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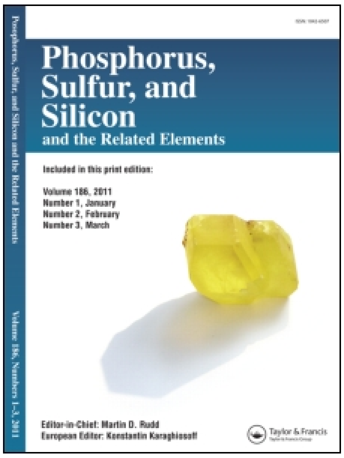

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PREPARATION AND SOME CHEMISTRY OF TETRANEOPENTYLOXYPHENYLPHOSPHORANE AND TETRACYCLOPENTYLOXYPHENYLPHOSPHORANE

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PREPARATION AND SOME CHEMISTRY OF TETRANEOPENTYLOXYPHENYLPHOSPHORANE AND TETRACYCLOPENTYLOXYPHENYLPHOSPHORANE

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The title compounds were prepared by allowing the appropriate dialkylphenylphosphonite to react with neopentyl and cyclopentyl benzenesulfenates. Extensive variable temperature ^{13}C nmr studies on tetraneopentyloxyphenylphosphorane showed no changes. ^{18}O labeled benzoic acid was allowed to react with tetraneopentyloxyphosphorane to give neopentyl benzoate. The isotope study shows that the benzoic acid attacks on the methylene carbon of the neopentyl moiety.

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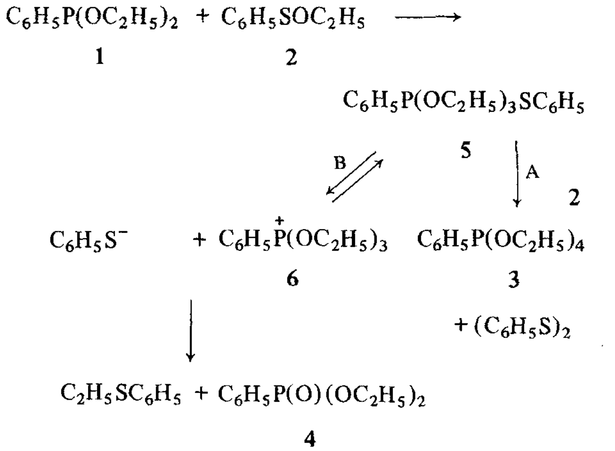
Recently, it was reported that trisubstituted phosphites react with alkyl benzenesulfenates to give pentaalkoxyphosphoranes and diphenyl disulfide.[1,2] The reaction

$$(RO)_3P + 2C_6H_5SOR \longrightarrow (RO)_5P + (C_6H_5S)_2$$

proceeds through the intermediacy of a mixed oxythiophosphorane, $(RO)_4PSC_6H_5$. This material reacts with another mole of alkyl benzenesulfenate to give the phosphorane and diphenyl disulfide. It was also reported that diethoxy phenylphosphonite, **1**, reacts with ethyl benzene-sulfenate, **2**, to give tetraethoxyphenylphosphorane, **3**, 65%, along with diethyl phenylphosphonate, **4**, 35%, this latter material probably arises by dissociation of the intermediate phosphorane, **5**, followed by attack of the thiophenoxide ion on **6** in an Arbusov reaction. Ethyl phenyl sulfide was found to be the other product.



$$\begin{tikzcd}[column sep=small]
\underset{1}{C_6H_5P(OC_2H_5)_2} + \underset{2}{C_6H_5SOC_2H_5} \arrow[r] & {} \\
& \underset{5}{C_6H_5P(OC_2H_5)_3SC_6H_5} \arrow[dl, shift left, "B"'] \arrow[d, "A", "2"'] \\
C_6H_5S^- + \underset{6}{C_6H_5\overset{+}{P}(OC_2H_5)_3} \arrow[ur, shift left] \arrow[d] & \underset{3}{C_6H_5P(OC_2H_5)_4} + (C_6H_5S)_2 \\
\underset{4}{C_2H_5SC_6H_5 + C_6H_5P(O)(OC_2H_5)_2} &
\end{tikzcd}$$

Other reactions of various trivalent phosphorus compounds with alkyl arylsulfenates are under investigation. It is the purpose of these investigations to establish how general the reaction is and to learn more about its mechanism.

Two of these reactants are the two phosphonites, **7** and **8**. They have been prepared by standard procedures and each has been allowed to react with its corresponding alkyl benzenesulfenate, **9** and **10**, respectively. In each case phosphoranes, **11** and **12**, were formed.

$$\begin{array}{lll} C_6H_5P(OR)_2 & + 2C_6H_5SOR \rightarrow & C_6H_5P(OR)_4 \\ \mathbf{7, 8} & \quad \mathbf{9} \text{ and } \mathbf{10} & \mathbf{11} \text{ and } \mathbf{12} \end{array}$$

$$\mathbf{7, 9, 11},\ R = CH_2C(CH_3)_3$$
$$\mathbf{8, 10, 12},\ R = C\text{–}C_5H_9$$

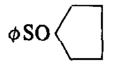
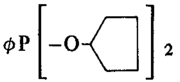
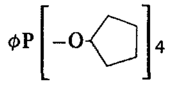
These materials were isolated as crystalline solids. Their ^1H, ^{13}C, and ^{31}P nmr spectral parameters are collected in Table I as are those of the starting materials.

One of the more interesting aspects of phosphorane chemistry is the tendency for these materials to undergo intramolecular permutational isomerization, pseudorotation.[3] The ^{13}C nmr spectra of **11** and **12** conclusively show that the respective carbons of the alkyl groups are equivalent to each other. Extensive low temperature ^{13}C nmr studies of **11** led to no significant changes, and thus it is not possible to comment on just how the equivalency arises.

Recently Westheimer and co-workers[4] have prepared

TABLE I

Nmr Spectra data[a]

Compound	^{1}H nmr α	β	γ	Aromatic	^{13}C nmr α	β	γ	α'	β' or γ		γ'	^{31}P nmr
$\phi SOCH_2C(CH_3)_3$	3.46	0.90		7.23	88.9	32.9	26.3	140.8	123.6	128.8	126.3	
	4.10	1.65[b]		7.0	89.5	33.4	23.6	141.6	123.2	128.8	125.9	
$\phi P(OCH_2C(CH_3)_3)_2$	3.45[b]	0.94		7.50	76.2 (7.2)	32.5 (5.6)	26.5	141.3 (21.3)	128.7 (22.6)	129.9 (14.8)	127.9	+153.5
	4.50	1.50[b]										+150.0
$\phi\overset{\displaystyle O}{\overset{\|}{P}}-(OCH_2C(CH_3)_3)_2$	3.70[b]	0.94		7.50	75.2 (6.6)	32.1 (7.3)	26.1	128.3 (189.5)	131.8 (9.7)	128.4 (14.9)	132.2 (2.9)	+18.0
$\phi P(OCH_2C(CH_3)_3)_4$	3.42 (4)	0.90		7.32	76.4 (11.7)	32.7 (7.9)	27.0	139.0 (227.7)	127.1 (17.3)	129.3 (9.0)	128.1 (3.2)	−60.0
	4.5[b]	i.6[b]		7.30	79.5 (10.9)	36.5 (4.9)	17.0	144.9 (200)	128.8 (10.9)	131.5 (9.4)	129.7 (3.7)	−57.5

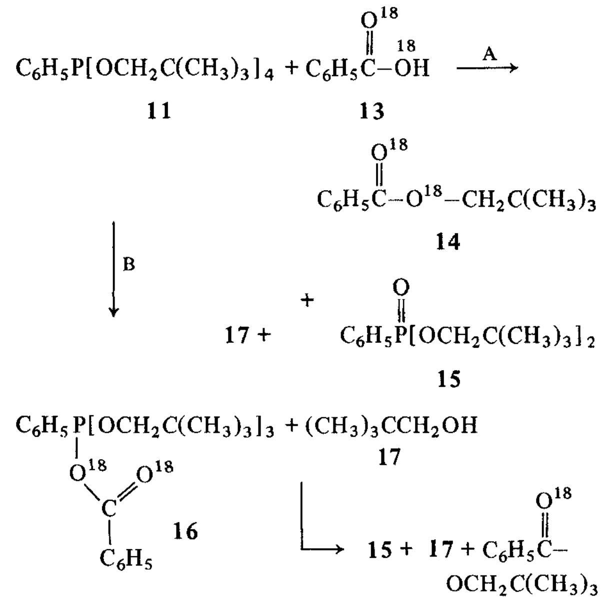
[a] In the ^{1}H spectra all integrated areas are correct to better than 10%. The aromatic hydrogens, in all cases, show complex multiple absorptions. The ^{13}C nmr spectra are fully proton decoupled. The coupling constants, listed in parentheses are J_{HCCH}, J_{HCOP}, J_{COP} and J_{CCOP}. The numbering system is as shown in i. ^{31}P shifts are reported as positive downfield from the standard, 85% phosphoric acid. All nmr spectra were obtained in methylene chloride and TMS is the standard for ^{1}H and ^{13}C spectra.

i

[b] These absorptions appear as multiplets in the ^{1}H nmr.

methyltetrakis(2,6-dimethylphenyl)phosphorane. This material is highly sterically congested. Its variable temperature ^{1}H nmr spectra revealed that there is an intramolecular ligand reorganization that renders the hydrogens of the 2,6-dimethyl groups equivalent. The activation energy for this process was found to be 7.7 kcal/mole. The finding of this very low activation energy for this highly hindered material indicates that the barrier for pseudorotation for **11** must be very small indeed.

One of the fairly general chemical reactions of acyclic oxyphosphoranes is their ability to alkylate acidic materials such as benzoic acid or phenol.[5] In general it appears that the acid attacks on carbon in a nucleophilic displacement reaction, path A. It was found that **11** reacts with benzoic acid to form neopentyl benzoate and the phosphonate, **15**. Because of the known difficulty of effecting S_N2 displacements on neopentyl groups, it seemed worthwhile to consider an alternative mechanism (path B) in which benzoic



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acid exchanged with **11** to give **16** and neopentyl alcohol, **17**. Further reaction could occur by attack on the carbonyl carbon of **16**. Such a pathway would circumvent the need for attack on the highly hindered carbon of the neopentyl group. Reaction of **11** with ^{18}O labeled benzoic acid gave ^{18}O neopentyl benzoate which contained twice as much ^{18}O as did neopentyl benzoate prepared by the sequence: labeled **13** to labeled benzoyl chloride by reaction with thionyl chloride, to labeled neopentyl benzoate by reaction with neopentyl alcohol. These results establish, that within experimental error path A is the correct one. Evidently the driving force for this reaction is provided by the formation of the phosphoryl bond which is potent enough to overcome the hindrance to attack on the neopentyl group.

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EXPERIMENTAL

Melting points were obtained with a Mel temp apparatus. Proton nmr spectra were obtained with a Varian T-60 nmr spectrometer. Phosphorus nmr were obtained with Varian HA-100 and CFT-20 nmr spectrometers. Mass spectra were obtained with a Perkin Elmer Hitachi RMU-7E Mass spectrometer.

Benzenesulphenyl chloride. This material, bp 40°C (0.5 mm) was prepared in 80% yield by a known procedure.[6]

Dineopentyl phenylphosphonite, 7. Neopentyl alcohol, 35.8 g (0.407 mol), triethylamine, 41.1 g (0.407 mol) and 200 ml of diethyl either were placed in a 500 ml three-necked round-bottom flask. The flask was flushed with nitrogen and cooled to 0°C. To the stirred contents of the flask was added dropwise 36.4 g (0.206 mol) of phenylphosphorus dichloride. After 2 hr the ether solution was separated from the precipitated triethylamine hydrochloride by forcing it under nitrogen pressure through a fine filter stick. The product was distilled, bp 90°C (0.15 mm) to give 36 g, 63% yield.

Tetraneopentyloxyphenylphosphorane, 11. Dineopentyl phosphonite, 14.6 g (0.052 mol) and 100 ml of dry *n*-pentane were placed in a 250 ml three-necked flask. The stirred reaction mixture was cooled to −78°C. Neopentyl benzenesulfenate, 20.4 g (0.104 mol) was added dropwise under an atomsphere of nitrogen. After 2 hr the solution was separated from precipitated diphenyl disulfide by forcing it through a fine filter stick under nitrogen pressure. This operation was conducted at −78°; diphenyl disulfide is quite soluble in the reaction mixture at higher temperatures. The *n*-pentane solution at room temperature was washed with three 100-ml portions of propylene carbonate. The *n*-pentane was removed to give a white solid, mp 48–50°C.[7] The mass spectrum had a molecular ion at *m/e* 486.

Dicyclopentyl phenylphosphonite, 8. The procedure was the same as employed in the production of **7**. Phenylphosphorus dichloride was allowed to react with cyclopentanol, 37.1 g (0.432 mol) to yield **8** 46.0 g, 77%, bp 140°C (0.75 mm).

Cyclopentyl benzenesulfenate, 10. The same procedure was used as for the preparation of **9**. Benzenesulfenyl chloride, 53.7 g (0.35 mol) was allowed to react with cyclopentanol, 30.9 g (0.36 mol) to yield 59.5 g, 85% of **10**, bp 90°C (0.35 mm).

Tetracyclopentyloxyphenylphosphorane, 12. Following the procedure used for the preparation of **11**, cyclopentyl phenylsulfenate 48.8 g (0.25 mol) was allowed to react with 35.0 g (0.126 mol) of dicyclopentyl phenylphosphonite to give 40.1 g, 71% of **12**, mp 87–90°C.

Reaction of 11 with ^{18}O enriched benzoic acid. In a 250 ml round bottom flask 1.38 g (0.011 mol) of ^{18}O enriched benzoic acid[8] was dissolved in 50 ml of methylene chloride and to the solution was added, under an atmosphere of nitrogen, **11** 5.0 g (0.011 mol) in 50 ml of methylene chloride. After 10 hr an aliquot was concentrated. The ^{31}P nmr spectrum of this sample indicated that all of the phosphorane had reacted and an absorption was found at −18. This absorption was due to dineopentyl phenylphosphonate, which was prepared independently (see below). The methylene chloride was removed and neopentyl benzoate was separated from dineopentyl phenylphosphonate by glpc using a 2 ft silicone gum rubber column.

Preparation of ^{18}O carbonyl labeled neopentyl benzoate. The ^{18}O labeled benzoic acid was converted into benzoyl chloride by reaction with thionyl chloride. The acid chloride, 10.6 g (0.075 mol), neopentyl alcohol, 7.5 g (0.075 mol), and 6.6 g (0.075 mol) of triethylamine were heated in 150 ml of benzene under reflux for 2 hr. The reaction mixture was filtered to remove triethylamine hydrochloride. The benzene solution was washed with three 100-ml portions of 5% hydrochloric acid, three 100-ml portions of water and three 100-ml portions of saturated aqueous sodium bicarbonate solution. The resulting solution was dried over magnesium sulfate. Distillation afforded 8.2 g, 56% of the ester bp 60°C (0.3 mm). The ^{1}H nmr spectrum of this material showed a singlet at δ 1.03 CH_3 hydrogens, a singlet at δ 4.0 CH_2 hydrogens and multiplets at δ 7.4 and δ 8.1, aromatic hydrogens. Unlabeled neopentyl benzoate was prepared in a similar manner.

Dineopentyl phenylphosphonate. A stirred solution of neopentyl alcohol, 45.3 g (0.51 mol), and triethylamine, 51.8 g (0.51 mol), in 100 ml of diethyl ether was allowed to react at 0°C with phenylphosphonic dichloride, 50.0 g (0.26 mol). After 2 hr, the mixture was filtered and the reaction mixture was washed with four 50-ml portions of water. Distillation afforded 60 g, 78% of the product, bp 160° (3.0 mm). The mass spectrum exhibted a molecular ion, *m/e* 298.

Mass spectrometric analysis of ^{18}O labeled neopentyl benzoates. The ratios of the peak heights of the 192 peak and 194 peak were determined for neopentyl benzoate, normal isotopic abundance, monolabeled and the product of the reaction of the labeled benzoic acid. The % differences were 1.5% in comparing nonlabeled to monolabeled and 2.9% in comparing nonlabeled to the product. The data were obtained from three spectra of each compound.

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