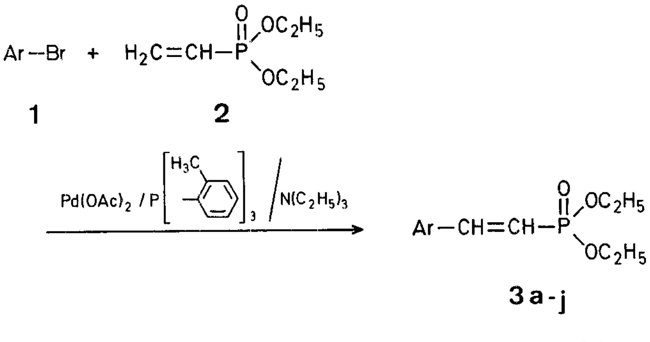
A Facile Synthesis of Diethyl 2-Arylethenephosphonates

YUANYAO XU*, XIAOLI JIN, GUOHUA HUANG, YAOZENG HUANG

Shanghai Institute of Organic Chemistry, Academia Sinica, 345 Lingling Lu, Shanghai, Peoples' Republic of China

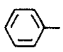
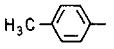
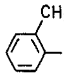
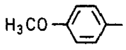
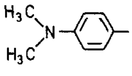
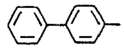
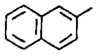
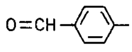
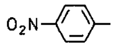
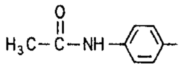
For the preparation of 2-arylethenephosphonates, only few synthetic methods are known. The reaction of an ethenephosphonate with aryldiazonium salts and subsequent dehydrohalogenation of the resulting 1-chloro-2-arylalkanephosphonates has the disadvantage that it involves two steps and the overall yield is quite low[1]. The nickel-catalyzed Arbusov reaction[2] and palladium-catalyzed phosphonylation[3] require vinyl halides as starting material and some of these are not easily available. Recently, Koizumi et al.[4] reported a synthetic method for 2-arylethenephosphonates based on the benzylation of the lithio derivative of phenylsulfenylmethanephosphonate and subsequent oxidative desulfurization, but it apparently suffers the limitation that functional groups which are vulnerable to the organolithium reagent may not be present.

We now report another method of preparing 2-arylethenephosphonates **3a–j**, i.e. the palladium-catalyzed arylation[5] of diethyl ethenephosphonate (**2**) with aryl bromides **1a–j**.



The experimental procedure is simple and the yields of **3** are moderate to good regardless of a wide variety of substituents on the ring of the aryl bromide **1**. Thus, this reaction provides a facile synthesis of the title compounds. Products **3a–j** are characterized by microanalyses, I.R., N.M.R., and mass spectroscopy. The results are summarized in Tables 1 and 2. *trans*-2-Arylethenephosphonates are formed exclusively and this can be rationalized by assuming that the reaction is largely sterically controlled[5].

Table 1. Diethyl 2-Arylethenephosphonates **3a-j**

Product No.	Ar	Reaction Condition Time/Temperature [°C]	Yield [%]	m.p.[a] [°C] or b.p. [°C]/torr	Molecular formula[b] or Lit. data	
3a		4 h/100°	78	156–158°/3	145–147°/2.5[1]	
3b		4 h/100°	72	142–144°/1	$C_{13}H_{19}O_3P$	(254.3)
3c		4 h/100°	67	160–161°/2	$C_{13}H_{19}O_3P$	(254.3)
3d		4 h/100°	76	160–161°/0.5	$C_{13}H_{19}O_4P$	(270.3)
3e		6 h/100°	65	200–201°/1	$C_{14}H_{22}NO_3P$	(283.3)
3f		4 h/100°	74	63.5–64.5°	$C_{18}H_{21}O_3P$	(316.3)
3g		4 h/100°	61	190–192°/1	$C_{16}H_{19}O_3P$	(290.3)
3h		4 h/100°	60	168–170°/1	$C_{13}H_{17}O_4P$	(268.3)
3i		3 h/100°	63	102–103.5°	$C_{12}H_{16}NO_5P$	(285.2)
3j		7 h/100°	62	185–186°	$C_{14}H_{20}NO_4P$	(297.3)

[a] Determined on a Kofler melting point apparatus.

[b] Satisfactory microanalyses obtained: C ±0.31, H ±0.20, N ±0.25, P ±0.31; exceptions: **3d**, C −0.45; **3f**, P +0.47.

Table 2. Spectral Data of Compounds **3a-j**

Product No.	I.R.[a] ν [cm^{-1}]						M.S.[b] m/e	^{1}H-N.M.R. (CCl_4 or $CDCl_3$/TMS)[c] δ [ppm]
	P=O	P—O—C		C=C	CH=CH(*trans*)	other		
3a	1240	1020	1150	1610	960		240 (M$^+$)	1.35 (t, 6H, J=7.5 Hz); 4.13 (quin, 4H, J=7.5 Hz); 6.35 (t, 1H, J=20 Hz); 7.35 (m, 5H+1H)
3b	1240	1020	1160	1610	960		254 (M$^+$)	1.33 (t, 6H, J=7.5 Hz); 2.40 (s, 3H); 4.15 (quin, 4H, J=7.5 Hz); 6.24 (t, 1H, J=18 Hz); 7.37 (m, 4H+1H)
3c	1260	1020	1170	1615	960		254 (M$^+$)	1.33 (t, 6H, J=7.0 Hz); 2.56 (s, 3H); 4.05 (quin, 4H, J=7.0 Hz); 6.02 (t, 1H, J=18 Hz); 7.07 (m, 4H+1H)
3d	1250	1020	1160	1595	960		270 (M$^+$)	1.33 (t, 6H, J=7.5 Hz); 3.78 (s, 3H); 4.03 (quin, 4H, J=7.5 Hz); 5.96 (t, 1H, J=18 Hz); 7.10 (m, 4H+1H)
3e	1230	1020	1150	1590	940		283 (M$^+$)	1.36 (t, 6H, J=7.5 Hz); 3.05 (s, 6H); 4.03 (quin, 4H, J=7.5 Hz); 5.80 (t, 1H, J=18 Hz); 6.95 (m, 4H+1H)
3f	1240	1015	1160	1595	950		316 (M$^+$)	1.33 (t, 6H, J=7.0 Hz); 4.05 (quin, 4H, J=7.0 Hz); 6.10 (t, 1H, J=18 Hz); 7.53 (m, 9H+1H)
3g	1240	1040	1150	1605	950		290 (M$^+$)	1.33 (t, 6H, J=7.5 Hz); 4.07 (quin, 4H, J=7.5 Hz); 6.28 (t, 1H, J=18 Hz); 7.68 (m, 7H+1H)
3h	1250	1020	1160	1605	960	1685 (C=O)	268 (M$^+$)	1.33 (t, 6H, J=7.0 Hz); 4.05 (quin, 4H, J=7.0 Hz); 6.33 (t, 1H, J=17 Hz); 7.50 (m, 4H+1H); 10.03 (s, 1H)
3i	1240	1020	1160	1595	970	1520, 1350 (NO_2)	285 (M$^+$)	1.37 (t, 6H, J=7.0 Hz); 4.18 (quin, 4H, J=7.0 Hz); 6.53 (t, 1H, J=18 Hz); 7.80 (m, 4H+1H)
3j	1260	1020	1170	1590	960	1680, 1520 (CO—NH)	297 (M$^+$)	1.33 (t, 6H, J=7.5 Hz); 2.20 (s, 3H); 4.07 (quin, 4H, J=7.5 Hz); 6.05 (t, 1H, J=18 Hz); 7.41 (m, 4H+1H); 8.95 (s, 1H)

[a] The I.R. spectra were recorded using a Specord 75-IR spectrometer.

[b] The mass spectra were recorded with a Finnigan 4021 spectrometer.

[c] The ^{1}H-N.M.R. spectra were recorded with a 60 MHz Varian EM 360 spectrometer.

Although the present study was concerned with diethyl ethenephosphonates, it is anticipated that this method should be applicable to other dialkyl ethenephosphonates as well.

Diethyl 2-Arylethenephosphonates 3a-j; General Procedure:

In a capped thick wall tube is placed a mixture of aryl bromide **1** (10 mmol), diethyl ethenephosphonate[6] (**2**; 1.97 g, 12 mmol), triethylamine (4.2 ml, 30 mmol), palladium acetate (22.4 mg, 0.1 mmol), tri-*o*-tolylphosphine (60.8 mg, 0.2 mmol), and acetonitrile (3 ml). The tube is flushed with nitrogen, capped and heated in an oil bath at 100 °C for several hours. After the reaction mixture has been cooled, it is diluted with ether (15 ml) and filtered. The filtrate is washed successively with 1% hydrochloric acid solution (2 × 15 ml) and water (3 × 15 ml), then dried with anhydrous sodium sulfate. The residue obtained after removal of solvent is purified by distillation or recrystallization. G.L.C. analysis (SE-30, 20% on Chromosorb W, 60-80 mesh) shows uniformly no impurities.

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