,2,4-dithiadiphosphetane-2,4-disulfide **1**a–d.

RESULTS AND DISCUSSION

Pyridinium phenacylides **7**a–c react with 2,4-Bis(4-Methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfid **1**a in methylenechloride at 60 °C to give the corresponding 9H-pyrido[2,1-d][1,4,2]thiazaphosphole-3-benzoyl-2-(4-methoxyphenyl) 2-sulfides **8**a–c and 2-(4-methoxyphenyl)4-N-pyridyl-1,3,2-oxathiaphosphole 2-sulfides **9**a–c in the ratio 2:1 respectively.



7 a-c 8 a-c 9 a-c

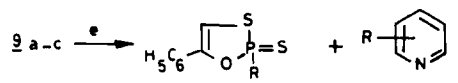
a, R = H
b, R = o-CH_3
c, R = p-CH_3

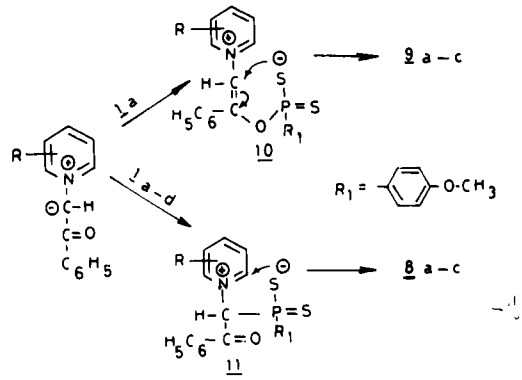
Scheme 1

The structure of compounds **8**a–c and **9**a–c are deduced from microanalysis, IR, ^{1}H NMR, ^{31}P, ^{13}C and MS (tables 1 and 2). Compounds **8**a–c showed the following assignments: The IR spectra had a strong ketone (C=O) 1680–1710 cm^{-1}, the ^{1}H NMR spectra of the thiazaphosphole moiety gave a 1H (CHS) at δ 6.2–6.5 and a 1H (CHP) at δ 5.3–5.5. Deshielding by S and P caused these two protons to appear at lowest field than the corresponding tetrahydroindolizines.[9] ^{13}C NMR spectra provided additional confirmation for the products **8**a–c, the ketone gave singlets at δ 189–190.

Beside the physical proofs for the structure of compounds **9**a–c (e.g. disappearance the ketone from the IR spectra . . .) there is a chemical reaction with nucleophiles to produce compounds **12**a–c.

The fragmentation of compounds **9**a–c in MS give a base peak at m/e 320 ($C_{15}H_{13}O_2PS_2$), due to the formation of 2-(4-methoxyphenyl)-1,3,2-oxathiaphosphole-2-sulfide. As to the formation of compounds **8**a–c and **9**a–c in the ratio

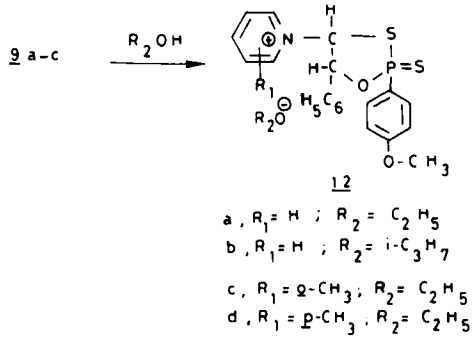




Scheme 2

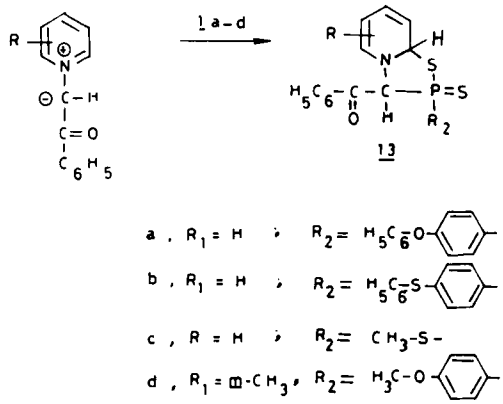
2:1 and unreactivity of compound **16** with **1**a, it is suggested that either nucleophilic attack of the carbonyl oxygen or the carbanion (1,3-dipolar cycloaddition) on phosphorus of **1**a–d gives the intermediates 10 and 11 respectively in the ratio 2:1.

Compounds **9**a–c react with nucleophiles e.g. ethyl alcohol and isopropyl alcohol to give the corresponding oxathiaphosphole-2-sulfide derivatives **12**a–d.



a , R_1= H ; R_2 = C_2H_5
b , R_1= H ; R_2= i-C_3H_7
c , R_1 = o-CH_3 ; R_2= C_2H_5
d , R_1 = p-CH_3 ; R_2= C_2H_5

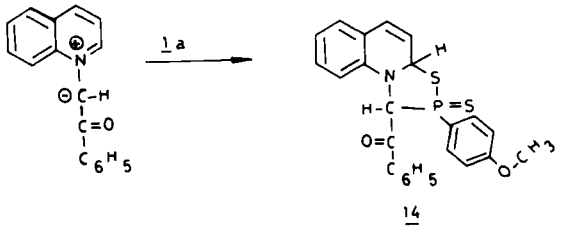
The reaction of compounds **1**b–d with pyridinium- and 3-methyl-pyridinium phenacylides at 60 °C yields the corresponding pyrido (2, 1-d)(1,4,2)thiazaphosphole-3-benzoyl-2-sulfide derivatives **13**a–d.

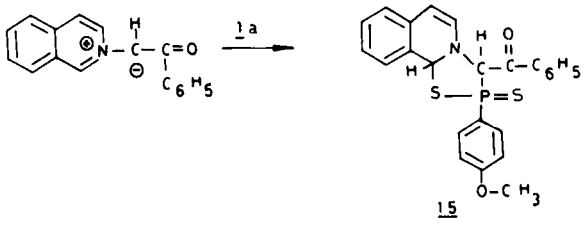


a , R_1 = H ; R_2= H_5C_6–C(=O)–O–
b , R_1 = H ; R_2= H_5C_6–C(=S)–S–
c , R = H ; R_2= CH_3-S-
d , R_1 = m-CH_3, R_2= H_3C-O–

The isolation of only product **13**a–d means that the corresponding intermediate 10 could not be formed, and the reaction goes through only the corresponding intermediate 11.

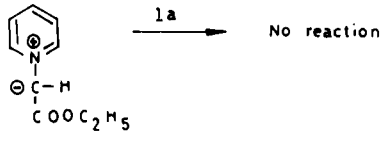
10-aH-Quinolo(2,1-d)(1,4,2)thiazaphosphole-3H-benzoyl-2-(4-methoxyphenyl)-2-sulfide **14** and 10-bH-isoquinolo(1,2-d)(1,4,2)thiazaphosphole-3H-3-benzoyl-2-(4-methoxyphenyl)-2-sulfide **15** are produced from the reaction of quinolinium- and isoquinolinium phenacylides with **1**a respectively.





The structural proofs of compounds **14** and **15** are based on microanalysis and spectroscopic data (IR, ^{1}HNMR, ^{13}C, ^{31}P) Tables I and II. Compounds **14** and **15** showed the following data:- ^{1}HNMR spectra of the thiazaphosphole moiety gave a 1H (CHP) at δ 5.2–5.4 and the other proton (CHS) obscured by overlapping with aromatic signals. The ketone appeared in the IR spectra at 1680–1700 cm^{-1}; and in the ^{13}C spectra gave singlets at 189.5–190.4.

Compound **16** does not react with compounds **1**a–d even at high temperature.



EXPERIMENTAL

^{1}HNMR spectra are recorded at 60 MHz on a Varian A-60 spectrometer. ^{13}C NMR spectra and ^{31}P NMR spectra were recorded at 20 MHz and 32 MHz, respectively, on a Varian CFT-20 spectrometer. TMS is used as internal standered and chemical shifts are expressed in δ-values. ^{31}P chemical shifts are related to 85% H_3PO_4. $CDCl_3$ is used as solvent. IR spectra are recorded on a Beckman IR-18 spectrometer. Mass spectra are recorded on a micromass 7070 Mass spectrometer operating at 70 ev using direct inlet. Elementary analysis are carried out by NRC. Egypt. M.P.s are not corrected.

TABLE 1

Experimental data and ^{1}HNMR for the reaction of pyridinium and related *N*-ylides with **1**a–d

Product	MP.P °C	Yield %	^{1}HNMR δ (ppm)
8a	89–90	62	3.7(3H, s, OCH_3), 5.5(1H, d, CHP), 6.5(1H, d, CHS), 7–8.1(12H, br, aromatics), 8.9(1H, d, 2 pyridyl).
b	79–80	55	2.7(3H, s, CH_3), 3.8(3H, s, OCH_3), 5.4(1H, d, CHP), 6.3(1H, d, CHS), 7–8.4(11H, br, aromatics), 9.0(1H, d, 2 pyridyl).
c	87–88	61	2.5(3H, s, CH_3), 3.7(3H, s, OCH_3), 5.3(1H, d, CHP), 6.2(1H, d, CHS), 7–8(11H, br, aromatic), 8.7(1H, d, 2 pyridyl).
9a	165–166	34	3.7(3H, s, OCH_3), 4.9(1H, d, CHS), 6.9–7.9(12H, br, aromatics), 8.5(2H, d, 2 pyridyl).
b	166	35	2.3(3H, s, CH_3), 3.7(3H, s, OCH_3), 4.6(1H, d, CHS), 7–8(12H, br, aromatics), 8.8(1H, d, 2 pyridyl).
c	183–184	33	2.3(3H, s, CH_3), 3.7(3H, s, OCH_3), 4.9(1H, d, CHS), 7–8(11H, br, atomatic), 8.9(2H, d, 2 pyridyl).
12a	110	83	1.1(3H, t, CH_3), 3.5(2H, d, CH_2), 3.7(3H, s, OCH_3), 5–5.3(2H, dd, CHO + CHS), 7.2–8.3(12H, br, aromatic), 8.8(2H, d, 2 pyridyl).
b	140	80	1–1.5(7H, br, $2CH_3$ + CH), 3.6(3H, s, OCH_3), 5.1–5.3(2H, dd, CHO + CHS), 7.1–8.5(12H, br, aromatic), 8.9(2H, d, 2 pyridyl).
c	53	75	1.1(3H, t, CH_3), 2.5(3H, s, CH_3), 3.4(2H, d, CH_2), 3.7 (3H, s, OCH_3), 4.8–5(2H, dd, CHO + CHS), 7–8.4(12H, br, aromatic), 9.2(1H, d, 2 pyridyl).
d	135–136	80	1.0(3H, t, CH_3), 2.5(3H, s, CH_3), 3.4(2H, d, CH_2S), 3.7(3H, s, OCH_3), 4.6–5(2H, dd, CHO + CHS), 7–8(11H, br, aromatic), 9.0(1H, d, 2 pyridyl).
13a	90–91	90	5.5(1H, d, CHP), 6.4(1H, d, CHS), 6.9–8.4(17H, br, aromatic), 8.8(1H, 2 pyridyl).
13b	70–71	69	5.3(1H, d, CHP), 7–9(18H, Br, aromatic).
c	25	30	2.6(3H, d, CH_3—S), 5.4(1H, d, CHP), 6.5(1H, d, CH), 7–8(8H, br, aromatic), 8.6(1H, d, 2 pyridyl).
d	88–90	85	2.3(3H, s, CH_3), 3.7(3H, s, OCH_3), 5.4(1H, d, CHP), 6.2(1H, d, CHS), 7–8.4(11H, br, aromatic), 8.8(1H, 1H, d, 2 pyridyl).
14	85–86	76	3.6(3H, s, OCH_3), 5.2(1H, d, CHP), 6.5–8.8(15H, br, aromatic).
15	82	80	3.7(3H, s, OCH_3), 5.4(1H, d, CHP), 6.9–8.9(15H, br, aromatic).

1) The reaction condition for the preparation of the products **8**a–c, **9**a–c, **13**, **14**, and **15** is CH_2Cl_2 at 60°C.

2) Satisfactory microanalysis (C, H, S) could be obtained for all the products.

3) The solvent of crystallization (experimental part).

4) All the products give M + in MS.

5) The solvent used for ^{1}HNMR is DMSO for compounds **9**a–c and $CDCl_3$ for the others.

6) Compound **14**d 2.5–2.7 (CH_3: δ, $^3J_{PH} = 12$) and for the others 5.2–5.5 (CHP: $^2J_{PH} = 18$–20); 6.2–6.5 (CHS: $^3J_{PH} = 14$).

Reaction of pyridinium phenacylides **7***a–c with* **1***a* The starting pyridinium phenacylides[12] (0.01 mole), and 2.02 g (0.005 mole) of **1**a in 10 ml anhydrous methylene chloride are heated at 60 °C with stirring for 15 mins. The solid formed is filtered then crystallized from CH_3CN to give the compounds **9**a–c; and the filtrate is concentrated and crystallized from CH_2Cl_2- Pet. ether to give the compounds **8**a–c.

General procedure for the preparation of compounds **12***a–d* 0.01 Mole of compounds **9**a–c in 20 ml of corresponding alcohol is heated at 70 °C for 15 min, at room temperature the crystal formed is collected to give the corresponding products **12**a–d.

General procedure for the preparation of thiazaphosphole-2-sulfide derivatives **13***a–d*, **14**, *and* **15** The starting N-ylides (0.01 mole) and compounds **1**a–d (0.006 mole) in 10 ml anhydrous CH_2Cl_2 are heated at 60°C for 20 min, the solvent is evaporated under reduced pressure and the solid formed is purified by crystallization from CH_2Cl_2- Pet. ether (80:20) to give the desired products.

TABLE II

^{13}C NMR, ^{31}P NMR ($CDCl_3$) and IR(KBr) data for the products **8**a–c, **12**a–d, **13**a–d, **14** and **15**.

Product	IR(C=O) cm	^{13}C δ (C=O)	^{31}P
8a	1690–1700	189.7	124.0
b	1680–1710	189.9	121.5
c	1680–1690	190.1	120.9
12a	—	—	27.4
b	—	—	28.6
c	—	—	27.7
d	—	—	27.4
13a	1690–1700	190.0	123.3
b	1680–1690	189.9	121.1
c	1690–1710	190.0	122.9
d	1690–1710	189.9	120.0
14	1680–1690	190.4	95.1
15	1690–1700	189.5	92.4

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