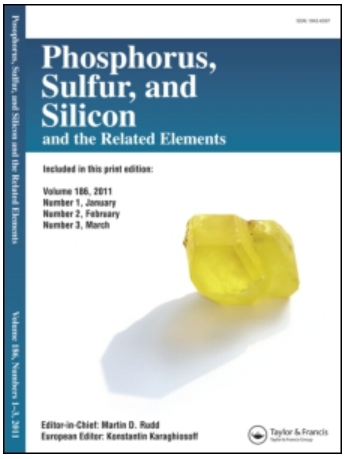

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ALKOXYLATION OF HYDRIDOPHOSPHORANE III. FURTHER STUDIES ON THE REACTION OF HYDRIDOPHOSPHORANE WITH BENZENESULFENIC ESTERS

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ALKOXYLATION OF HYDRIDOPHOSPHORANE III. FURTHER STUDIES ON THE REACTION OF HYDRIDOPHOSPHORANE WITH BENZENESULFENIC ESTERS

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The bicyclic hydridophosphorane **2** was shown to undergo alkoxylation reaction with a series of benzenesulfenic esters **3** to give the corresponding isolable alkoxyphosphoranes in preparatively useful amounts (72–89%). The reaction pathway is interpreted in terms of a two-step process: the first step involves formation of alkoxyphosphorane **4** and thiaphosphorane **5**, the second step involves the reaction of **5** with alcohol, converting to **4**.

Key words: Alkoxylation; hydridophosphorane; alkoxyphosphoranes; benzenesulfenic esters; thiaphosphoranes.

INTRODUCTION

It is well-known that tricoordinated phosphorus compounds react with benzenesulfenic esters via biphilic mechanism to form pentacoordinated phosphorus compounds.[1] It is known that the S—O bond in benzenesulfenic esters could readily undergo cleavage. This reaction was first found by D. B. Denney. Bentrude[3] recently reported a scission reaction, initiated by AIBN or UV light, of hydridophosphorane with alkyl disulfides or dialkyl peroxide via free-radical mechanism to give corresponding thiaphosphorane or alkoxyphosphorane. It indicated that the P—H bond in phosphorane could also readily undergo cleavage.

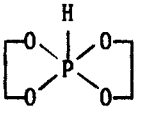
The work made by Denney and Bentrude led us to investigate the reaction of P—H bond with the S—O bond.

In the previous paper,[2] we reported the reaction of **1** with benzenesulfenic esters, leading to the corresponding isolable alkoxyphosphorane formation. In this paper, we report the reaction of **2** with benzenesulfenic esters and provide further understanding of this reaction.

The principal advantages of this reaction are: the operation is simple, the reaction proceeds smoothly under mild conditions, the yield and purity of the corresponding alkoxyphosphoranes are excellent.

RESULTS AND DISCUSSION

Compound **2** reacted in benzene with benzenesulfenic esters **3** at 14°C for 4–5 hrs to convert completely to the corresponding alkoxyphosphoranes **4** and phenylthia-



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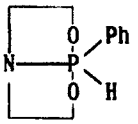
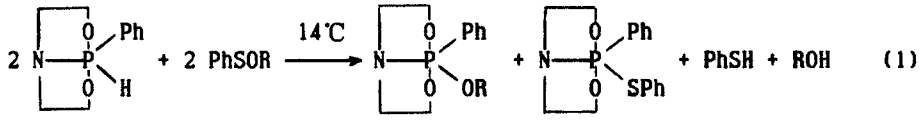


2

phosphorane **5**. The reaction process was monitored by ^{31}P NMR. When no signal was detected for the starting material **2**, the following reaction sequence was observed.

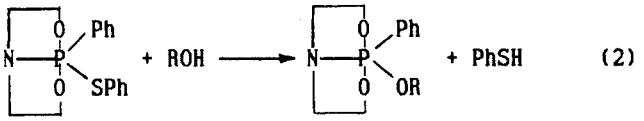


(1)

2 **3** **4** **5**

a R=Me; **b** R=Et; **c** R=n-Pr; **d** R=i-Pr;
e R=n-Bu; **f** R=i-Bu; **g** R=n-Pen; **h** R=n-Hex;

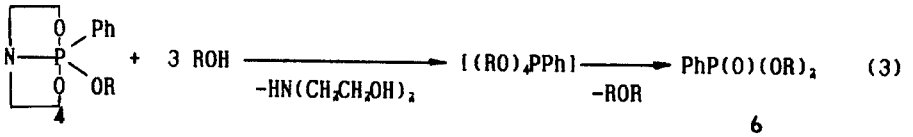
The reaction mixture was then heated to 40–50°C for some hours until compound **5** disappeared largely and the by-product **6** just appeared. It is an exchange reaction between compound **5** and alcohol.



(2)

5 **4**

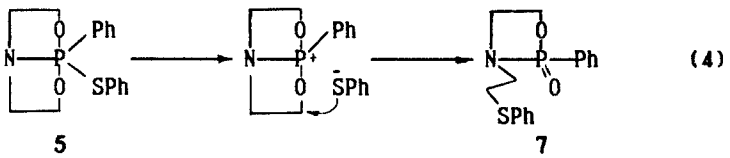
The major by-product is O,O-dialkyl phenyl phosphonate **6** which probably was transformed via alcoholyses of **4**.[5]



(3)

6

It was reported that compound **5** was easily decomposed to the phosphoryl compound **7** during distillation.[3] At 50°C in benzene compound **5** is reasonably stable and is not converted to compound **7**.



(4)

5 **7**

We had been unable to isolate compound **5** owing to its instability, but its structure was characterized by ^{31}P NMR spectroscopy and entirely consistent with that reported previously.[3]

The yields of **4** were monitored quantitatively by ^{31}P NMR with trimethyl phosphate added as an external standard. High NMR yields (72–89%) were found (Table IV).

Products **4** were also easily isolable in pure form by distillation, and the structure was confirmed by spectroscopic criteria (Tables I, II, III) and quantitative elemental analysis.

Although **2** is known to undergo reaction in its tricoordinated form **8**,[4] the tautomerization was dependent of solvent and temperature. The ^{31}P NMR spectrum of **2** exhibits only one single high-field signal in benzene, even at higher temperature (50°C). This excludes the possibility of a biphilic mechanism in Equation (1) (see Equation (5)).

TABLE I

^{1}H and ^{31}P NMR data of compounds **4a–h**[a]

compd.	^{1}H chemical shifts					^{31}P
	RO[b]	NCH_2[b]	OCH_2[b]	m,p-C_6H_5P[b]	o-C_6H_5P[b]	
4a	3.70(d, J_{HP}=14.4Hz, CH_3O)	3.05-3.43	3.74-4.05	7.23-7.40	7.49-7.80	-37.42
4b	1.16-1.34(d of t, $\underline{CH_3}CH_2O$) 3.69-4.14(d of q, $CH_3\underline{CH_2}O$)	3.01-3.28	3.69-4.14	7.26-7.37	7.46-7.75	-38.23
4c	0.95(t, $\underline{CH_3}CH_2CH_2O$) 1.51-1.92(m, $CH_3\underline{CH_2}CH_2O$) 3.73-4.08(m, $CH_3CH_2\underline{CH_2}O$)	3.06-3.33	3.73-4.08	7.28-7.46	7.49-7.81	-38.09
4d	1.28(d, J_{HP}=6.1Hz, $(\underline{CH_3})_2CHO$) 4.47-4.80(m, $(CH_3)_2\underline{CH}O$)	3.05-3.33	3.76-4.06	7.31-7.41	7.49-7.84	-39.57
4e	0.91(t, $\underline{CH_3}(CH_2)_2CH_2O$) 1.20-1.79(m, $CH_3\underline{(CH_2)_2}CH_2O$) 3.73-4.04(m, $CH_3(CH_2)_2\underline{CH_2}O$)	3.04-3.31	3.73-4.04	7.28-7.41	7.47-7.78	-38.69
4f	1.02(d, J_{HP}=7.2Hz, $(\underline{CH_3})_2CHCH_2O$) 1.85-2.16(m, $(CH_3)_2\underline{CH}CH_2O$) 3.65-4.05(m, $(CH_3)_2CH\underline{CH_2}O$)	3.05-3.33	3.67-4.05	7.24-7.40	7.47-7.81	-39.17
4g	0.96(t, $\underline{CH_3}(CH_2)_2CH_2CH_2O$) 1.33-1.46(m, $CH_3\underline{(CH_2)_2}CH_2CH_2O$) 1.58-1.81(m, $CH_3(CH_2)_2\underline{CH_2}CH_2O$) 3.79-4.08(m, $CH_3(CH_2)_2CH_2\underline{CH_2}O$)	3.09-3.37	3.79-4.08	7.31-7.43	7.49-7.80	-38.09
4h	0.92(t, $\underline{CH_3}(CH_2)_3CH_2CH_2O$) 1.23-1.45(m, $CH_3\underline{(CH_2)_3}CH_2CH_2O$) 1.54-1.76(m, $CH_3(CH_2)_3\underline{CH_2}CH_2O$) 3.72-4.08(m, $CH_3(CH_2)_3CH_2\underline{CH_2}O$)	3.05-3.32	3.72-4.08	7.22-7.44	7.47-7.83	-38.23

a. Solvent is $CDCl_3$

b. Unresolved multiplets

TABLE II

^{13}C NMR data of compounds **4a–h**[a,b]

compd.	NCH_2	OCH_2	RO		C_6H_5P
4a	43.34(19.5)	58.40	$\underline{CH_3}$	54.55(7.3)	140.66(166.0) ipso 126.01(48.8) o 127.79(17.1) m 129.26(14.6) p
4b	43.28(16.9)	58.29	$\underline{CH_3}CH_2$ $CH_3\underline{CH_2}$	16.85(7.3) 62.84(9.8)	139.82(227.1) ipso 127.20(4.9) p 128.50(19.5) o 129.47(9.8) m
4c	43.45(19.5)	58.40	$\underline{CH_3}CH_2CH_2$ $CH_3\underline{CH_2}CH_2$ $CH_3CH_2\underline{CH_2}$	10.51 24.32(7.3) 68.85(7.3)	139.98(229.5) ipso 127.69(17.1) o 128.93(4.9) p 129.09(9.8) m
4d	43.45(19.5)	58.50	$(\underline{CH_3})_2CH$ $(CH_3)_2\underline{CH}$	24.43(7.3) 69.77(9.8)	140.85(229.5) ipso 127.66(13.4) o 128.93(4.9) p 129.09(9.8) m
4e	43.08(17.1)	58.07	$\underline{CH_3}CH_2CH_2CH_2$ $CH_3\underline{CH_2}CH_2CH_2$ $CH_3CH_2\underline{CH_2}CH_2$ $CH_3CH_2CH_2\underline{CH_2}$	13.54 18.85 32.83(9.8) 66.63(9.8)	139.66(229.5) ipso 127.36(17.1) o 128.55(7.3) p 129.37(9.8) m
4f	43.23(19.5)	58.18	$(\underline{CH_3})_2CHCH_2$ $(CH_3)_2\underline{CH}CH_2$ $(CH_3)_2CH\underline{CH_2}$	19.18 29.25(9.8) 73.35(9.8)	140.09(229.5) ipso 127.47(17.1) o 128.66(7.3) p 129.47(9.8) m
4g	43.18(17.1)	58.18	$\underline{CH_3}CH_2CH_2CH_2CH_2$ $CH_3\underline{CH_2}CH_2CH_2CH_2$ $CH_3CH_2\underline{CH_2}CH_2CH_2$ $CH_3CH_2CH_2\underline{CH_2}CH_2$ $CH_3CH_2CH_2CH_2\underline{CH_2}$	13.87 22.21 27.85 30.55(9.8) 67.01(7.3)	139.77(229.5) ipso 127.44(18.3) o 128.66(7.3) p 129.47(9.8) m
4h	43.34(19.5)	58.40	$\underline{CH_3}CH_2CH_2CH_2CH_2CH_2$ $CH_3\underline{CH_2}CH_2CH_2CH_2CH_2$ $CH_3CH_2\underline{CH_2}CH_2CH_2CH_2$ $CH_3CH_2CH_2\underline{CH_2}CH_2CH_2$ $CH_3CH_2CH_2CH_2\underline{CH_2}CH_2$ $CH_3CH_2CH_2CH_2CH_2\underline{CH_2}$	13.98 22.54 25.57 30.77 31.31(9.8) 67.23(7.3)	139.88(229.5) ipso 127.47(7.3) p 128.39(19.5) o 129.47(9.8) m

a. Solvent is $CDCl_3$.
b. ^{13}C-^{31}P coupling constants (Hz) in parenthesis.

Evidently, this reaction proceeded by a different mechanism, possibly via a hexacoordinated phosphorus compound as transition state which subsequently eliminated alcohol or thiophenol to give **4** and **5** respectively (as depicted in sequence (6)).

TABLE III

Mass spectral data of compounds **4a–h**

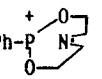
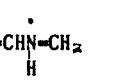
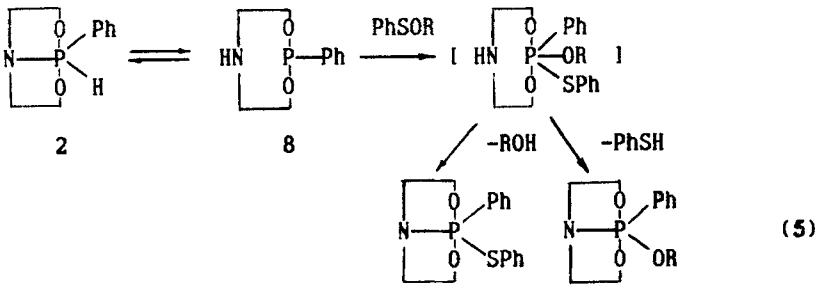
compd	Fragment m/e (rel intensity)				
	M^+	Ph^+ / RO–P=O	Ph^+ / HO–P=O		
4a	241 (10)	155 (8)	141 (20)	210 (11)	56 (83)
4b	255 (4)	169 (23)	141 (57)	210 (11)	56 (75)
4c	269 (15)	183 (23)	141 (100)	210 (50)	56 (57)
4d	269 (5)	183 (2)	141 (51)	210 (14)	56 (100)
4e	283 (8)	197 (19)	141 (48)	210 (34)	56 (100)
4f	283 (4)	197 (22)	141 (100)	210 (64)	56 (61)
4g	297 (3)	211 (4)	141 (19)	210 (18)	56 (100)
4h	311 (7)	225 (4)	141 (49)	210 (42)	56 (100)

TABLE IV

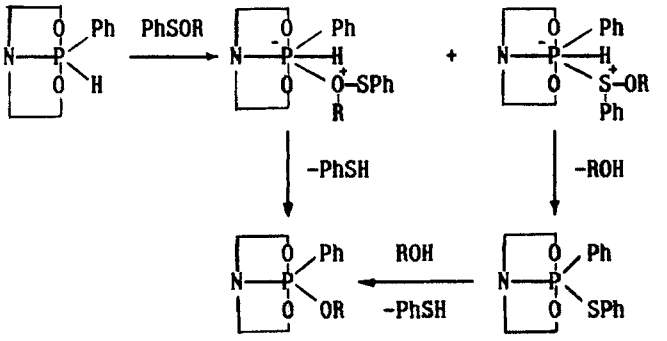
The results and conditions of reaction of 2 with PhSOR[a]

R	first step			second step				
	conditions t (℃) (4–5 hr)	results		conditions T (hr) (40–50℃)	results			
		content of compd 4 (%)	content of compd 5 (%)		content of compd 4 (%)	content of compd 5 (%)	content of compd 6 (%)	yields of compd 4 (%)
Me	14	28.77	71.23	21.5	72.30	27.70	—	72.30
Et	14	33.12	66.88	18.0	75.64	16.80	7.56	75.64
n-Pr	14	19.08	80.92	29.5	78.39	18.16	3.45	78.39
i-Pr	12	11.18	88.82	59.0	73.00	27.00	—	73.00
n-Bu	12	27.54	72.46	21.5	80.57	13.24	6.19	80.57
i-Bu	14	24.00	76.00	28.0	80.41	13.12	6.47	80.41
$n\text{-}C_5H_{11}$	14	19.12	80.88	44.0	77.01	13.49	9.50	77.01
$n\text{-}C_6H_{13}$	11	48.31	51.69	15.0	89.33	3.90	6.77	89.33

a. The contents and yields were determined by ^{31}P NMR spectroscopy.



(5)



(6)

EXPERIMENTAL

^1H, ^{13}C, ^{31}P NMR spectra were run on a JEOL FX-90Q spectrometer. ^1H and ^{13}C chemical shifts are reported in parts per million relative to internal tetramethylsilane. All ^{31}P chemical shifts are reported in parts per million relative to 85% phosphoric acid (external). In all cases the nuclei which are deshielded relative to their respective standard are assigned a positive chemical shift. ^{13}C, ^{31}P NMR spectra were obtained by using full proton coupling. ^{31}P NMR spectra were acquired by using a 90° tip angle and a 2–4s repetition rate with no pulse delay. Quantitative elemental analyses were run on a Yana MT-3. Mass spectra were recorded on a Hewlett-Packard 5988. All manipulations were carried out in a nitrogen atmosphere. All solvents were scrupulously dried and freshly distilled.

Hydridophosphorane/benzenesulfenic esters reaction monitored by ^{31}P NMR spectroscopy. To a stirred solution of hydridophosphorane **2**[6] (10 mmol) in absolute benzene (20 ml) was added benzenesulfenic esters **3**[2] (10 mmol) at 14°C. The mixture was stirred for 4–5 hours at 14°C and occasionally inspected by ^{31}P NMR spectroscopy. A sealed capillary tube containing trimethyl phosphate was placed in the NMR tube. When no signal was detected for **2**, the ^{31}P NMR spectra were taken to give compounds **4**, **5** to trimethyl phosphate ratios, from which amounts of compounds **4**, **5** were determined. The mixture was then heated to 40–50°C for some hours until compound **5** disappeared mostly and the by-product **6** just appeared. The yields of the products **4a–h** were calculated in like manner.

General procedure for preparation of alkoxyphosphoranes **4**. The above reaction, inspected by ^{31}P NMR spectroscopy, was carried out, and then the reaction mixture was concentrated. The residue was vacuum distilled to give the desired alkoxyphosphoranes **4**.

4a. 33.20% yield, bp 116–117°C/0.05 mmHg. Anal. Calcd. for $C_{11}H_{16}NO_3P$: C, 54.77; H, 6.64; N, 5.81. Found: C, 54.58; H, 6.16; N, 5.80

4b. 42.04% yield, bp 123.8–124°C/0.05 mmHg. Anal. Calcd. for $C_{12}H_{18}NO_3P$: C, 56.47; H, 7.06; N, 5.49. Found: C, 56.34; H, 7.14; N, 5.69

4c. 40.89% yield, bp 128.8–129°C/0.05 mmHg. Anal. Calcd. for $C_{13}H_{20}NO_3P$: C, 57.99; H, 7.43; N, 5.20. Found: C, 57.94; H, 7.05; N, 4.98

4d. 44.61% yield, bp 109.8–110°C/0.05 mmHg. Anal. Calcd. for $C_{13}H_{20}NO_3P$: C, 57.99; H, 7.43; N, 5.20. Found: C, 57.76; H, 7.06; N, 5.32

4e. 53.00% yield, bp 133.8–134°C/0.05 mmHg. Anal. Calcd. for $C_{14}H_{22}NO_3P$: C, 59.36; H, 7.77; N, 4.95. Found: C, 59.08; H, 7.33; N, 4.74

4f. 42.40% yield, bp 100.8–101°C/0.03 mmHg. Anal. Calcd. for $C_{14}H_{22}NO_3P$: C, 59.36; H, 7.77; N, 4.95. Found: C, 59.91; H, 7.31; N, 4.70

4g. 43.77% yield, bp 127.8–128°C/0.03 mmHg. Anal. Calcd. for $C_{15}H_{24}NO_3P$: C, 60.61; H, 8.08; N, 4.71. Found: C, 60.30; H, 7.81; N, 4.18

4h. 57.88% yield, bp 135.8–136°C/0.05 mmHg. Anal. Calcd. for $C_{16}H_{26}NO_3P$: C, 61.74; H, 8.36; N, 4.50. Found: C, 61.41; H, 8.60; N, 4.30

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