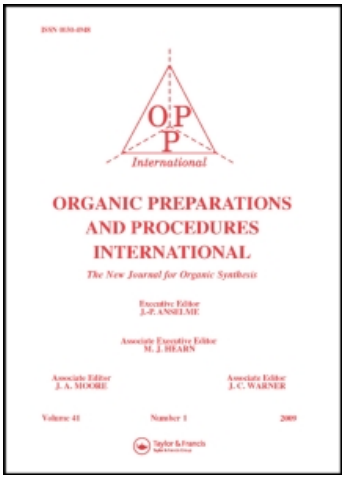

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SYNTHESIS OF PENTACOORDINATE PHOSPHORUS COMPOUNDS BY THE ATHERTON-TODD REACTION

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suspension was centrifuged and the residue, washed with $CHCl_3$ (2 x 1 mL), proved to be unreacted **1** (as its hydrochloride, 84 mg, 36%). ^1H NMR (D_2O): δ 1.87-2.38 (m, 4 H, H-C_3 and H-C_4), 3.20-3.32 (m, 2 H, H-C_5) and 4.27 (t, 1 H, J = 6.7, H-C_2). The combined chloroform supernatants were concentrated *in vacuo* and analyzed, indicating **3** as the sole product. ^1H NMR ($CDCl_3$): δ 1.80-2.46 (m, 4 H, H-C_3 and H-C_4), 3.50 -3.88 (m, 2 H, H-C_5), 4.50 (dd, 0.6 H, J = 3.7 and 8.5, H-C_2 rotamer), 4.62 (dd, 0.4 H, J = 2.8 and 8.5, H-C_2 rotamer) and 9.28 (br s, 1 H, $w_{1/2}$ = 25, CO_2H).

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SYNTHESIS OF PENTACOORDINATE PHOSPHORUS COMPOUNDS BY THE ATHERTON-TODD REACTION

Submitted by (11/13/95)

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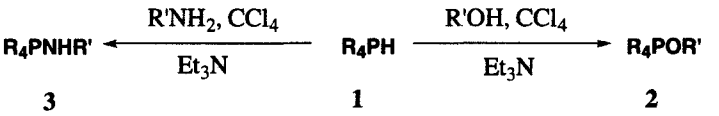
The Atherton-Todd reaction is a synthetically valuable method for the preparation of tetracoordinate phosphorus compounds.[1] The reaction has recently been extended to some hydridophosphoranes by Houalla[2] and by us.[3] It is the purpose of this work to further explore the scope of the reaction using a variety of hydridophosphoranes. The principal advantages of this reaction are that the starting materials are readily obtained, the operation is simple (one-pot reaction) and the reaction proceeds smoothly under mild conditions.

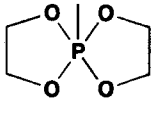
Scheme

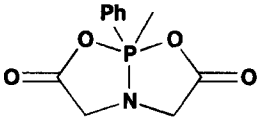


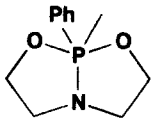
3 **1** **2**

a) R' = n-C_3H_7, R_4P = A
b) R' = i-C_3H_7, R_4P = A

a) R' = CH_3, R_4P = B
b) R' = C_2H_5, R_4P = B
a) R' = n-C_3H_7, R_4P = C
b) R' = n-C_4H_9, R_4P = C

A = 

B = 

C = 

EXPERIMENTAL SECTION

^1H and ^{31}P NMR spectra were taken on a JEOL FX-90 Q spectrometer. ^1H NMR chemical shifts are reported in parts per million relative to internal TMS. ^{31}P NMR chemical shifts are reported in parts per million relative to 85% phosphoric acid (external). ^{31}P NMR spectra were obtained by using full proton decoupling. Quantitative elemental analyses were run on a Yana MT-3 instrument. All manipulations were carried out in a nitrogen atmosphere. Melting points are uncorrected. Hydridophosphoranes **1** were prepared as described (**1A**[4], **1B**[5] and **1C**[6]).

General Procedure for Preparation of Phosphoranes 2 or 3.- To a stirred solution of hydridophosphoranes **1** (20 mmol) in 10 mL acetonitrile or dichloromethane were added tetrachloromethane (40 mmol) triethylamine (60 mmol) and the nucleophilic reagent (40 mmol) at room temperature. The reaction mixture was stirred at ambient temperature for 24 hrs until the ^{31}P NMR signal of hydridophosphorane **1** disappeared, then the mixture was filtered and the filter cake was washed with ethyl ether. The filtrate was concentrated in vacuum at about 60° by use of a rotary evaporator. The residue was mixed with 40 mL ethyl ether and filtered, this being immediately followed by further concentration of the filtrate which was then distilled under reduced pressure or recrystallized from the mixture of benzene and petroleum in ratio 1:5 to give the desired compounds (**3**) or (**2**).

Compound **3a**: Yield 65%: mp. 91-92°. ^1H NMR ($CDCl_3$): δ 0.84 (t. $^3J_{HH}$ 7.2, CH_3), 1.12-1.70 (m. CH_2), 2.40-3.12 (m, $NHCH_2$), 3.82 (d, $^3J_{HP}$, 14.4, OCH_2). ^{31}P NMR ($CDCl_3$): δ -31.36.

Anal. Calcd for $C_7H_{16}NO_4P$: C, 40.19; H, 7.65; N, 6.70. Found: C, 39.90; H, 7.56; N, 6.58

Compound **3b**: Yield 66%; mp. 30-31°. ^1H NMR ($CDCl_3$): δ 1.12(dd, $^3J_{HH}$ 72, $^4J_{HH}$ 2.4. CH_3). 2.28-2.76 (m, CH), 3.38-3.64(m, NH), 3.88 (d, $^3J_{HP}$ 14.4, OCH_2). ^{31}P NMR ($CDCl_3$): δ -32.57.

Anal. Calcd for $C_7H_{16}NO_4P$: C, 40.19; H, 7.65; N, 6.70. Found: C, 39.91; H, 7.44; N, 6.46

Compound **2a**: Yield 54%; mp. 110-111°. ^1H NMR ($CDCl_3$): δ 3.87 (d, $^3J_{HP}$ 14.4, CH_3), 3.90 (d, $^3J_{HP}$ 13.3, NCH_2), 7.34-7.84 (m, C_6H_5). ^{31}P NMR ($CDCl_3$): δ -40.38.

Anal. Calcd. for $C_{11}H_{12}NO_5P$: C, 49.08; H, 4.46; N, 5.20. Found: C, 49.50; H, 4.55; N, 5.34

Compound **2b**: Yield 48%; mp. 138-140°, ^1H NMR ($CDCl_3$): δ 1.33 (dt, $^3J_{HH}$ 7.2, $^4J_{HP}$ 2.1, CH_3), 4.19 (dq, $^3J_{HH}$ 7.2, $^3J_{HP}$ 10, CH_2), 3.87 (d, $^3J_{HP}$ 13.3, NCH_2), 7.32-7.82 (m, C_6H_5). ^{31}P NMR ($CDCl_3$): δ -41.32.

Anal. Calcd for $C_{12}H_{14}NO_5P$: C, 50.88; H, 4.95; N, 4.95. Found: C, 51.24; H, 5.02; N, 4.69

Compound **2c**: Yield 51%; bp. 128-129°/0.05mmHg. ^1H NMR ($CDCl_3$): δ 0.95 (t, $^3J_{HH}$ 7.2, CH_3). 1.511.92 (m, CH_2), 3.73-4.08 (m, CH_2), 3.06-3.33(m, NCH_2), 3.73-4.08 (m, OCH_2), 7.28-7.81 (m, C_6H_5). ^{31}P NMR ($CDCl_3$): δ -38.09.

Anal. Calcd for $C_{13}H_{20}NO_3P$: C, 57.99; H, 7.43; N, 5.20. Found: C, 57.94; H, 7.05; N, 4.98

Compound **2d**: Yield 54%; bp. 133-134°/0.05mmHg ^1H NMR ($CDCl_3$): δ 0.91 (t, $^3J_{HH}$ 7.2, CH_3). 1.20-1.79 (m, CH_2CH_2). 3.73-4.04 (m, CH_2), 3.04-3.31 (m, NCH_2), 3.73-4.04 (m, OCH_2), 7.28-7.78 (m, C_6H_5). ^{31}P NMR ($CDCl_3$): δ -38.69.

Anal. Calcd. for $C_{14}H_{32}NO_3P$: C, 59.36; H, 7.77; N, 4.95. Found: C, 59.08; H, 7.33; N, 4.74

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CONVERSION OF ALCOHOLS TO ALKYL CHLORIDES WITH SILICA CHLORIDE

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The importance of alkyl halides in the formation of carbon-carbon bonds by nucleophilic substitution is well established. A variety of procedures for converting alcohols, the most common precursors of alkyl halides, have been developed.[1] The choice of the appropriate reagent is usually dictated by the sensitivity of the alcohol and other functional groups present in the molecule. The last two decades have witnessed an explosive growth in the use of organosilicon reagents in organic chemistry.[2,3] For example, alcohols can be converted to alkyl iodides with iodotrimethylsilane.[4] However, the reaction of alcohols with chlorotrimethylsilane generates trimethylsilyl ethers and not alkyl chlorides.[4] We now report a simple and efficient method for the conversion of alcohols into chlorides under mild conditions *via* treatment of the alcohols with silica chloride.

This reagent converts primary, secondary, and tertiary alcohols to corresponding alkyl chlorides in high yield. A racemic mixture of the alkyl chloride was obtained from the reaction of an optically pure (+)-2-butanol with silica chloride. A comparison of the present results with those reported earlier,[7,8] clearly indicates that silica chloride is a more effective reagent than thionyl chloride because