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LETTERS TO THE EDITOR

Effective Catalyst for C=X Electrophiles Phosphonylation

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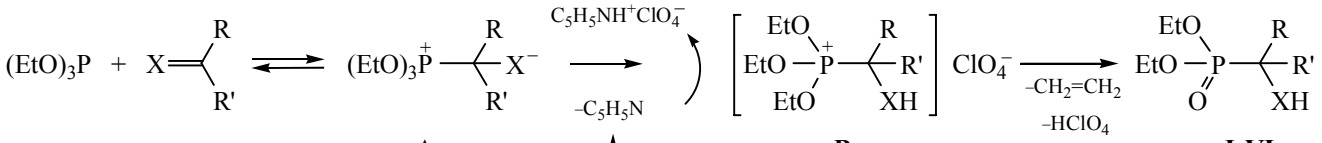
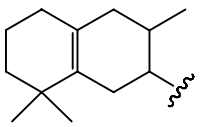
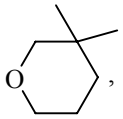
We found that pyridinium perchlorate is extremely active catalyst for phosphonylation of various C=X electrophiles, namely aldehydes, ketones, aldimines, ketimines, isocyanates, and others by trialkylphosphites, to give the corresponding α-substituted phosphonates in high yields. The reaction was carried out solvent-free or in methylene chloride at room temperature or at cooling to 0°C. In the presence of pyridinium perchlorate the reaction of triethylphosphite with C=X electrophiles proceeds vigorously with the heat release. Catalyst is not consumed in the course of the reaction; it can be isolated from the reaction mixture and used repeatedly without noticeable loss of catalytic activity. Catalytic action of pyridinium perchlorate is explained by the scheme below. Probably, the reaction of triethylphosphite with C=X electrophiles results in unstable betaine **A**, which reacts with pyridinium perchlorate to form alkoxyphosphonium perchlorate **B** and pyridine (cf. [1]). The unstable salt **B** is decomposed affording phosphonates **I–VI**, ethylene and perchloric acid, which reacts with pyridine to regenerate pyridinium perchlorate.



R =  , R' = H, X = O (**I**); R = 3-$CF_3C_6H_4$, R' = Me, X = O (**II**); RR'C =  , X = O (**III**);

R = Ph, R' = H, X = $PhCH_2N$ (**IV**); RR'C = *cis*-C_6H_{10}. X = PhN (**V**); RR'C = CO, X = PrNH (**VI**).

Pyridinium perchlorate can be readily prepared by the reaction of pyridine with perchloric acid in water, from which it is isolated as crystals. It is ready for use after careful drying. The most significant advantages of the offered catalyst are the availability, high products yields and mild reaction conditions. Below we describe some examples of synthesis of α-substituted phosphonates **I–VI** using pyridinium perchlorate.

Diethyl hydroxy(3,8,8-trimethyl-1,2,3,4,5,6,7,8-octahydro-2-naphthyl)methylphosphonate (I). To a mixture of aldehyde (10 mmol), triethylphosphite (10 mmol), and 3 ml of dichloromethane was gradually added 8 mmol of pyridinium perchlorate at cooling to 0°C under stirring. The mixture was stirred for 30–60 min at 0°C and 60–90 min at room temperature. Catalyst (8 mmol) was filtered off and washed with diethyl ether. After solvent removal the residue was

distilled in a vacuum and recrystallized from hexane. Yield 80%, bp 190°C (0.1 mm Hg), mp 107–110°C (hexane). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.96 d (3H, CH_3C, *J* 6); 0.97 s (6H, CH_3); 1.34 t (6H, CH_3CH_2O, *J* 7); 1.43 m (2H, CH_2); 1.6 m (4H, CH_2); 1.8 m (2H, CH_2); 1.9 m (1H, CH); 2.0 m (1H, CH); 2.19 m (2H, CH_2); 2.91 br (1H, OH); 4.2 m (5H, CH_2O + PCH). ^{31}P NMR spectrum ($CDCl_3$), δ, ppm: δ_P 25.63. Found, %: C 62.61; H 9.68; P 9.14. $C_{18}H_{33}O_4P$. Calculated, %: C 62.77; H 9.66; P 8.99.

Diethyl 1-hydroxy-1-(3-trifluoromethylphenyl)-ethylphosphonate (II) was prepared similarly. Reaction proceeds for 6 h at room temperature. Yield 80%, mp 125–128°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.24 t (6H, CH_3, *J* 7); 1.83 d (3H, CH_3CP, *J* 15.6); 4.04 m (2H, OCH_2); 4.12 m (2H, OCH_2); 4.66 br (1H, NH); 7.44–7.9 m (4H, C_6H_4). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 16.17 (CH_3); 26.33 (CH_3); 63.5 d (OCH_2, *J* 94); 73.5 d (PC, *J* 161); 127 q (CF_3, *J* 271); 123.1, 123.88, 128.16, 130.01, 130.27, 143.00 (C_6H_4). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 57.67. ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 25.3. Found, %: C 47.86; H 5.56; P 9.49. $C_{13}H_{18}F_3O_4P$. Calculated, %: C 47.82; H 5.51; P 9.55.

Diethyl 4-hydroxy(tetrahydro-2,2-dimethyl-2*H*-pyran-4-yl)phosphonate (III) was prepared similarly. Yield 80%, bp 130–135°C (0.08 mm Hg), mp 72–75°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.19 s [3H, $(CH_3)_2C$]; 1,43 s [3H, $(CH_3)_2C$]; 1.64–19 m (4H, CH_2); 3.65 m (2H CH_2O); 3.95 br (1H, OH); 3.65 m (1H, CH_2); 4.05 m (1H, CH_2); 4.15 d.q (4H, CH_3CH_2O, *J* 7, *J* 8). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 16.45 (CH_3CH_2); 24.29 (CH_2); 31.09 (CH_3); 32.61 (CH_3); 39.87 (CH_2); 56.1 d ($PCCH_2$, *J* 12.5); 62.8 d (OCH_2, *J* 8.5); 63.0 d (CH_2, *J* 7.5); 70 d (PC, *J* 183.5); 70.57 (CMe_2). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 23.6. Found, %: P 11.66. $C_{11}H_{23}O_5P$. Calculated, %: P 11.63.

Dimethyl phenyl[1-methyl[(benzyl)amino]methyl-phosphonate (IV) was prepared similarly. Yield 70%, mp 60°C. ^{1}H NMR spectrum ($CDCl_3$), δ, (*J*, Hz): 1.4 d (3H, CH_3, *J* 7); 3.51 m (1H, NH); 3.79 d (3H, *J* 11.8, CH_3); 3.83 d (3H, CH_3, *J* 10.1); 5.2 d (1H, PCH, *J* 24); 6.8–7.28 m (5H, C_6H_5); 7.3 d (2H, *J* 8.5); 7.5 d (2H, C_6H_5, *J* 8.5). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 16 d (CH_3); 56.1 d (OCH_3, $^2J_{PC}$ 7.0), 56.2 d (OCH_3, $^2J_{PC}$ 6.8); 57.2 d (CH, $^1J_{PC}$ 150); 114.3 (CH); 120.0 (CH); 128.2 d (CH, $^3J_{PC}$ 5.8); 128.4 d (CH, $^3J_{PC}$ 3.1); 130.1 (CH); 131.2, 140.0, 146.6 d (CH, $^2J_{PC}$ 14.5). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 24, that corresponds to the reported earlier compound [2].

Diethyl 1-anilinocyclohexylphosphonate (V) was obtained similarly. Reaction proceeds for 12 h at 40°C. Yield 60%, mp 100°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.07 t (6H, OCH_2Me, J_{HH} 7.0); 1.33–1.46 m (C_6H_4); 1.59–2.10 m (4H, CH_2); 3.86–3.93 m (4H, OCH_2CH_3); 5.38 br (1H, NH); 6.63 t (1H, ArH, *J* 7.1); 6.86 d (2H, ArH, *J* 8.1); 6.99 t (2H, ArH, *J* 8.1). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 31. Found, %: N 4.56; P 9.85. $C_{16}H_{26}NO_3P$. Calculated, %: N 4.50; P 9.95 [3].

Diethyl (propylamino)carbonylphosphonate (VI) was prepared similarly. Yield 90%, bp 100-110°C (0.08 mm Hg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.87 t (3H, CH_3, *J* 7.5); 1.3 t (6H, CH_3CH_2O, *J* 7); 1.51 m (2H, $CH_3CH_2CH_2$); 3.2 q (4H, NCH_2, *J* 7); 4.15 m (4H, CH_2O): 7.34 br (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm (*J,* Hz): 11.2 d (*C*CC, *J* 8); 16.15 d (CH_3CO, *J* 15); 22.6 (C*C*CN); 40.98 (CN), 64.15 d (OC, *J* 8); 165 d (PC, J_{PC} 221). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 0.71. Found, %: N 6.15; P 13.92. $C_8H_{18}NO_4P$. Calculated, %: N 6.28; P 13.88.

NMR spectra were recorded on a Varian-300 instrument, reference TMS (^{1}H and ^{13}C) and 85% H_3PO_4 in D_2O (^{31}P).

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