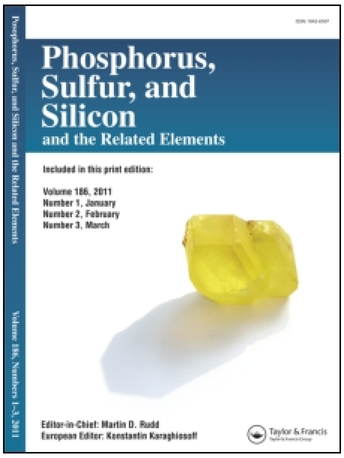

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One Step Synthesis of 1,4-Dialkyl-1,4-Diphospha 2,3,5,6-Tetra - Hydroxycyclohexanes from Primary Alkylphosphines and Glyoxal

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ONE STEP SYNTHESIS OF 1,4-DIALKYL-1,4-DIPHOSPHA 2,3,5,6-TETRA - HYDROXYCYCLOHEXANES FROM PRIMARY ALKYLPHOSPHINES AND GLYOXAL

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Abstract High yields of 1,4-dialkyl 1,4-diphospha 2,3,5,6 tetrahydroxycyclohexanes are produced when equal molar portions of glyoxal are added to primary alkylphosphines. The reactions take place at low temperatures and without the aid of an acid catalyst. The cyclic products are readily converted to the corresponding 1,4 diphosphoryl or dithiophosphoryl derivatives with the addition of a slight excess of H_2O_2 or sulphur. Of particular importance are the order and rates of addition of the two reagents. Reversal of the addition of the reagents results in an entirely different product. This synthesis offers an easy route to 1,4-diphosphacyclohexanes. In addition, the oxides of the lower homologs have utility as flame retardants for polymethymethacrylate and other plastics.

Nucleophilic additions of phosphine(s) to carboxyl functional groups are well known. Phosphine and acetaldehyde or propanaldehyde in the presence of HCl or HBr will form tetrahydroxy ethyl or propyl phosphonium salts (1). A similar reaction with formaldehyde will produce tetrahydroxymethylphosphonium salts (2). If the aldehyde has an alpha branch such as isobutyraldehyde, cyclic 2,4,6-trialkyl-1,3-dioxa-5-phosphacyclohexanes are the main product (3). The initial alpha hydroxy substituted phosphine derived from aromatic aldehydes will under go an oxygen transfer to produce a phosphine oxide (3). These and many other examples are extensively reviewed by K.A. Petrov and V.A. Parshina (4).

S.A. Buckler and V.P. Wystrach have reported the synthesis of spiro cyclic phosphonium salts from the addition of phosphine or alkyl phosphines to dialdehydes such as glutaraldehyde and succinaldehyde (3). Analogous reactions using glyoxal were unsuccessful. Only a low molecular weight polymer was reported from phosphine and glyoxal under similar conditions.

Generally speaking, all of the above reactions require an acid catalyst - usually a strong mineral acid - and heating at some elevated temperature.

This paper discusses the novel synthesis of 1,4-dialkyl-1,4-diphospha 2,3,5,6-tetrahydroxycyclohexanes from the addition of primary phosphines to glyoxal. High yields (80-90%) are obtained in 2-3 hours at 35-60°C without the use of an acid catalyst.

Several homologues were prepared using primary alkylphosphines containing three to eight carbons. The alkyl groups can be straight, branched or cyclic. Commercially available 40% aqueous glyoxal (i) is added in a slight molar excess to the alkylphosphine in a mutually miscible solvent such as isopropanol or THF. The addition takes place over 1-2 hours at 35-60°C. There is very little exotherm and within a short period of time the product begins to precipitate from the reaction mixture.

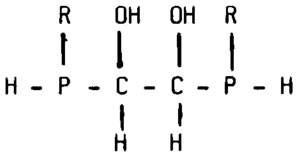
The products all have a characteristic IR band at 970-990 cm^{-1}. They are insoluble in both polar and non polar solvents. The cyclic phosphines are readily converted to the corresponding phosphine oxides or sulphides with the addition of H_2O_2 or S_8 at 50-60°C. The oxides and sulphides are also insoluble. The 970-990 cm^{-1} IR band of the phosphines is replaced by corresponding bands at 1140 cm^{-1} or 590 cm^{-1} respectively.

The four hydroxy groups can be totally silylated to solubilize the products for GC/MS analysis. The mass spectrum of the silylated oxide of the isobutyl homologue (Figure 1) did not indicate a molecular ion with m/e of 616.35 but did have a strong M-CH_3 ion with m/e of 601.35 amu and other ions expected from such a structure. The corresponding phosphine and phosphine sulphide had M-CH_3 ions of 569.35 and 633.35.

The sulphide of the isobutyl homologue was recrystalized from pyridine. Single crystal XRD (Figure 2) confirmed that the product was 1,4-diisobutyl-1,4-dithiophosphoryl-2,3,5,6-tetrahydroxycyclohexane. In addition there were two molecules of pyridine co-ordinated to the 2 and 5 hydroxy groups.

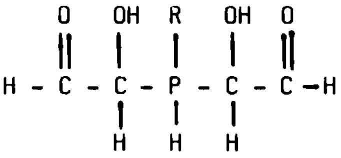
(i) CYANACHEM 40D - American Cyanamid Company

The order of addition of the two reagents is very important. Slow addition of glyoxal to the phosphine produces high yields of the desired crystalline product. On the other hand, addition of the primary phosphine to the glyoxal or simultaneous addition of both reagents produces an exothermic reaction which results in a telemeric solution of phosphine oxides. The conflicting products result from the differing reactivities of the respective intermediates A and B. B undergoes a well known oxygen transfer (3) prior to further reaction while A adds to another mole of glyoxal and cyclizes to form the subject compound.



$\mathrm{H-\overset{R}{P}-\underset{H}{\overset{OH}{C}}-\underset{H}{\overset{OH}{C}}-\overset{R}{P}-H}$

A



$\mathrm{H-\overset{O}{\overset{\|}{C}}-\underset{H}{\overset{OH}{C}}-\underset{H}{\overset{R}{P}}-\underset{H}{\overset{OH}{C}}-\overset{O}{\overset{\|}{C}}-H}$

B

1,4 diphosphacyclohexanes have been reported but these require more laborious techniques (5-7). This straight forward synthesis offers a more direct and easy route. In addition the four hydroxy groups are available for further reactions.

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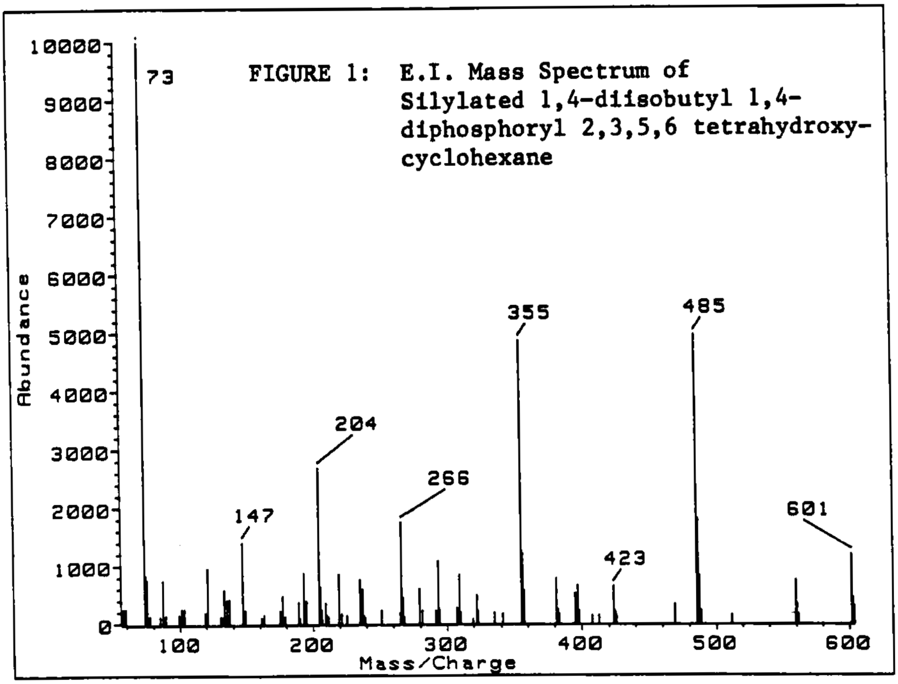

FIGURE 1: E.I. Mass Spectrum of Silylated 1,4-diisobutyl 1,4-diphosphoryl 2,3,5,6 tetrahydroxy-cyclohexane

FIGURE 2: 1,4-diisobutyl 1,4-dithiophosphoryl 2,3,5,6-tetrahydroxycyclohexane . 2 pyr.