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# A Convenient and Direct Route to 1,2-Dichlorovinylphosphine Oxides *via* Copper-catalyzed addition of H-phosphine Oxides to 1,2-Dichloroethyne

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ABSTRACT

**An efficient, convenient and inexpensive CuI-catalyzed method for the synthesis of 1,2-dichlorovinylphosphine oxides from substituted phosphites, diphenylphosphine oxide and 1,2-dichloroethyne has been developed in moderate-good yields, and the reactions provided mainly regioselective *anti* addition products.**

KEYWORDS

**Copper-catalyzed addition reaction, 1,2-dichlorovinylphosphine oxides.**

Alkenylphosphine oxides are an attractive class of compounds useful in organic synthesis. For example, they are used as biological active compounds,[1] are the key intermediates in the preparation of palladium ligands[2] and have been identified as common building blocks in constructing a broad variety of compounds bearing functional groups and phosphorus heterocycles.[3] Nucleophiles of amines,[4] phosphines,[5] carbanion species[6] and 1,3-dipoles[7] readily add to the olefinic bond in alkenylphosphine oxides to give useful bifunctional adducts. 1,2-Dichlorovinylphosphine oxides are one of the most promising alkenylphosphine oxide compounds.[8] As part of our programme to acquire these starting materials for further synthetic elaboration, it is necessary to develop convenient and efficient methodology for the synthesis of 1,2-dichlorovinylphosphonates and 1,2-dichlorovinylphosphine oxides. Several efficient methods for metal-catalyzed synthesis of alkenylphosphine oxides have recently been developed including palladium,[9] nickel,[10] rhodium,[11] ytterbiumimine complex-catalyzed[12] and CuI/ethylenediamine[13] additions of P(O)H compounds to alkynes, but relatively few papers on the synthesis of 1,2-dichloro vinylphosphine oxide derivatives have been reported. There is only Ismailov's report on the synthesis of 1,2-dichlorovinylphosphonates from 1,1-dichloro-2-oxoethylphosphonate and triphenylphosphine.[14] This sparked our interest to further investigate efficient methods for the synthesis of these compounds. Here, we report a more convenient and inexpensive copper-catalyzed method for the synthesis of 1,2-dichlorovinylphosphonates and 1,2-dichlorovinylphosphine oxides.

In our attempts to search for a more convenient procedure to provide 1,2-dichlorovinylphosphine oxides, we first chose diethylphosphate and 1,2-dichloroethyne as the model substrates to optimize the catalysis conditions. The addition reaction of the diethylphosphate to 1,2-dichloroethyne did not proceed using L-proline or cinchonidine as catalyst even at elevated temperature. Addition reaction slowly proceeded when $BF_3 \cdot O(C_2H_5)_2$, $AgNO_3$, and $ZnCl_2$ was used separately as the catalyst to give very poor yield of product after being stirred at room temperature. Dramatically, however, the addition reaction took place readily to afford the adducts using CuI as catalyst in a good yield at room temperature (Scheme 1). Several solvents, namely benzene, ether, DCM and acetonitrile, were also tested in the progress of the reaction. It was found that moderate yields of adduct were obtained when ether was used as the solvent. After optimization of the procedure, other substituted phosphite esters were used in the reaction with 1,2-dichloroethyne in the presence of CuI to afford the corresponding products in moderate yields as shown in Table 1.

The data indicated that the yields depended primarily upon the electronic or steric properties of the P(O)H compounds. The substituted phosphites containing bulky groups could provide higher yield in contrast with ones containing smaller groups. Diphenylphosphine oxide displayed higher reactivity than other substituted phosphites. All addition reactions of P(O)H compounds to 1,2-dichloroethyne showed regioselectivity; the *anti* addition products were mainly obtained with the exception of diphenylphosphine oxide by the regioselective addition of the phosphorus atom at the carbon of the triple bond. The addition of diphenylphosphine to 1,2-dichloroethyne exclusively gave *syn* addition products **4h**, which was confirmed by single crystal structural analysis.[15] This result is possibly from the electronnegativity of aromatic substituent groups compared with aliphatic ones. The structures of all products were confirmed by $^1H$, $^{13}C$, $^{31}P$ NMR spectroscopy.

In conclusion, we have developed an efficient, convenient and inexpensive copper-catalyzed method for the synthesis of 1,2-dichlorovinylphosphine oxides regioselectively in moderately good yields. Further mechanistic investigations, related synthetic applications and extensions are now in progress.

## 1. Experimental

All melting points were determined on a Yanaco apparatus and they are uncorrected. NMR spectra were measured on a Bruker 400 NMR instrument in $CDCl_3$ with TMS as an internal standard for $^1H$ NMR, $^{13}C$ NMR. 85 % $H_3PO_4$ was used as an external standard for $^{31}P$ NMR spectroscopy. IR spectra were determined as KBr pellets on an Avatar 360 FT-IR spectrophotometer. Elemental analysis was carried out with a Yanaco Chncorder MT-3 analyzer.

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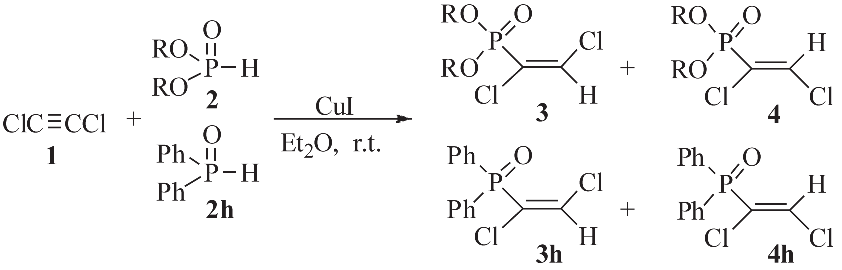


**a**, R= Me; **b**, R= Et; **c,** R= n-Pr; **d**, R= i-Pr;
**e**, R= n-Bu; **f**, R= i-Am; **g**, R= $C_6H_{12}$;

**Scheme 1**
CuI-catalyzed addition of phosphite esters with dichloroacetylene.

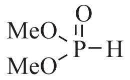
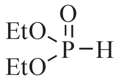
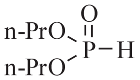
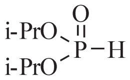
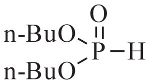
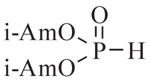
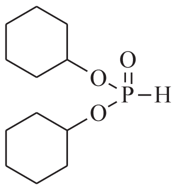
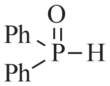
### 1.1 General Procedure

Ether was distilled from sodium. To a stirred solution of 1,2-dichloroethyne (1.88 g, 20 mmol) in anhydrous ether (40 mL), a solution of phosphite ester (12 mmol) or diphenylphosphine oxide (2.23 g, 12 mmol) in ether (10 mL) was added dropwise in the presence of CuI (0.229 g, 1.2 mmol) at room temperature in nitrogen atmosphere for between 4 and 24 hours. After completion of the reaction as indicated by thin-layer chromatography, the mixture was filtered and rinsed with ethyl acetate. The organic layer was washed with brine (3 × 10 mL) and dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The products were purified by flash chromatography on silica gel.

1.1.1. *(E)-dimethyl (1,2-dichlorovinyl)phosphonate* (**3a**)

Yellow viscous oil; IR (KBr)/cm$^{-1}$: ( P=O) 1188, ( P-O-C) 1034, (C=C-H )3065, (C=C)1590; $\delta_H$ (400 MHz, $CDCl_3$): 7.21 (d, 1H, J =

**Table 1** Addition of various substituted phosphites and diphenylphosphine oxide to 1,2-dichloroethyne.[a]

| Entry | **2** | Time /h | Products | Yield /% [b] | Regioselectivity [c] (*anti:syn*) 3:4 |
|---|---|---|---|---|---|
| 1 |  $(MeO)_2P(O)H$ | 4.5 | **3a** | 51 | 90:10 |
| 2 |  $(EtO)_2P(O)H$ | 18 | **3b** | 57 | 61:39 |
| 3 |  $(n\text{-}PrO)_2P(O)H$ | 7 | **3c** | 66 | 60:40 |
| 4 |  $(i\text{-}PrO)_2P(O)H$ | 11 | **3d** | 54 | 70 :30 |
| 5 |  $(n\text{-}BuO)_2P(O)H$ | 4.5 | **3e** | 73 | 84:16 |
| 6 |  $(i\text{-}AmO)_2P(O)H$ | 6 | **3f** | 64 | 70:30 |
| 7 |  | 4.5 | **3g** | 68 | 66:34 |
| 8 |  $Ph_2P(O)H$ | 3 | **4h** | 82 | 0:100 |

[a] Reaction conditions: using CuI as catalyst, $Et_2O$ as solvent.
[b] Isolated yield.
[c] Determined ratio of *anti* to *syn* by $^{31}P$ NMR.

80 Hz, C=CH), 3.74-3.79 (m, 6H, $CH_3$); $\delta_C$ (100 MHz, $CDCl_3$): 130.9, 128.8(d, J = 208 Hz), 125.2 (d, J = 2 Hz), 54.5 (d, J = 6 Hz); $\delta_P$ (162 MHz, $CDCl_3$): 14.94; Found: C, 23.5; H, 3.43 %. Calc. for $C_4H_7Cl_2O_3P$ (204.98); C, 23.4; H, 3.44 %.

### 1.1.2. *(E)-diethyl (1,2-dichlorovinyl)phosphonate* (**3b**)

Yellow viscous oil; IR (KBr)/$cm^{-1}$: (P=O) 1080, (P-O-C) 1019, (C=C-H) 3050, (C=C)1600; $\delta_H$ (400 MHz, $CDCl_3$): 7.20 (d,1H, J = 124 Hz, C=CH), 4.08-4.16 (m,4H, $CH_2$), 1.29-1.33 (m, 6H, $CH_3$); $\delta_C$ (100 MHz, $CDCl_3$): 127.8 (d, J = 11 Hz), 124.8 (d, J = 78 Hz), 63.1, 63.3, 15.2, 15.1; $\delta_P$ (162 MHz, $CDCl_3$): 19.84; Found: C, 30.88; H, 4.67 %. Calc. for $C_6H_{11}C_{l2}O_3P$ (233.03); C, 30.92; H, 4.76 %.

### 1.1.3. *(E)-dipropyl (1,2-dichlorovinyl)phosphonate* (**3c**)

Yellow viscous oil; IR (KBr)/$cm^{-1}$: (P=O) 1160, (P-O-C) 1267, (C=C)1550, (C=C-H) 3060; $\delta_H$ (400 MHz, $CDCl_3$): 7.20,( d, 1H, J = 124 Hz, C=CH), 3.94-4.08 (m,4H, $CH_2$), 1.63-1.69(m, 4H, $CH_2$), 0.88-0.92 (m, 6H, $CH_3$); $\delta_C$ (100 MHz, $CDCl_3$): 138.0(d, J = 28 Hz), 130.4 (d, J = 210 Hz), 68.5, 68.7, 22.6, 22.8, 9.94, 9.97; $\delta_P$ (162 MHz, $CDCl_3$): 22.17; Found: C, 36.81; H, 5.80 %. Calc. for $C_8H_{15}Cl_2O_3P$ (261.08); C, 36.80; H, 5.79 %.

### 1.1.4. *(E)-diisopropyl (1,2-dichlorovinyl)phosphonate* (**3d**)

Yellow viscous oil; IR (KBr)/$cm^{-1}$: (P=O) 1182, (P-O-C) 1096, (C=C)1017, (C=C-H) 3073; $\delta_H$ (400 MHz, $CDCl_3$): 7.29,( d, 1H, J = 120 Hz, C=CH), 4.78-4.80 (m, 2H, CH), 1.35-1.41 (m,12H, $CH_3$); $\delta_C$ (100 MHz, $CDCl_3$): 127.7(d, J = 282 Hz), 123.7, 72.4, 72.7, 22.7, 23.0; $\delta_P$ (162 MHz, $CDCl_3$): 9.03; Anal. Calc. for $C_8H_{15}Cl_2O_3P$ (261.08); C, 36.80; H, 5.79 %. Found: C, 36.79; H, 5.81 %.

### 1.1.5. *(E)-dibutyl(1,2-dichlorovinyl)phosphonate* (**3e**)

Yellow viscous oil; IR (KBr)/$cm^{-1}$: (P=O) 1196, (P-O-C) 1074, (C=C)1021, (C=C-H) 3050; $\delta_H$ (400 MHz, $CDCl_3$): 7.17,( d, 1H, J = 121 Hz, C=CH), 4.00-4.05(m, 4H, $CH_2$), 1.60-1.63(m, 4H, $CH_2$), 1.32-1.33(m, 4H, $CH_2$), 0.83-0.87(m, 6H, $CH_3$); $\delta_C$ (100 MHz, $CDCl_3$): 125.2 (d, J = 280 Hz), 124.1, 67.3(d, J = 19.7 Hz), 67.2, 67.0, 67.1, 31.6, 31.4, 17.9, 12.7; $\delta_P$ (162 MHz, $CDCl_3$): 11.85; Anal. Calc. for $C_{10}H_{19}Cl_2O_3P$ (288.04); C, 41.54; H, 6.62 %. Found: C, 41.35; H, 6.80 %.

### 1.1.6. *(Z)-diethyl (1,2-dichlorovinyl)phosphonate* (**4b**)

Yellow viscous oil; IR (KBr)/$cm^{-1}$: (P=O) 1180, (P-O-C) 1022, (C=C-H) 3060, (C=C)1400; $\delta_H$ (400 MHz, $CDCl_3$): 7.04 (d,1H, J = 168 Hz, C=CH), 4.08-4.16 (m,4H, $CH_2$), 1.28-1.32 (m, 6H, $CH_3$); $\delta_C$ (100 MHz, $CDCl_3$): 130.7, 127.8 (d, J = 210 Hz), 53.1, 53.4, 18.1, 15.1; $\delta_P$ (162 MHz, $CDCl_3$): 20.56; Found: C, 30.88; H, 4.67 %. Calc. for $C_6H_{11}C_{l2}O_3P$ (233.03); C, 30.72; H, 4.77 %.

### 1.1.7. *(Z)-(1,2-Dichlorovinyl)diphenylphosphine oxide* (**4h**)

Colourless solid, m.p. 114.5–116.8 °C; IR (KBr)/$cm^{-1}$: (P=O) 1194, (P-O-C) 1245, (C=C)1580, (C=C-H) 3088; $\delta_H$ (400 MHz, $CDCl_3$): 7.48-7.81 (m,11H, Ar and C=CH ); $\delta_C$ (100 MHz, $CDCl_3$): 133.4 (d, J = 23 Hz), 132.9, 132.9, 132.3, 132.2, 130.1 (d, J = 103 Hz), 129.5 (d, J = 100 Hz), 128.8; $\delta_P$ (162 MHz, CDCl3): 25.61; Found: C, 56.56; H, 3.70 %. Calc. for $C_{14}H_{11}Cl_2OP$(251.28); C, 56.59; H, 3.73 %.

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