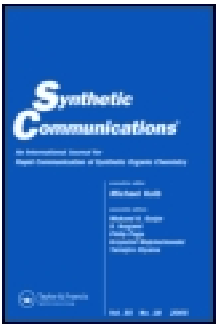

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Synthesis of Aryl Phosphonates by Reaction of Grignard Reagents with Diethyl Cyanophosphonate

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Synthesis of Aryl Phosphonates by Reaction of Grignard Reagents with Diethyl Cyanophosphonate

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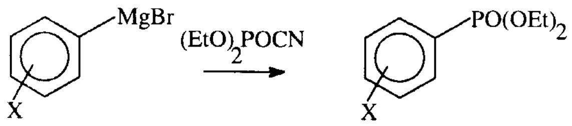
Abstract: Reaction of Grignard reagents with diethyl cyanophosponate gave aryl phosphonates under mild conditions and in good yield

The Arbuzov reaction is a facile procedure for the formation of carbon-phosphorus bonds[1], however, is not applicable to the formation of sp^2 hybridized carbon-phosphorus bonds. The synthesis of aryl phosphonates as precursors of phosphorous heterocycles or phosphorus analogs of heterocyclic compounds[2-4], is of considerable interest. A number of methods have been described for the synthesis of aryl phosphonates . For example , the esterification of arylphosphonic dichlorides with alcohols[5] or the decarbonylation of arylketophosphonates[6]. Coupling methods as the nickel(II) catalyzed reaction of aryl halides with trialkyl phosphites[7] , and the photostimulated condensation of aryl iodides with phosphites[8] or with phosphite salts[9]. Alternative methods also described are the palladium catalyzed reaction of aryl halides[10] and aryl polyfluoroalkanesulfonates[11] with O,O-dialkyl phosphites or the cooper (I) iodide promoted arylation of phosphite anions with aryl iodides[12]. Aryl phosphonates also have been prepared by electrochemical oxidation of silylphosphites[13] or trialkyl phosphites[14] in the presence of aromatic compounds. However, all of these methods have certain disadvantages, such as the use of excess of phosphites, harsh reaction conditions, or low yield.

As part of our investigation on synthetic applications of diethyl cyanophosphonate, we have investigated the reaction with Grignard reagents. In this communication we report a convenient synthesis of arenephosphonates by the reaction of diferent Grignard reagents with diethyl cyanophosphonate. The present method has the advantages of easy availability of starting materials, mild reactions conditions, simple workups and good yields.

We have found that the reaction of 10 equivalents of diethyl cyanophosphonate with 15 equivalents of the corresponding arylmagnesium bromide (THF solution) at 0° C in methylene chloride solution was complete within less than 30 minutes, (Eq.), affording the correspondent phosphonates in satisfactory yields (Table).



The reaction is compatible with different functional groups (Entry 3,4,8) and the yields range from 53 to 95%. The products were characterized by ^{1}H, ^{13}C NMR and H.R. MS spectroscopies.

EXPERIMENTAL

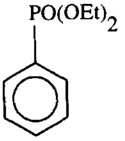
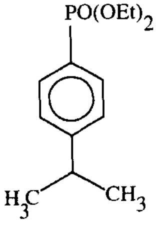
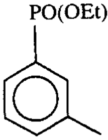
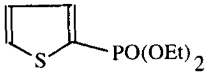
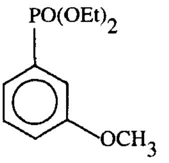
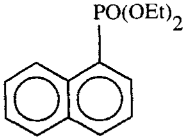
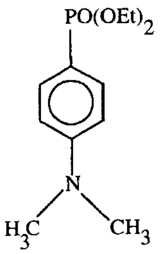
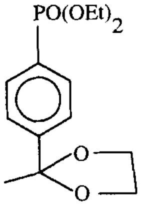
IR spectra were recorded on a Nicolet Magna 750 spectrometer. NMR spectra were determinated in $CDCl_3$ solution with a Varian Gemini 200 using tetramethylsilane as an internal standard. Mass and high resolution mass spectra were determinated on a Jeol-SX 102A instrument, using PEG as internal reference for FAB technique.

General Procedure

A representative experimental procedure (entry 1 in table): To a solution of 1.63g (10 mmol) of diethyl cyanophosphonate in 20 mL of methylene chloride, cooled to 0^{0}C, 24.1 ml, (20mmol) of a 0.83N solution of phenylmagnesium bromide were added under argon. After being stirred for 30 min, the reaction was poured in 20 ml of aqueous saturated solution of oxalic acid, filtered through celite and the filtrated extracted with methylene chloride (3X20), the organic extracts were dried over sodium sulfate and concentrated in vacuum. The residue was purified by silica gel flash chromatography to give diethyl phenyl phosphonate1 (2.1 g, 92%) oil; bp, 100-101/0.3; ^{1}H-NMR ($CDCl_3$) δ 1.32 (t, 6H), 4.12 (m, 4H), 7.46 (m, 2H) 7.55 (m, 1H), (m, 2H); H.R. MS calc. For $C_{10}H_{15}O_3P$: 214.0837. Found: 214.0844

2: Oil (Lit[16]). IR (neat) 2985, 1394, 1248, 1025, 967 cm^{-1} . ^{1}H-NMR δ_{ppm} ($CDCl_3$) : 7.63 (1H, m), 7.61 (1H, m), 7.35 (2H, m), 4.19 (4H, m), 2.40 (3H, s), 1.32 (6H, dt,). HRMS (FAB): calcd for $C_{11}H_{17}O_3P$ 228.0915; found: 228.0907

TABLE

Entry	Phosphonate	Yield %	Entry	Phosphonate	Yield %
1		81[15]	**5**		90[15]
2		93[16]	**6**		90[18]
3		73[17]	**7**		80[19]
4		95[20]	**8**		53

3: Oil (Lit[17]). IR (neat) 2984, 1253, 1025, 966 cm^{-1}. ^{1}H-NMR δ_{ppm} (CDCl$_3$): 7.36 (1H, m), 7.35 (1H, m), 7.32 (1H,m), 7.06 1H, m), 4.09 (4H, m), 3.89 (3H,m), 1.3 (6H, t). HRMS (FAB) calcd for $C_{11}H_{17}O_4P$ 244.0864, found 244.0865.

4:Oil (Lit[20]). IR (neat) 2984, 1603, 1237, 1025, 961 cm^{-1}. ^{1}H-NMR δ_{ppm} (CDCl$_3$) : 7.64 (2H, dd), 6.70 (2H, dd), 4.05 (4H, m), 3.02 (6H, s), 1.3 (6H, t). HRMS (FAB): calcd. for $C_{12}H_{21}NO_3P$ 258.1259, found 258.1251.

5:Oil (Lit[15]). IR (neat) 2964, 1249, 1024, 964 cm^{-1}. ^{1}H-NMR δ_{ppm} (CDCl$_3$) : 7.5 (2H, m), 7.27 (2H, m), 4.05 (4H, m), 2.91 (1H,hep), 1.22 (6H, d). HRMS (FAB): calcd for $C_{13}H_{22}O_3P$ 257.1307, found 257.1302.

6: Oil (Lit[18]). IR (neat) 3074, 2983, 1409, 1255, 1024, 970 cm^{-1}. ^{1}H-NMR δ_{ppm} ($CDCl_3$) : 7.70 (1H, dd, $J_{2\text{-}3}=5.1$, $J_{2\text{-}4}=1.2$, $J_{3\text{-}4}=3.3$), 7.66 (1H, ddd, $J_{P\text{-}H4}=8.4$, $J_{3\text{-}4}=3.3$, $J_{2\text{-}4}=1.2$), 7.18 (1H, ddd), 4.13 (4H, m), 1.34 (6H, t). HRMS (FAB) calcd for $C_8H_{13}O_3PS$ 220.0323, found 220.0321.

7: Oil (Lit[19]). IR (neat) 3059, 2983, 1392, 1249, 1024, 966 cm^{-1}. ^{1}H-NMR δ_{ppm} ($CDCl_3$): 8.25 (1H, ddd), 8.3 (1H, d), 8.048 (1H,bd), 7.89 (1H, bd), 7.61 (1H, bd), 7.54 (1H, m) , 4.19 (2H, m), 4.09 (2H, m), 1.30 (6H, dt) . HRMS (FAB) calcd for $C_{14}H_{17}O_3P$ 264.0915; found: 264.0909.

8: Oil; IR (neat) 2989, 1251, 1031, 972 cm^{-1}. ^{1}H-NMR δppm ($CDCl_3$): 7.72 (2H, m), 7.51 (2H, m), 4.07 (4H, m), 3.98 (2H, m), 3.69 (2H, m), 1.58 (3H, s), 1.26 (6H, t). HRMS (FAB): calcd for $C_{14}H_{22}O_5P$ 301.1205, found 301.1207.

References and Notes

(1) Worms, K.H.; Schmidt-Dunker, M.In *Organic Phosphorus Compounds*, Vol. 7; Kosolapoff, G.M. ;: Maier, L., Ed.; John Wiley &, Sons New York, **1976**; p 1

(2) Balthazor, T.M. *J. Org. Chem.*, **1978**, 43, 4538.

(3) Balthazor, T.M. *J. Org. Chem.*, **1980**, 45, 2519.

(4) Balthazor, T.M. *The Heterocyclic Chemistry of Phosporus*, John Wiley & Sons, New York, **1981.**

(5) Siddall, T.H.; Prohaska, C.A. *J. Am. Chem Soc.*, **1962**, 84, 3467.

(6) Nakazawa, H.; Matsuoka, Y.; Yamaguchi, H.; Kuroiwa, T.; Miyoshi, K.; Yoneda, H. *Organometallics*, **1989**, 8, 2272.

(7) Tavs, P. *Chem. Ber.*, **1970**, 103, 2428.

(8) Obrycki, R.; Griffin C.E. *J. Org. Chem.*, **1968**, 33, 632.

(9) Bunnett, J.F.; Weisis, R.H. *Org. Syn.*,Coll. Vol. 6, , 451, **1988.**

(10) Hirao, T.; Masunaga, T.; Yamada, N.; Ohshiro, Y.; Agawa, T. *Bull Chem. Soc. Jpn.*, **1982**, 55, 909.

(11) Lu, X.; Zhu, J. *Synthesis,* **1987,** 726.

(12) Osuka, A.; Ohmasa, N.; Yoshida, Y.; Suzuki, H. *Synthesis,* **1983**, 69.

(13) Nikitin, E.V., Ignatev, Yu. A.; Malaev, V.G.;Romakhin, A.S.; Parakin, O.V.; Podovik, A.N. *Zh. Obshch. Khim.*, **1983**, 53, 233.

(14) Kargin, Yu.M.; Nikitin, E.V.; Parakin, O.V.; Romanov, G.V.; Podokiv, A.N. *Phosphorus Sulfur*, **1980**, 8, 55.

(15) Yuan, Ch., Feng, H. *Synthesis,* **1990**, 140.

(16) Allen, W. D.,Hutley, B.G., Mellor, M.T.J. *J. Chem. Soc. Perkin II*, **1977**, 789.

(17) Effenberg, F, Kottman, H. *Tetrahedron,* **1985**, 41, 4171.

(18) Allen, D.W., Hutley, B.G., Mellor, M.T.J., *J. Chem. Soc. Perkin II,* **1972**, 63

(19) Yasuda, M., Yamashita,T., Shima, K. *Bull. Chem. Soc. Jpn.*, **1990**, 63, 938.

(20) Yuan, Ch., Yeh, H., Ko, M., Chou, L. *Chem. Abstr.*,**1965**, 62, 8958d.

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