Palladium-Catalyzed Reaction of Aryl Polyfluoroalkanesulfonates with *O,O*-Dialkyl Phosphonates

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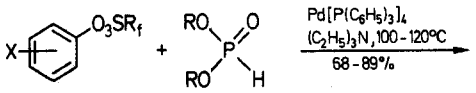
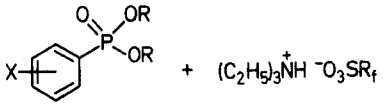
Arylphosphonates were synthesized by the reaction of aryl polyfluoroalkanesulfonates with *O,O*-dialkyl phosphonates in the presence of triethylamine under palladium catalysis in good to excellent yield.

Arylphosphonates can be used as precursors of phosphorus heterocycles which constitute a class of compounds possessing potent biological activity.[1] Several reports dealing with the synthesis of arylphosphonates from aryl halides have appeared.[2,3] Recently, palladium catalyzed reaction of enol triflates, aryl triflates and aryl perfluoroalkanesulfonates to form an arylpalladium(II) species[4] which can undergo carbonylation,[5] olefination, alkynylation[4] and reduction[6,7] reactions have been reported. However, the reaction of aryl polyfluoroalkanesulfonates with nucleophiles has not been reported. Here, we wish to present our results on the reaction of aryl polyfluoroalkanesulfonates **1** with *O,O*-dialkyl phosphonates **2** in the presence of triethylamine under palladium catalysis to give dialkyl arylphosphonates **3** in high yields.



1a-d **2a-c**



3aa-da

1	X
a	H
b	2-Cl
c	4-OCH_3
d	4-Cl

2	R
a	C_2H_5
b	*n*-C_4H_9
c	*i*-C_3H_7

Neither an electron withdrawing group nor an electron donating group on the benzene ring has any effect on the reaction, also the substituents on phosphorus atom have very little influence on the reaction. The results are shown in Table 1.

Owing to the accessibility of a wide variety of per- and polyfluoroalkanesulfonates,[8,9] the new method provides an effective means for the specific transformation of phenols into arylphosphonates. Bis(cyclooctadiene)nickel failed to catalyze this reaction under the same conditions.

Table 1. Arylphosphonates **3** Prepared[a]

Entry	Reactants	Temp. (°C)	Time (h)	Product	Yield (%)	b.p.[b] (°C)/mbar	Molecular Formula or Lit. b.p. (°C)/mbar
1	**1a** + **2a**	100	4	**3aa**	77	120/3	96–98/0.3[10]
2	**1a** + **2b**	100	4	**3ab**	68	140/3	166/5[11]
3	**1a** + **2c**	100	2	**3ac**	69	120/3	96–97/0.13[10]
4	**1b** + **2a**	120	4	**3ba**	70	130/3	113–115/0.4[10]
5	**1b** + **2b**	120	2	**3bb**	73	160/3	$C_{14}H_{22}ClO_3P$ (304.7)[c]
6	**1c** + **2a**	110	2	**3ca**	74	150/0.7	168–169/2[10]
7	**1c** + **2b**	110	4	**3cb**	82	150/0.7	$C_{15}H_{25}O_4P$ (300.3)[d]
8	**1d** + **2a**	110	2	**3da**	89	160/1.3	105–108/0.2[10]

[a] 4 mol% of $Pd(PPh_3)_4$ was used.
[b] Bath temperature of short-path distillation is given.
[c] calc. C 55.18 H 7.28 P 10.16; found 54.93 7.65 10.31
[d] calc. C 59.99 H 8.39 P 10.31; found 59.94 8.93 10.13

Table 2. Spectral Data of Arylphosphonates **3**

Compound	^{1}H-NMR (CCl_4/TMS)[a] δ, J (Hz)	IR (Neat)[b] (cm^{-1}) $\nu_{P=O}$	ν_{P-O-C}	MS[c] *m/e*
3aa	1.16 (t, 6H, J = 7); 3.63–4.18 (m, 4H); 7.16–7.85 (m, 5H)	1245	1020	215 (M^++1), 214 (M^+), 186, 158, 141, 77
3ab	0.83–1.86 (m, 14H); 3.83–4.22 (m, 4H); 7.38–8.03 (m, 5H)	1240	1010	271 (M^++1), 270 (M^+), 215, 159, 141, 77
3ac	1.11 (d, 6H, J = 6); 1.27 (d, 6H, J = 6); 4.25–4.84 (m, 2H); 7.24–7.91 (m, 5H)	1240	985	243 (M^++1), 201, 159, 141, 77
3ba	1.35 (t, 6H, J = 7); 3.80–4.32 (m, 4H); 7.25–7.50 (m, 3H); 7.76–8.20 (m, 1H)	1240	1020	251 (M^++3), 250 (M^++2), 249 (M^++1), 248 (M^+), 221, 213, 177, 175, 111
3bb	0.83–1.83 (m, 14H); 3,77–4.20 (m, 4H); 7.16–7.48 (m, 3H); 7.70–8.18 (m, 1H)	1245	1020	307 (M^++3), 305 (M^++1), 269, 249, 193, 177, 175, 111
3ca	1.27 (t, 6H, J = 7); 3.70–4.35 (m, 4H); 3.78 (s, 3H); 6.75–7.05 (m, 2H); 7.43–7.87 (m, 2H)	1240	1240	245 (M^++1), 244 (M^+), 216, 188, 171, 108
3cb	0.83–1.93 (m, 14H); 3.76–4.18 (m, 4H); 3.85 (s, 3H); 6.77–7.05 (m, 2H); 7.46–7.88 (m, 2H)	1240	1030	301 (M^++1), 300 (M^+), 245, 189, 188, 171, 108
3da	1.30 (t, 6H, J = 7); 3.74–4.31 (m, 4H); 7.24–7.92 (m, 4H)	1250	1020	251 (M^++3), 250 (M^++2), 249 (M^++1), 248 (M^+), 220, 192, 177, 175, 111

[a] The ^{1}H-NMR spectra were recorded on an EM 360 spectrometer.
[b] The IR spectra were taken using an IR-440 spectrometer.
[c] The mass spectra were recorded on a Finnigan 4021 GC/MS/DC instruments.

Arylphosphonates 3; General Procedure:
In a capped thick wall tube are placed aryl polyfluoroalkanesulfonate **1** (1 mmol), *O,O*-dialkyl phosphonate **2** (1.1 mmol), triethylamine (4 mL) and tetrakis(triphenylphosphine)palladium (50 mg, 0.04 mmol). The tube is flushed with nitrogen, capped and heated in an oil bath at 100–120 °C for 2–4 h. The crude product obtained after the removal of solvent is purified by column chromatography (silica gel, petroleum ether/ethyl acetate, 2:1) and distilled under vacuum (Tables 1 and 2).

We wish to thank the National Science Foundation of China for partial financial support.

Received: 10 November 1986; revised: 19 February 1987

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