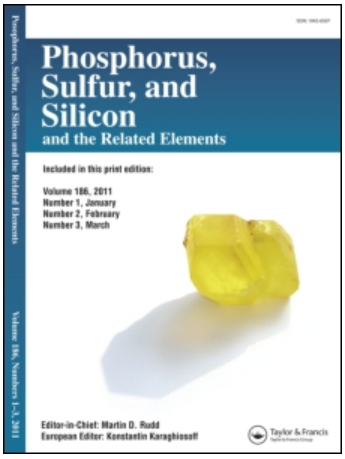

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ALKOXYLATION OF HYDRIDOPHOSPHORANES

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ALKOXYLATION OF HYDRIDOPHOSPHORANES

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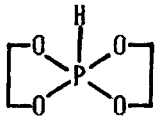
The bicyclic hydridophosphorane **3** reacted with a series of alcohols in the presence of phenyl disulfide to give the corresponding isolable alkoxyphosphoranes. The reactivities of the alcohols in this reaction were seen to be dependent on the steric hindrance of the R groups. The mechanism was suggested in terms of experimental observation.

Key words: Alkoxylation; hydridophosphoranes; scission reaction; phenyl disulfide; alkoxyphosphoranes; steric size.

INTRODUCTION

The reactivities of the hydridophosphoranes have been thoroughly studied.[1] However, the alkoxylation in which hydridophosphoranes react with alcohol in the presence of a hydrogen acceptor to give alkoxyphosphoranes is much less well-understood. The first successful attempts to obtain alkoxyphosphoranes using **1** with alcohols in the presence of enamine were made by Burgada *et al.* in 1976.[2] Bentrude *et al.* recently reported[3] that the alkylthiylation reaction, initiated by UV-light, of hydridophosphorane **2** with alkyl disulfides yielded the corresponding isolable thiaphosphoranes, which then reacted with alcohols to give alkoxyphosphoranes. These results indicated that the P—H bond in hydridophosphoranes could readily undergo a scission reaction.



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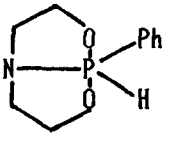

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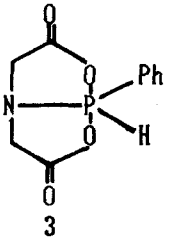

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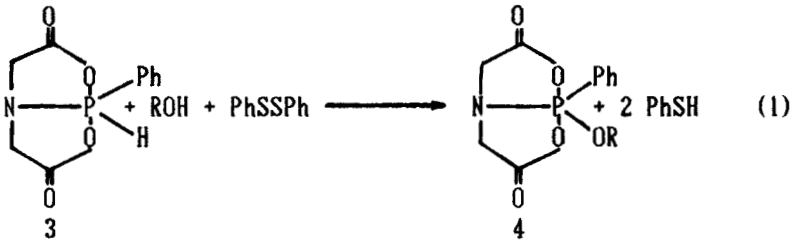
It was the purpose of this work to investigate the one pot reaction of **3** with alcohols in the presence of phenyl disulfide, to see what the effects of phenyl disulfide is this reaction and the scission mechanism of P—H bond could be. It was hoped that the results of this investigation would provide information on the nature of this reaction and also on the properties of the hydridophosphoranes that might result therefrom.

RESULTS AND DISCUSSION

The hydridophosphoranes **3**, can be prepared by the method of Munoz *et al.*,[4] which was improved by us. Unlike compounds **1** and **2**, which readily reacted with phenyl disulfide at room temperature, compound **3** did not react with phenyl disulfide even under reflux in benzene for 24 hr. However, when excess alcohol was added to the benzene solution of **3** and PhSSPh, and the reaction mixture was monitored by ^{31}P NMR, the following reaction sequence was observed.



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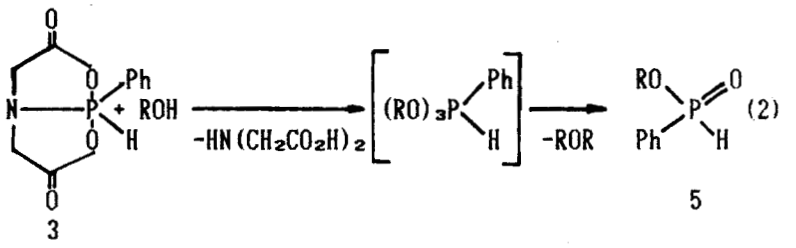
4a R = CH_3; **4b** R = C_2H_5; **4c** R = n-C_3H_7;

4d R = n-C_4H_9; **4e** R = n-C_6H_{13}; **4f** R = i-C_3H_7.

Products **4a–d** were isolated in pure form, as indicated by quantitative elemental analysis and spectroscopic criteria. Compounds **4e** and **4f** were characterized by ^{31}P NMR spectroscopy, but had not been isolated because of their lower content in the reaction mixture. ^{1}H, ^{31}P, ^{13}C NMR data and mass spectrometry are collected in Tables I, II and III.

The major by-products in equation (1) were (RO)PhP(O)H **5**, $(RO)_2PhP(O)$ **6** and iminodiacetic acid, which were determined by NMR data (see Table IV). Their formation was reasonably understood in terms of the reaction sequence (2) and (3):



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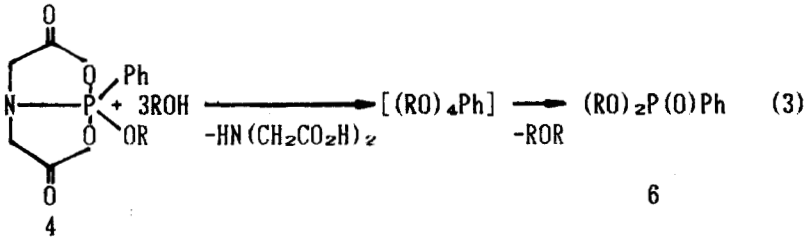

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TABLE I

^1H and ^{31}P NMR data[a,b]

Compd	^1H chemical shifts				^{31}P
	RO	NCH_2	m, p-C_6H_5P	o-C_6H_5P	
4a	3.87(d, J 14.4, CH_3)	3.90(d, J 13.3)	7.34–7.64	7.64–7.84	−40.38
4b	1.33(d of t, CH_3) 4.19(d of q, CH_2)	3.87(d, J 13.3)	7.32–7.62	7.62–7.82	−42.00
4c	0.97(t, CH_3) 1.70(m, CH_2) 4.07(d of t, CH_2O)	3.90(d, J 13.3)	7.32–7.62	7.62–7.82	−41.19
4d	0.93(t, CH_3) 1.10–1.88(m, CH_2CH_2) 4.10(d of t, CH_2O)	3.87(d, J 12.6)	7.32–7.62	7.62–7.82	−41.05
4e[c]					−41.32
4f[c]					−42.41

[a]Solvent is $CDCl_3$.
[b]^1H-^{31}P coupling constants (Hz) in parentheses.
[c]External lock.

TABLE II

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

Compd	m/e (rel intensity)
4a*	225(45, M—CO_2), 197(71, M—CO_2—CO), 173(44), 155(100), 77(34), 42(12)
4b	283(0.2, M^+), 239(44, M—CO_2), 211(42, M—CO_2—CO), 187(27), 159(22), 141(100), 77(42), 42(24)
4c*	253(34, M—CO_2), 225(17, M—CO_2—CO), 201(22), 184(42), 159(50), 141(100), 77(41), 42(35)
4d*	267(37, M—CO_2), 239(6, M—CO_2—CO), 215(22), 184(63), 159(70), 141(100), 77(64), 42(94)

*Molecular ion (m/e **4a** 269, **4c** 297, **4d** 311) not observed.

TABLE III

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

Compd	N—CH_2	C=O	RO	C_6H_5P
4a	47.08(7.33)	166.20(4.88)	57.04(7.33) CH_3	141.28(151.36) ipso 131.74(4.89) para 130.50(12.20) meta 128.61(19.53) ortho
4b	47.07(7.33)	166.32(4.89)	16.29(7.33) CH_3 66.52(9.76) CH_2	131.63(141.60) ipso 131.64 para 130.49(12.21) meta 128.49(19.53) ortho
4c	47.08(7.33)	166.42(4.89)	10.18 CH_3 23.84(9.77) CH_2 72.05(9.76) CH_2O	135.01(156.25) ipso 131.64(4.89) para 130.50(12.20) meta 128.50(19.53) ortho
4d	46.97(7.33)	166.53(4.88)	13.65 CH_3 18.74 CH_2CH_3 32.45(7.33) CH_2 70.32(9.77) CH_2O	135.32(146.48) ipso 131.53(4.88) para 130.29(12.21) meta 128.50(19.53) ortho

[a]Solvent is $CDCl_3$.
[b]^{13}C—^{31}P coupling constants (Hz) in parentheses.

TABLE IV

^{31}P NMR data* of compounds **5** and **6**

R	Me	Et	n-Pr	n-Bu	n-C_6H_{13}	i-Pr	t-Bu
5	28.00	24.63	25.57	24.76	24.90	22.61	17.36
6	21.26	18.17	18.44	18.17	18.57	17.09	14.53
ratio 5/6	1/3.3	1/2.4	1/2.4	1/1.1	1/0.33	1/0.33	1/0.14

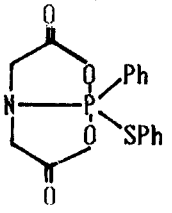
*External lock.

These side reactions were confirmed by reaction of **3** with ethanol as well as **4c** with n-propanol respectively. It is interesting to note that the ratio of **5** to **6** was evidently different with change of R groups. ^{31}P NMR techniques showed that **5** and **6** were formed in the ratio 1:1. 1—3.3, when R was C_{1-4} alkyl. On the contrary, when R is n-C_6H_{13}, i-C_3H_7, the ratio is 1:0.33. The most reasonable explanation for this observation isthat Equations (1), (2) and (3) are the intermolecular competition reactions, which were influenced by the steric size of the R groups.

A more quantitative investigation of Equation (1) has now been conducted. Reaction of **3** with lower alcohols (C_1–C_4) in the presence of phenyl disulfide under reflux in benzene proceeded smoothly and after 8 hr, more than 30% yield of **4a–d** were obtained. n-Hexanol or isopropanol required 20 hr, 50 hr under the same conditions and formed about 5% yield of **4e**, **4f** respectively. In the case of tertiary butanol, the corresponding **5** was obtained, but **4** was not monitored by ^{31}P NMR after 56 hr. These results demonstrated that the reactivities of alcohols with **3** in Equation (1) were seen to be dependent on the steric hindrance of the R groups. The following order of steric effects were observed.

$$CH_3,\ C_2H_5,\ \text{n-}C_3H_7,\ \text{n-}C_4H_9 < \text{n-}C_6H_{13} < \text{i-}C_3H_7 < \text{t-}C_4H_9$$

As noted above, **3** did not react with phenyl disulfide. This means the thiaphosphoranes **7** cannot be present as an intermediate or transition state in Equation



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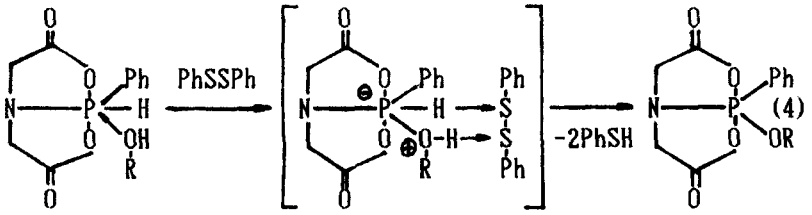
(1). Evidently, this reaction proceeded by a different mechanism, possibly as depicted in sequence (4):



EXPERIMENTAL

^1H, ^{13}C, ^{31}P NMR spectra were run on a JEOL FX-90 Q 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 decoupling. ^{31}P NMR spectra were acquired by using a 90° flip angle and a 2-4 s 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. Melting points were uncorrected.

Preparation of hydridophosphorane **3**. To a stirred solution of iminodiacetic acid (7.8 g, 0.06 mol) in DMF (60 ml) at −35°C was added phenyl phosphinous dichloride (10.8 g, 0.06 mol). The reaction mixture was allowed to stir at −20° ~ −30°C for 40 min, then concentrated below 30°C in vacuum until DMF (50 ml) was removed. Then residue was poured into cooled water (180 ml) to give a sticky solid. The solid was immediately filtered, and washed with cooled water, ether successively, then dissolved in methylene chloride (60 ml). The undissolved material was filtered, the filtrate was dried over magnesium sulfate. The volume of filtrate was reduced by two-thirds. Ether (30 ml) was added resulting in a white solid. The solid was filtered, and washed with ether, then dried in vacuum to yield **3** (6.99 g, 48.7% yield). mp 110–112°C. ^{31}P NMR ($CDCl_3$): −52.50 (−51.4)[4]; ^1H NMR 3.81 (CH_2, d, $^3J_{HP}$ 10.55), 7.81 (P—H, d, $^1J_{HP}$ 767.71), 7.20–7.92 (C_6H_5, m); ^{13}C NMR: 46.48 (CH_2, d, $^2J_{cp}$ 9.76), 128.88 (ortho-C, d, $^2J_{cp}$ 17.09), 131.70 (meta-C, d, $^3J_{cp}$ 12.21), 132.54 (ipso-C, d, $^1J_{cp}$ 126.95), 132.83 (para-C, d, $^4J_{cp}$ 4.90), 167.39 (C═O, s).

Alcoholysis of hydridophosphorane **3**. Hydridophosphorane **3** (0.956 g, 4 mmol) and ethanol (20 ml) were dissolved in benzene (20 ml). The reaction mixture was stirred and heated at reflux for 11 hr. The solid formed was removed by filtration, and determined by NMR spectra to assign iminodiacetic acid. The filtrate was concentrated to yield a sticky material, and ether (10 ml) was added to give a white solid, then filtered. ^1H, ^{31}P NMR showed the solid was unreacted **3**. The ether filtrate was concentrated to give a liquid (0.32 g), which was assigned ethyl phenylphosphinate **5b**. ^{31}P NMR ($CDCl_3$): 24.63; ^1H NMR: 1.54 (t, 3H, CH_3), 4.10 (d of q, 2H, CH_2), 7.31 (d, 1H, P—H, $^1J_{HP}$ 562.81), 7.82 (m, 5H, C_6H_5); ^{13}C NMR: 16.28 (d, $^3J_{cp}$ 7.32, CH_3), 62.03 (d, $^2J_{cp}$ 7.32, CH_2), 128.72 (d, $^2J_{cp}$ 14.64, ortho-C), 130.77 (d, $^3J_{cp}$ 9.76, meta-C), 132.94 (s, para-C), 129.80 (d, $^1J_{cp}$ 131.83, ipso-C).

General procedure for preparation of alkoxyphosphoranes **4a–c**. Hydridophosphoranes **3** (0.72 g, 3 mmol) and phenyl disulfide (0.66 g, 3 mmol) were dissolved in absolute alcohol (15 ml) and benzene (15 ml). The reaction mixture was heated at reflux for 8 hr under stirring, then cooled, and filtered (to remove iminodiacetic acid as by-product). The filtrate was concentrated on a rotary evaporator to give a sticky material. Petroleum (15 ml) was added resulting in the precipitation of white solid. The solid was filtered and dried in vacuum. Recrystallization, from the mixture of benzene and petroleum in ratio 1:5, gave the desired alkoxyphosphoranes.

4a. 33.5% yield, mp 110–112°C. Anal. Calcd. for $C_{11}H_{12}NO_5P$: C, 49.08; H, 4.49; N. 5.20. Found: C, 49.50; H, 4.55; N, 5.34

4b. 31.8% yield, mp 138–140°C. Anal. Calcd. for $C_{12}H_{14}NO_5P$: C, 50.91; H, 4.95; N, 4.95. Found: C, 51.24; H, 5.42; N, 4.69.

4c. 30.3% yield, mp 98–100°C. Anal. Calcd. for $C_{13}H_{16}NO_5P$: C, 52.53; H, 5.43; N, 4.71. Found: C, 52.03; H, 5.40; N, 4.62.

Preparation of n-butoxyphosphorane **4d**. Hydridophosphorane **3** (1.195 g, 5 mmol), phenyl disulfide (1.09 g, 5 mmol), n-butanol (35 ml) and benzene (25 ml) were allowed to stir at reflux for 7.5 hr, then cooled, and filtered. The solvent was stripped off on a rotary evaporator. To the remaining material was added petroleum to separate a pale yellow thick liquid, then washed with petroleum. The liquid was assigned n-butoxyphosphorane **4d** (0.48 g, 30.8% yield). Anal. Calcd. for $C_{14}H_{18}NO_5P$: C, 54.02; H, 5.83; N, 4.50. Found: C, 54.16; H, 5.69; N, 4.22.

Alcoholysis of n-propoxyphosphorane **4c**. n-Propoxyphosphorane **4c** (0.04 g, 0.13 mmol), n-propanol (0.8 ml) and benzene (0.7 ml) were heated at reflux for 10 hr. A ^{31}P NMR spectrum taken after 10 hr showed peaks at 18.30 and −41.86 ppm. The former is assigned dipropyl phenyl phosphonate **5c** in comparison with the standard sample, the latter is unreacted n-propoxyphosphorane **4c**.

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