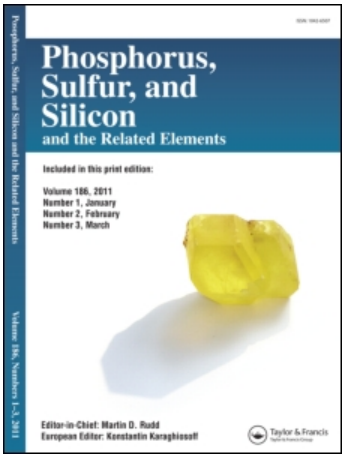

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PREPARATION OF PHOSPHORANES FROM TRIVALENT PHOSPHORUS COMPOUNDS AND 1,2-DIOXANE

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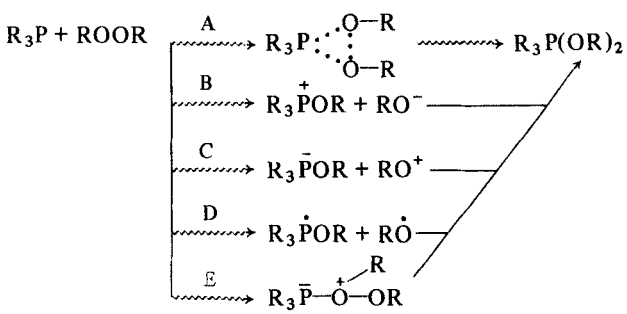
1,2-Dioxane has been allowed to react with a variety of trivalent phosphorus compounds. In some cases penta-coordinate phosphorus compounds were formed, whereas in others tetrahydrofuran and the appropriate phosphoryl containing compound were produced. The mechanism of the reaction is discussed.

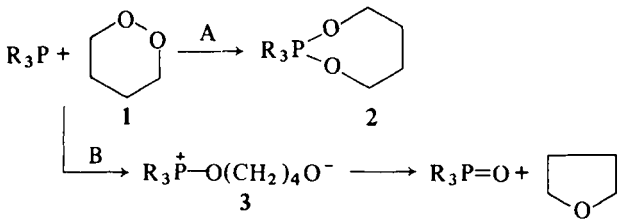
INTRODUCTION

It has been shown that various dialkyl peroxides often react with trivalent phosphorus compounds to give phosphoranes.[1-11] This reaction is of interest because it has been one of the best methods of preparing oxyphosphoranes and because of the intriguing mechanistic possibilities that it presents. Previous work has suggested that the reaction involves biphilic insertion of the trivalent phosphorus compound into the oxygen-oxygen bond of the peroxide to give the phosphorane without the intervention of intermediates, path A.[5,8] It should be recognized that some polarization may arise in the transition state of such a reaction and thus some degree of ionic character is not precluded. Other possible mechanisms are B, C, D, E. Of these four C and D seem extremely unlikely, generation of $R-O^+$ and its subsequent capture without rearrangement or decomposition has *not* been recorded. In the case of D no evidence for the known reactions of RO· has ever been noted in any of these reactions; in fact when mixtures of trivalent phosphorus compounds and peroxides are irradiated, phosphoranes are not formed.[12] Pathway E involves the trivalent phosphorus compound functioning as an electrophile in an initial association followed by product formation via ionization or by an intramolecular rearrangement. Phosphorus trichloride does not react with diethyl peroxide under conditions where more nucelophilic trivalent phosphorus compounds do,[13] and thus a purely electrophilic interaction in the rate determining step is not supported by the data. Ramirez and his co-workers have studied the deoxygenation of pyridine-*N*-oxide by trivalent phosphorus compounds. In this reaction a truly electrophilic rate order was observed i.e. $PCl_3 > C_6H_5PCl_2 > (C_6H_5)_2PCl > (C_2H_5O)_2P > (C_2H_5O)_3P > (C_6H_5)_3P$.[14] Clearly electrophilic attack by trivalent phosphorus compounds has been demonstrated; however it does not seem to dominate in the peroxide reaction. On the other hand path B involves a nucleophilic displacement with the trivalent phosphorus compound functioning as the nucleophile and RO^- as the leaving group. Such a mechanism has long been accepted for the reaction of benzoyl peroxide with trivalent phosphorus compounds.[15] It should be noted that the reactions of dialkyl peroxides proceed in indifferent solvents such as pentane; thus if B is the correct pathway clearly the products would have to be formed as very tight ion pairs. Other evidence which has been provided against path B in nonhydroxylic solvents includes studies of structural variations in the trivalent phosphorus compound which show that the rates of the various reactions do not follow known changes in nucleophilicity. Also it has been shown that large changes in dielectric constant of the medium have only small effects on the rate of the reaction.[16] It should be noted that these results pertain to nonhydoroxylic media. There is some evidence which suggests that in hydroxylic media path B competes with insertion.[17] Such competition is understandable because the forming alkoxide



ion can be stabilized by hydrogen bonding under these conditions.

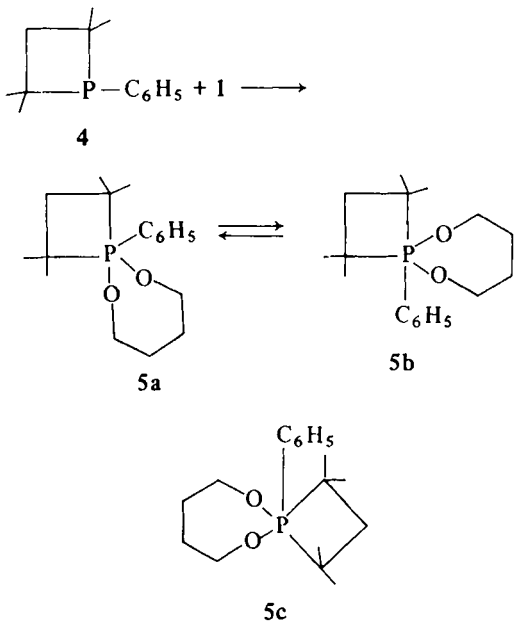
It was of interest to investigate the reactions of 1,2-dioxane, **1**, with trivalent phosphorus compounds. One reason was to determine if phosphoranes were formed and another was to learn something about the potential phosphoranes. It was felt that a study of these reactions would provide some further information concerning the mechanism of the reaction. For example, insertion should lead directly to the phosphorane, **2**, whereas if path B was followed then the zwitterion, **3**, would result. Decomposition of **3**



could lead to **2**, however intramolecular displacement can yield tetrahydrofuran and the appropriate phosphoryl compound. Previous work has shown that alkoxy-containing phosphoranes often react with 1,4-butanediol to give tetrahydrofuran; thus triphenyldiethoxyphosphorane reacts vigorously to give triphenylphosphine oxide and tetrahydrofuran.[18] Formation of tetrahydrofuran does not in itself rule out path A. Compound **2** could be formed and then ionize to **3** which then would decompose. Ionization of dialkoxyphosphoranes has been noted and the process has been found to be solvent dependent.[8] Similar behavior has been found by Ramirez and coworkers with a number of cyclic phosphoranes.[19] With these thoughts in mind a number of trivalent phosphorus compounds have been allowed to react with **1**.

RESULTS AND DISCUSSION

The phosphetane, **4**, was allowed to react with **1** in methylene chloride. A material was formed, *ca.* 95% yield, which showed one absorption in its ^{31}P NMR spectrum at δ + 21 relative to 85% phosphoric acid. The positive absorption relative to phosphoric acid is clearly indicative of the formation of a phosphorane. The ^1H nmr spectrum at room temperature has a doublet at δ 1.22 (J_{PCCH} = 15.5 Hz) which is assignable to the absorptions of hydrogens of four equivalent methyl groups. Complex absorptions are found between δ 0.95-1.95, these are assigned to β-CH_2

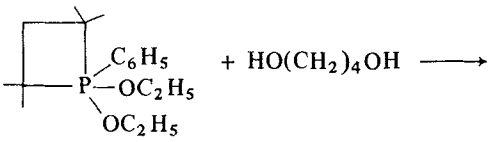


hydrogens on the 4 and 7-membered rings. The postulation of the formation of a phosphorane containing a 7-membered ring is based primarily on the simplicity of the ^1H nmr spectrum. If oligomeric materials had been formed, one might certainly have expected more complicated ^1H nmr spectra than have been found for the various materials which have been assigned phosphorane structures. Absorptions between δ 3.5-3.9 are assigned to the α-CH_2 hydrogens of the 7-membered ring. Absorptions for aromatic hydrogens are found between δ 7.2-7.75. On cooling a broad signal was found at −10° for the absorptions of the hydrogens of the methyl groups. At −43.5° the absorption had split into two doublets of equal intensity at δ 1.05 (J_{PCCH} = 18 Hz) and 1.37 (J_{PCCH} = 14 Hz). The activation energy associated with the process which renders the hydrogens of the methyl groups equivalent is $\Delta G\ddagger$ = 13.5 kcal/mole.

One explanation for the temperature dependent ^1H nmr spectra is that the most stable conformer is **5a** and this is undergoing rapid pseudorotation at −40° so that the two ring carbons exchange positions as do the two oxygens with the phenyl group remaining in an equatorial position of the assumed trigonal bipyramidal, TBP, structure. At higher temperatures the hydrogens of the methyl groups can become equivalent if **5b** is formed as an intermediate or transition state. In **5b** the hydrogens of the methyl groups are not equivalent, however they are allowed to interchange sites and thus they experience the same time-averaged environment. There is another explanation for the

low temperature spectrum: that the molecule favors a tetragonal pyramid, TP, structure, **5c**. If this is the case, then it is easily seen that there are two sets of methyl groups. Recently it has been shown that a number of spirocyclic phosphoranes exist in the crystalline state as TP's or as structures intermediate between TBP's and TP's.[20,21] These observations certainly complicate any explanation of variable temperature NMR data; in fact in many cases, such as **5**, it is not possible to specify the most stable structure in solution on the basis of nmr data.

The fact that **5** was formed supports path A for the mechanism of the reaction. When the phosphorane, **6**, was treated with 1,4-butanediol in an attempt to prepare **5**, only the phosphetane oxide **7** was formed.



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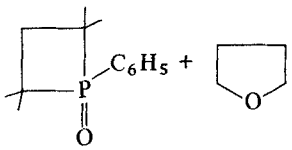

7

In other systems it has been shown that the glycol undergoes monoexchange to give a new phosphorane which decomposes by intramolecular displacement.[18] It would seem that a zwitterion from **4** and **1** should also behave in the same manner; however this negative evidence can be only considered as supportive of path A.

Other phosphines gave phosphine oxides and tetrahydrofuran when they were allowed to react with **1**. These phosphines were tri-*n*-butyl, tri-*o*-tolyl and triphenyl. In the latter case a small absorption was observed at δ 54.5 during the course of the reaction and this may have been due to the formation of a phosphorane. It had been previously shown that tri-*n*-butylphosphine reacts with diethyl peroxide to give an equilibrium mixture of a phosphorane and a phosphonium alkoxide ion pair.[8] It is thus not surprising that a phosphorane was not obtained from tri-*n*-butylphosphine and **1**. Similarly tri-*o*-tolylphosphine does not give a phosphorane when it is allowed to react with diethyl peroxide.[13] Triphenylphosphine and diethyl peroxide react to give a rather stable phosphorane. This material presumably has both ethoxy groups present in apical positions of the TBP structure. The phosphorane from **1** and triphenylphosphine cannot achieve such stabilization and this undoubtedly accounts for its instability.

Methylcatecholphosphite, **8**, and trimethylphosphite, **9**, gave phosphoranes when they were allowed to react with **1**. These materials are reasonably stable. Tri-t-butylphosphite reacted very slowly with **1** and, after three and one half weeks, there was formed a 60% yield of tri-t-butyl phosphate and tetrahydrofuran. Triphenylphosphite reacted with **1** quite slowly to give only a small quantity of triphenyl phosphate. The results from the above reactions are very similar to those observed when the various phosphites were allowed to react with diethyl peroxide.

The results of this study show that a variety of seven membered ring phosphoranes can be prepared from 1,2-dioxane and the data support the biphilic insertion mechanism for the reaction in nonhydroxylic media.

EXPERIMENTAL

1,2-Dioxane was prepared by the method of Criegee[22] in 24–29% yield. ^{1}H nmr spectra were obtained on Varian A-60, T-60 and HA-100 instruments. The ^{31}P nmr spectra were recorded on a Varian HA-100 instrument operating at 40.5 MHz with 85% phosphoric acid as an external reference.

Reaction of the Phosphetane, **4**, *with* **1**. The peroxide, 0.44 g (0.005 mole) in 1 ml of methylene chloride was added to a stirred solution of **4**, 1.03 g (0.005 mole) in 1 ml of methylene chloride at *ca.* −50°C. The reaction mixture was allowed to warm to room temperature over 1 hr and the reaction mixture was then allowed to stand at room temperature for a further 3 hr. The spectral data on the material are reported in the text. An attempt to isolate the phosphorane by distillation at reduced pressure led to decomposition with the production of the phosphetane oxide, **7**.

Attempted Exchange of **6** *with 1,4-Butanediol.* Initially molar quantities of 1,4-butanediol and **6** were mixed neat. Two layers formed which did not become miscible on pumping overnight. Addition of methylene chloride gave a homogeneous solution which was allowed to stand 3 hr. The solvent was removed *in vacuo*. The ^{31}P nmr spectrum of the residue showed only one absorption at −51 ppm which is that of the phosphetane oxide, **7**.

Reaction of **1** *with Methylcatecholphosphite.* 1,2-Dioxane, **1**, 0.88 g (0.01 mole) was added to the phosphite, 1.70 g (0.01 mole) at −20°. The reaction mixture was stirred overnight at room temperature. After 18 hr the ^{1}H nmr spectrum showed 70% reaction. After 2 days the ^{31}P nmr spectrum showed one major absorption at +41 ppm. This absorption corresponded to at least 90% of the phosphorus containing materials. The ^{1}H nmr spectrum showed absorption for aromatic hydrogens, and there was a doublet at δ 3.7 (J_{POCH} = 14 Hz) for the methoxyl group hydrogens of the phosphorane.

Reaction of **1** *with Trimethylphosphite.* Trimethylphosphite, 1.24 g (0.01 mole), freshly distilled from sodium, and 1,2-dioxane, 0.088 g (0.01 mole) were mixed at −10°. The reaction mixture was allowed to warm to room temperature over 1 hr and it was stirred at room temperature for three days. The ^{1}H nmr spectrum showed two absorptions centered at δ 3.45 (J_{POCH} = 11 Hz) one of which was due to unreacted trimethylphosphite, and the other (J_{POCH} = 12 Hz) which was assigned to the methoxyl group hydrogens of the phosphorane. The ^{31}P nmr spectrum after 4 days had an absorption at −141, unreacted trimethylphosphite, 25%, a small amount of phosphate(s) at −5, and phosphorane at +61, 65%.

Reaction of **1** *with Triphenylphosphine.* Triphenylphosphine, 1.31 g (0.05 mole) and 0.44 g (0.05 mole) of **1** were allowed to react at room temperature for 24 hr. At this time there was a 45% yield of triphenylphosphine oxide. The remainder of the phosphorus containing compounds were triphenylphosphine and a material which absorbed at +54.5, not greater than 10%. The formation of tetrahydrofuran was verified by ^{1}H nmr and glpc.

Reaction of Tri-n-butylphosphine with 1,2-Dioxane. Equimolar, 0.01 mole, quantities of the two reactants were mixed with cooling in an ice-water bath. After two hrs there was formed 80% of tributylphosphine oxide, −44.5. Glpc analysis indicated a 76% yield of tetrahydrofuran.

ACKNOWLEDGEMENT

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