

# Alkoxylation of Hydridophosphorane. II. Reaction of Hydridophosphorane with Benzenesulphenic Esters

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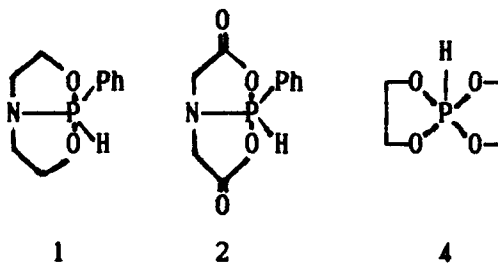
## ABSTRACT

The spirophosphorane **4** underwent reaction with a series of benzene-sulphenic esters **3** to give the corresponding isolable alkoxyphosphoranes. The reactivities of benzenesulphenic esters **3** in this reaction were seen to be dependent on steric hindrance of the R groups. The yields of alkoxyphosphoranes were influenced by the reaction temperature. The probable mechanism was suggested in terms of experimental observations.

## INTRODUCTION

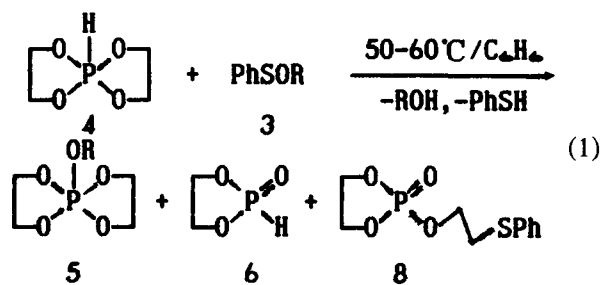
The alkoxylation reactions of hydridophosphoranes have been studied previously [1,2]. Bentrude [3] reported in 1987 that alkylthiation, initiated by UV light, of the bicyclic hydridophosphorane **1** with dialkyl disulfides yielded the corresponding isolable thiaphosphoranes, which then reacted with alcohols to give alkoxyphosphoranes. Recently, we studied [4] the reactions of the bicyclic hydridophosphorane **2** with alcohols in the presence of diphenyl disulfide to give the corresponding isolable alkoxyphosphoranes. It was hoped in the present research that the benzenesulphenic esters **3** would act as both hydrogen acceptors and nucleophilic reagents in the reactions of spirohydridophosphorane **4** with **3**. The results of this investigation were

consistent with these hopes. It was also hoped that the results of this study would provide information on the mechanism of these reactions and also on the properties of the hydridophosphoranes that might result from them.



## RESULTS AND DISCUSSION

5-Hydro-1,4,6,9-tetraoxa-5-phosphaspiro[4.4]nonane **4** reacted in benzene with benzenesulphenic esters **3** at 50–60°C to give the corresponding isolable 5-alkoxy-1,4,6,9-tetraoxa-5-phosphaspiro[4.4]nonanes **5** as the main products (yield 68–94%), but some by-products **6** and **8** were also detected (Equation 1):



\*To whom correspondence should be addressed. Dedicated to Prof. Yao-Zeng Huang on the occasion of his eightieth birthday.

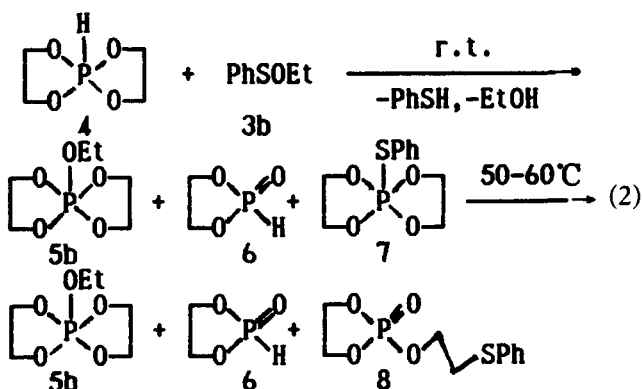
a: R = Me; b: R = Et; c: R = *n*-Pr;

d: R = *n*-Bu; e: R = *n*-C<sub>6</sub>H<sub>13</sub>(*n*-Hex).

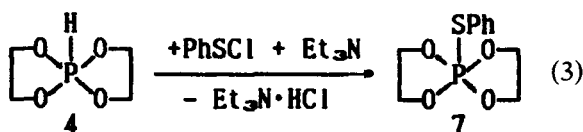
Products **5a–e** were easily isolable in pure form by distillation, and the structures were confirmed by spectroscopic criteria. Thus, the alkoxylation reactions are preparatively useful; <sup>1</sup>H, <sup>31</sup>P, and <sup>13</sup>C NMR data are given in Table 1.

In an attempt to determine what the scission mechanism of the P–H bond and the effect of the R groups in this reaction might be, the reactions of **4** with **3a–e** during different time periods and at different temperatures were studied. The types of phosphorus compounds formed in these reaction mixtures were determined by <sup>31</sup>P NMR techniques. The results and conditions of the reactions (Equation 1) are collected in Table 2.

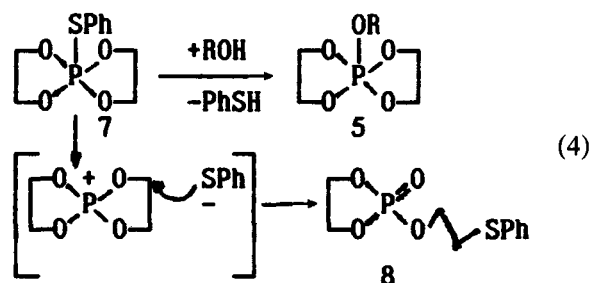
When **4** was caused to react with **3b** at room temperature for 5.5 hours, <sup>31</sup>P NMR spectroscopy showed that **5b** as well as the by-products **6** ( $\delta_p$  8.20) and **7** ( $\delta_p$  – 8.72) were formed. The reaction mixture was then heated to 50–60°C. It was found that after a reaction period of 6.4 hours compound **7** disappeared and the amount of the product **5b** increased. Also, compound **8** ( $\delta_p$  17.36) appeared.



The overall result of the two-step reaction (Equation 2) was the same as that of the one-step reaction (Equation 1). We had been unable to isolate compound **7** owing to its instability, but its structure was confirmed by the reaction of **4** with benzenesulfonyl chloride (Equation 3).

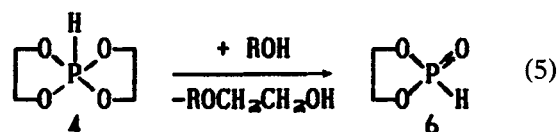


The authentic compound **7** (Equation 3) was the same as the by-product **7** (Equation 2), as shown by comparison of their <sup>31</sup>P, <sup>13</sup>C, and <sup>1</sup>H NMR spectra. Authentic **7** also underwent alcoholysis to **5** as well as rearrangement to **8**.



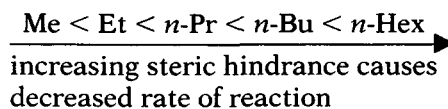
The result (Equation 4) was entirely consistent with that observed (Equation 2) and similar to that reported previously [3].

The formation of the by-product **6** is reasonably understood in terms of the alcoholysis of **4**.



Therefore, the complete reaction pathway (Equation 1) may be described as shown in Scheme 1.

The magnitude of the steric effects of **3** observed in Equation 1 is very apparent in the data of Table 2. These data demonstrated that the reactivities of PhSOR toward **4** were dependent on the steric hindrance of the R groups. The following order of steric effects was observed.



When R was an isopropyl, *s*-butyl or *t*-butyl group, PhSOR reacted with **4** only very sluggishly. For example, no more than 10% of **4** had undergone reaction with PhSOBu-*t* in a week.

## EXPERIMENTAL SECTION

The <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectra were run on a JEOL FX-90Q spectrometer. The <sup>1</sup>H and <sup>13</sup>C chemical shifts are reported in parts per million relative to internal tetramethylsilane. All <sup>31</sup>P chemical shifts are reported in parts per million relative to 85% phosphoric acid (external). In all cases, nuclei which are deshielded relative to their respective standards are assigned a positive chemical shift. The <sup>13</sup>C and <sup>31</sup>P NMR spectra were obtained by broadband proton decoupling. All manipulations were carried out in a nitrogen atmosphere. All solvents were scrupulously dried and freshly distilled.

### General Procedure for Preparation of Benzenesulphenic Esters **3a–e**

Anhydrous ethyl ether (100 mL) and triethylamine (0.11 mol) which had been treated with potassium

TABLE 1  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  NMR Data <sup>a,b</sup> of Compounds 5a–e<sup>c</sup>

Compound	$^{31}\text{P}$	$^1\text{H}$ NMR		$^{13}\text{C}$ NMR	
		Cyclic-CH <sub>2</sub>	R	Cyclic-CH <sub>2</sub> ( $^2J_{\text{CP}}$ )	R
5a	-27.19 <sup>d</sup>	3.93 (d, $J$ 14.4)	3.69 (d, $J$ 14.4, CH <sub>3</sub> )	59.92 (d, 4.88)	54.77 (d, $^2J_{\text{CP}}$ 7.33, CH <sub>3</sub> )
5b	-28.94 <sup>e</sup>	3.86 (d, $J$ 14.4)	1.23 (dt, CH <sub>3</sub> )	60.02 (d, 4.88)	16.41 (d, $^3J_{\text{CP}}$ 7.32, CH <sub>3</sub> )
5c	-27.86	3.92 (d, $J$ 14.4)	3.91 (dq, CH <sub>2</sub> O)	60.02 (d, 4.89)	63.38 (d, $^2J_{\text{CP}}$ 9.76, OCH <sub>2</sub> )
			0.96 (t, CH <sub>3</sub> )	60.02 (d, 4.88)	10.29 (s, CH <sub>3</sub> )
5d	-28.13	3.92 (d, $J$ 14.4)	1.67 (m, CH <sub>2</sub> )	59.92 (d, 4.88)	23.99 (d, $^3J_{\text{CP}}$ 7.33, CH <sub>2</sub> )
			3.91 (dt, OCH <sub>2</sub> )		69.12 (d, $^2J_{\text{CP}}$ 9.77, OCH <sub>2</sub> )
			0.95 (t, CH <sub>3</sub> )		13.54 (s, CH <sub>3</sub> )
5e	-28.26	3.90 (d, $J$ 14.4)	1.20–1.80 (m, CH <sub>2</sub> CH <sub>2</sub> )	60.02 (s)	18.74 (d, $^4J_{\text{CP}}$ 4.88, CH <sub>2</sub> )
			3.60–4.40 (m, OCH <sub>2</sub> )		32.66 (d, $^3J_{\text{CP}}$ 7.32, CH <sub>2</sub> )
			0.96 (t, CH <sub>3</sub> )		67.28 (d, $^2J_{\text{CP}}$ 9.76, OCH <sub>2</sub> )
			1.20–1.80 (m, CH <sub>2</sub> )		14.08 (s, CH <sub>3</sub> )
			2.56–4.36 (m, OCH <sub>2</sub> )		22.64 (s, CH <sub>2</sub> )
					25.35 (s, CH <sub>2</sub> )
					30.60 (d, $^4J_{\text{CP}}$ 7.32, CH <sub>2</sub> )
					31.52 (d, $^3J_{\text{CP}}$ 4.89, CH <sub>2</sub> )
					67.60 (d, $^2J_{\text{CP}}$ 9.77, OCH <sub>2</sub> )

<sup>a</sup>Solvent is CDCl<sub>3</sub>.<sup>b</sup> $^1\text{H}$   $^{31}\text{P}$ , and  $^{13}\text{C}$ - $^{31}\text{P}$  coupling constants (Hz) in parentheses.<sup>c</sup>Satisfactory microanalyses obtained: C,  $\pm$ 0.05%; H,  $\pm$ 0.05%.<sup>d</sup>Ref. [1]: -27 ppm.<sup>e</sup>Ref. [8]: -28 ppm.TABLE 2 The Results and Conditions of the Reaction of 4 with PhSOR<sup>a</sup>

R	Number <sup>b</sup>	Conditions		Contents of Phosphorus Compounds (%)					Yields of 5a–e
		$t$ (°C)	$T$ (hour)	4	5	6	7	8	
Me	A	25	7		80.8	6.8	4.1	2.7	80.8
Et	B	15–20	5.5		53.2	3.7	43.1		53.2
		50–60	6.5		84.6	3.1		6.8	84.6
<i>n</i> -Pr	B	50–60	5.5		94.8	2.1		3.1	94.8
		15	7		48.1	5.6	41.1		48.1
<i>n</i> -Bu	B	50–60	7		68.1	10.1	3.9	10.1	68.1
		20	5.5	66.7	13.6	12.9	6.8		40.8
<i>n</i> -Hex	A	50–60	11	33.7	46.5	10.1	3.2	6.5	70.1
		50	100	35.9	53.4	1.9		2.4	83.3

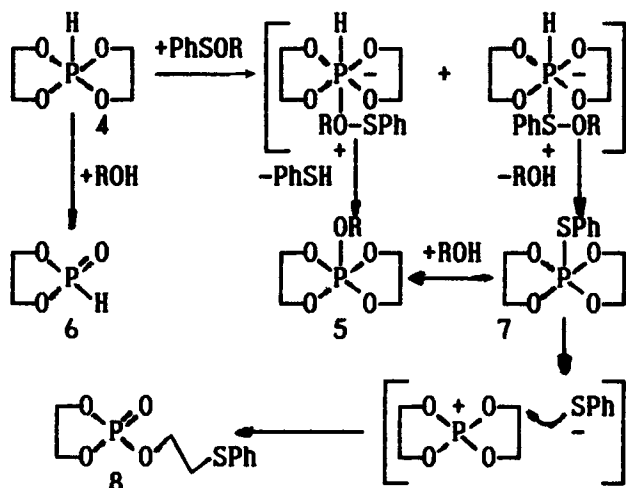
<sup>a</sup>The contents and yields were determined by  $^{31}\text{P}$  NMR spectroscopy.<sup>b</sup>A—representative of a one-step reaction.

B—representative of a two-step reaction.

hydroxide pellets and alcohol (0.11 mol) were added to a 250 mL reaction flask. The mixture was cooled in an ice-salt bath. Benzenesulphenyl chloride was added to the mixture dropwise over 2 hours at -10–0°C with vigorous stirring [5] (0.1 mol). At the end of the addition, the mixture was filtered to remove the precipitated Et<sub>3</sub>N·HCl. The filter cake was washed with two 15 mL portions of ether, the ether was evaporated in vacuo, and the residue was distilled to give the benzenesulphenic esters 3a–e.

3a: yield 60.7%; bp 58–60°C/10 mm Hg,

 $n_{\text{D}}^{25}$  1.5613. (Ref. [6]: bp 50°C/1 mm Hg,  $n_{\text{D}}^{20}$  1.5630.)3b: yield 69.6%. bp. 54–56°C/0.3 mm Hg,  $n_{\text{D}}^{25}$  1.5462. (lit [6]: bp. 76°C/1.5 mm Hg,  $n_{\text{D}}^{20}$  1.5480)3c: yield 47.6%. bp. 82–88°C/1.5 mm Hg,  $n_{\text{D}}^{25}$  1.5393. (lit [6]: bp. 56°C/0.2 mm Hg,  $n_{\text{D}}^{20}$  1.5390)3d: yield 52.2%. bp. 84–88°C/0.8 mm Hg,  $n_{\text{D}}^{25}$  1.5337. (lit [6]: bp. 66°C/0.1 mm Hg,  $n_{\text{D}}^{20}$  1.5330)



SCHEME 1

**3e**: yield 50.5%. bp. 116–120°C/0.8 mm Hg,  $n_D^{25}$  1.5260.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 0.92 (t, 3H,  $\text{CH}_3$ ), 1.16–1.88 (m, 8H,  $\text{CH}_2$ ), 3.84 (t, 2H,  $\text{OCH}_2$ ), 7.24–7.46 (m, 5H,  $\text{C}_6\text{H}_5$ ).

#### Hydridophosphorane/Benzensulphenic Ester Reaction Monitored by $^{31}\text{P}$ NMR Spectroscopy

Benzenesulphenic ester **3** (10 mmol) and spirohydridophosphorane **4** [7] (10 mmol) were added to anhydrous benzene (20 mL). The mixture was stirred at the indicated temperature (Table 2) and occasionally inspected by  $^{31}\text{P}$  NMR spectroscopy. A sealed capillary tube containing trimethyl phosphate was placed in the NMR tube. The pulse delay time was 60 seconds. The  $^{31}\text{P}$  NMR spectra were taken to give compounds **4–8** to trimethyl phosphate ratios, from which amounts of compounds **4–8** were determined. The yields of the products **5a–e** were calculated based on the amount of hydridophosphorane **4** that was consumed in the reaction. The results and yields are given in Table 2.

#### General Procedure for Preparation of Alkoxyphosphoranes **5a–e**

Each of the above reaction mixtures, inspected by  $^{31}\text{P}$  NMR spectroscopy, was concentrated, and then the residue was vacuum distilled to give the desired alkoxyphosphoranes **5a–e**, which would crystallize when cooled.

**5a**: bp 78–82°C/0.03 mm Hg. (Ref. [1]: bp 90–98°C/0.01 mm Hg.)

**5b**: bp 90–94°C/0.01 mm Hg.

**5c**: bp. 92–94°C/0.05 mm Hg.

**5d**: bp. 102–106°C/0.05 mm Hg.

**5e**: bp. 118–121°C/0.05 mm Hg.

#### Preparation of Thiaphosphorane **7**

Spirohydridophosphorane **4** (1.52 g, 10 mmol) and triethylamine (1.01 g, 10 mmol) were added to anhydrous benzene (40 mL). Benzenesulphenic chloride (1.73 g, 12 mmol) in benzene (10 mL) was added to the stirred mixture during 30 minutes at 0–5°C. After having been stirred 5 hour at room temperature, the  $^{31}\text{P}$  NMR spectrum was taken and indicated the formation of compounds **7** ( $\delta_P$  –8.75). The filtrate was concentrated on a rotary evaporator to give a sticky material. Petroleum ether (10 mL) was added to give a white solid. The solid was filtered off and dried in vacuo to yield **7** (1.21 g, 46.5% yield),  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ): –8.48;  $^1\text{H}$  NMR: 7.16–7.44 (m, 2H, *meta*, *para*), 7.44–7.72 (m, 1 H, *ortho*), 3.76–4.08 (m, 8H,  $\text{CH}_2$ );  $^{13}\text{C}$  NMR: 61.10 (d,  $^2J_{\text{PC}}2.44$ ,  $\text{CH}_2$ ), 128.39 (s, *meta*-C, *para*-C), 129.20 (d,  $^2J_{\text{PC}}7.32$ , *ipso*-C), 135.11 (d,  $^3J_{\text{PC}}4.88$ , *ortho*-C).

#### Rearrangement of Compound **7** Monitored by $^{31}\text{P}$ NMR Spectroscopy

Compound **7** (0.52 g, 2 mmol) was added to benzene (4 mL). The mixture was stirred and heated to 50–60°C. After 2 hours, the  $^{31}\text{P}$  NMR spectrum indicated the formation of compound **8** ( $\delta_P$  17.09).

#### Alcoholysis of Compound **7** Monitored by $^{31}\text{P}$ NMR Spectroscopy

Compound **7** (0.52 g, 2 mmol) was added to ethanol (4 mL) and benzene (4 mL). The mixture was stirred and heated to 50–60°C. After 5 hours, the  $^{31}\text{P}$  NMR spectrum indicated the formation of compound **5b** ( $\delta_P$  –28.74).

#### ACKNOWLEDGMENTS

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