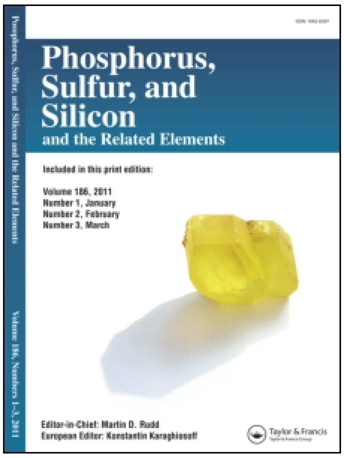

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REACTIONS OF DIPHENYL PHOSPHINE OXIDE WITH DIACETYL AND ETHYL PYRUVATE

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REACTIONS OF DIPHENYL PHOSPHINE OXIDE WITH DIACETYL AND ETHYL PYRUVATE

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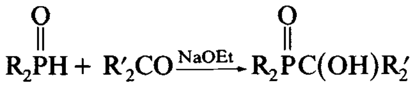
3-Hydroxy-3-diphenyloxophosphino-butanone-2 and 2-hydroxy-2-diphenyloxophosphino-propionic acid ethyl ester were synthesized by reacting diphenyl phosphine oxide with diacetyl or ethyl pyruvate respectively. The reaction of diphenyl phosphine oxide with diacetyl did not lead to an addition to both carbonyls of diacetyl although the reactants ratio utilized was 2 : 1. The structure of the aforementioned compounds was confirmed by elemental analysis, IR and ^{1}H-NMR spectroscopy.

INTRODUCTION

Primary phosphine oxides react with aldehydes by a nucleophilic addition to their carbonyl and form tertiary phosphine oxides.[1-3] These reactions are usually catalyzed by acids.

Secondary phosphine oxides in general undergo addition reactions with carbonyl compounds to give tertiary phosphine oxides in much the same manner as do primary phosphine oxides. Thus a number of α-hydroxy tertiary phosphine oxides have been obtained in good to excellent yields by the neutral or base-catalyzed addition of secondary phosphine oxides to aldehydes and ketones.[4-6]



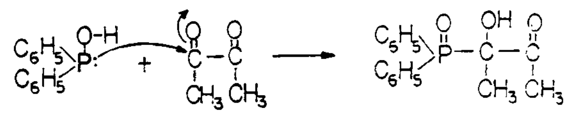
$$R_2\overset{O}{\overset{\|}{P}}H + R'_2CO \xrightarrow{NaOEt} R_2\overset{O}{\overset{\|}{P}}C(OH)R'_2$$

The α-hydroxy tertiary phosphine oxides obtained are thermally unstable. They are pyrolyzed to their starting materials.

In connection with our interest in studying the reactions of phosphorous acid diesters or secondary phosphine oxides with carbonyl compounds, we investigated the reactions of diphenyl phosphine oxide with diacetyl or ethyl pyruvate. (α-Hydroxyalkyl)phosphines obtained by reacting diphenylphosphine with diacetyl or ethyl pyruvate have been previously reported.[7] They can be oxidized to the corresponding α-hydroxy tertiary phosphine oxides.

RESULTS AND DISCUSSION

3-Hydroxy-3-diphenyloxophosphino-butanone-2 was synthesized by reacting diphenyl phosphine oxide with diacetyl. The reaction involves a nucleophilic attack of the phosphorus atom on the carbonyl carbon followed by a proton transfer which stabilizes the adduct:

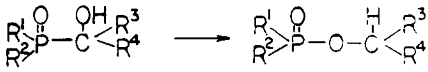


The reaction was carried out at ambient temperature without utilizing a solvent. The reaction product was obtained in nearly quantitative yield. Although the employed mole ratio of the reactants diphenyl phosphine oxide/diacetyl was 2 : 1, the product arising from a nucleophilic addition to both carbonyls was not obtained. In contrast, diphenyl phosphine oxide adds to glyoxal at both carbonyls under same experimental conditions.[8] The carbonyl carbon of diacetyl shows a lower electrophilicity as compared to that of glyoxal due to the presence of the electron-donating methyl group.

The IR spectrum of the reaction product exhibits absorption bands of hydroxyl (3310 cm^{-1}), carbonyl (1730 cm^{-1}), P=O (1195 cm^{-1}) and phenyl (1500, 1453 and 735 cm^{-1}). The absorptions of the OH and P=O groups are lain at lower frequency ranges than those encountered usually due to a hydrogen bonding formed between these groups.

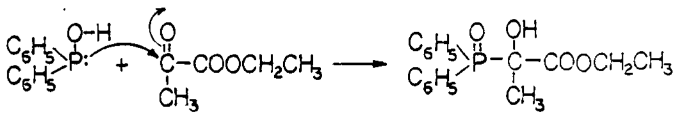
The ^{1}H-NMR spectrum of the reaction product shows a doublet peak at $\delta = 1.65$ assigned to the methyl protons of position 4 ($J_{PCCH} = 14.5$ Hz); singlets at $\delta = 2.53$ and 5.90 assigned to the methyl protons of position 1 and the hydroxyl proton, respectively, and finally a multiplet at $\delta = 7.26$–8.28 associated with the aromatic protons. It can be seen that the deshielding effect of the $(C_6H_5)_2P(O)$ and OH groups on the methyl protons of position 4 is lower than that of the carbonyl group on the methyl protons of position 1. The diphenyloxophosphino group is a moderately strong electron acceptor and possesses an inductive effect comparable to the effects of phenyl and carboalkoxy groups.[9]

It is well known[10–14] that substituted α-hydroxy phosphinyl or oxophosphino compounds can be isomerized to compounds having P—O—C bond:



R^1 and R^2 may be alkyl, aryl, alkoxy or aryloxy groups. The above reaction can be catalyzed by bases or occurs thermally. In the present case the IR and ^{1}H-NMR spectra of the reaction product reveal the presence of hydroxyl group thus indicating that an isomerization has not taken place. Note that the reaction of diacetyl with a phosphorous acid diester leads at first to the formation of the α-hydroxy phosphonate but with strong heating the corresponding phosphate is obtained.[11]

Diphenyl phosphine oxide reacts with ethyl pyruvate at the acetyl carbonyl leading to 2-hydroxy-2-diphenyloxophosphino-propionic acid ethyl ester:



An exotherm reaction was observed when the reagents were mixed. The reaction was completed by moderate heating. Water was the most preferred reaction solvent.

Characteristic absorption bands in the IR spectrum of the reaction product were observed at 3096 cm^{-1} (OH), 1754 cm^{-1} (ester carbonyl), 1253 cm^{-1} (P=O), and 1484, 1450, 735 cm^{-1} (phenyl). The hydroxyl and oxophosphino groups absorb usually at higher frequencies than those observed in the IR spectrum of 2-hydroxy-2-diphenyloxophosphino-propionic acid ethyl ester. This is attributed to a hydrogen bonding between the OH and P=O groups. The ^{1}H-NMR spectrum shows a triplet peak at $\delta = 1.13$ and a quartet at $\delta = 4.18$ assigned to the methyl and methylene protons respectively of the ester group, doublets at $\delta = 1.70$ ($J_{PCCH} = 14$ Hz) and $\delta = 3.90$ ($J_{PCOH} = 6$ Hz) assigned to the methyl protons of position 1 and the hydroxyl proton, respectively, and finally a multiplet at $\delta = 7.33$–8.27 associated with the aromatic protons. Since the IR and ^{1}H-NMR spectra of the reaction product show peaks associated with hydroxyl, an isomerization to the compound having the P—O—C bond did not occur. Note that Birum *et al.* prepared from the reaction of dialkyl phosphite with ethyl pyruvate the corresponding phosphate.[15]

EXPERIMENTAL

The melting points were determined with a Büchi apparatus and are uncorrected. IR spectra were determined in potassium bromide disks using a Perkin-Elmer Infracord Model 137 Spectrometer. ^{1}H-NMR spectra were obtained in deuteriochloroform at 60 MHz on a Varian T-60A spectrometer with tetramethylsilane as an internal standard on saturated solutions at ambient temperature.

3-Hydroxy-3-diphenyloxophosphino-butanone-2. A mixture of diacetyl (1.29 g, 15 mmol), diphenyl phosphine oxide (6.09 g, 30 mmol) and water (15 ml) was placed in a flask. The mixture was stirred at ambient temperature for 1 hour. The product precipitated was removed by filtration (4.0 g, mp 130–133°C, yield 92%). Recrystallizations from acetonitrile gave an analytical sample: mp 132–134°C. Anal. Calcd for $C_{16}H_{17}O_3P$ (288.3): C, 66.66%; H, 5.94%. Found: C, 66.65%; H, 5.76%.

2-Hydroxy-2-diphenyloxophosphino-propionic acid ethyl ester. To a vigorously stirred mixture of ethyl pyruvate (5.81 g, 50 mmol) and water (20 ml) diphenyl phosphine oxide (10.15 g, 50 mmol) was added portionwise. After subsidence of the exothermic reaction the mixture was heated at 90°C for 1 hour. The product precipitated was removed by filtration (13.41 g, mp 122–125°C, yield 84%). Recrystallizations from benzene-diethyl ether (2 : 1 vol/vol) gave an analytical sample having mp 128–130°C. Anal. Calcd for $C_{17}H_{19}O_4P$ (318.3): C, 64.15%; H, 6.01%. Found: C, 64.31%; H, 6.25%.

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