Synthesis of Arylphosphonates by Arylation of Phosphite Anions Using Diaryliodonium Salts[1]

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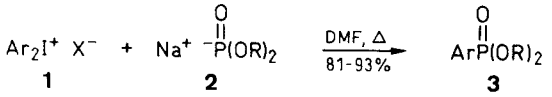
An efficient synthesis of arylphosphonates **3** is described. The method involves simple stirring of the dialkyl phosphite salts **2** with diaryliodonium salts **1** in dimethylformamide.

As part of our general interest in synthetic applications of diaryliodonium salts **1**,[1] we have examined their reaction with dialkyl phosphite salts **2**, in dimethylformamide, which constitutes a new, effective method for the preparation of arylphosphonates **3**.



1 **2** **3**

In contrast to trialkyl phosphite,[2,3] the reaction of dialkyl phosphite salts with diaryliodonium salts proceeds smoothly and affords satisfactory yields (Table).

The synthesis of arylphosphonates is of considerable current interest in that these can be used as precursors of phosphorus heterocycles or phosphorus analogs of heterocyclic compounds.[4-6] A number of methods have been reported for the synthesis of arylphosphonates: (a), the esterification of arylphosphonic dichlorides with alcohols;[7] (b), the decarbonylation of arylketophosphonates;[8] (c), the nickel(II) catalyzed reaction of aryl halides with trialkyl phosphites;[9] (d), the photolysis of aryl iodides in the presence of trialkyl phosphites;[10] (e), the photostimulated condensation of aryl iodides with phosphite salts;[11] (f), the palladium catalyzed reaction of aryl halides[12] or aryl polyfluoroalkanesulfonates[13] with *O,O*-dialkyl phosphites; (g), the copper(I) iodide promoted arylation of phosphite anions with aryl iodides;[14] and (h), the electrochemical oxidation of silylphosphites[15] or

Table. Arylphosphonates **3** Prepared

Product	R	Ar	Reaction Time (h)	Yield (%)	bp[a] (°C/Torr)	Lit bp (°C/Torr)	ν (cm^{-1}) P=O, P–O–C, P–Ar	^1H NMR ($CDCl_3$/TMS)
3a	Et	Ph	4	93	110/2	96–98/0.2[9]	1250, 1025, 965	1.32 (t, 6H, J = 7.5, $2CH_3$), 4.11 (m, 4H, $2CH_2$). 7.48 (m, 3H, H_{arom}), 7.75 (m, 2H, H_{arom}).
3b	Et	*p*-MeC_6H_4	4	87	170/1	118–119/0.05[9]	1245, 1020, 965	1,21 (t, 6H, J = 7.5 $2CH_3$), 2.25 (s, 3H, Arom-CH_3), 3.95 (m, 4H, $2CH_2$), 7.20 (m, 2H, H_{arom}), 7.55 (m, 2H, H_{arom}).
3c	Et	*p*-ClC_6H_4	7	85	170/1.5	105–108/0.15[9]	1250, 1025, 970	1.18 (t, 6H, J = 8.0, $2CH_3$), 3.99 (m, 4H, $2CH_2$), 7.28 (m, 2H, H_{arom}), 7.65 (m, 2H, H_{arom}).
3d	Pr	Ph	4	86	115/2	106–108/1[18]	1250, 1060, 995	0.87 (t, 6H, $2CH_3$), 1.60 (m, 4H, $2CH_2$), 3.91 (m, 4H, $2CH_2$), 7.42 (m, 5H. H_{arom}).
3e	Pr	*p*-MeC_6H_4	5	81	120/2	110–112/1[18]	1250, 1060, 990	0.95 (t, 6H, $2CH_3$), 1.69 (m, 4H, $2CH_2$), 2.34 (s, 3H, Arom-CH_3), 4.04 (m, 4H, $2CH_2$), 7.30 (m, 2H, H_{arom}), 7.65 (m, 2H, H_{arom}),
3f	*i*-Pr	Ph	5	89	120/1	96–97/0.1[9]	1250, 1025, 975	1.26 (m, 12H, $4CH_3$), 4.69 (m, 2H, 2CH), 7.48 (m, 3H, H_{arom}), 7.90 (m, 2H_{arom}).
3g	*i*-Pr	*p*-MeC_6H_4	5	79	115/1.5	98–100/1[18]	1250, 1025, 980	1.28 (m, 12H, $4CH_3$), 2.37 (s, 3H, Arom-CH_3), 7.22 (m, 2H, H_{arom}), 7.65 (m, 2H, H_{arom}).

[a] Bath temperature of short path distillation is given.

trialkylphosphites[16] in the presence of aromatic compounds.

These methods have certain disadvantages such as the necessity of using a large excess of phosphites (d, e) or of using a noble metallic catalyst (b, f), or of making starting materials by multistep reactions (a, b), or using harsh reaction conditions (c, d, e, g), a toxic and carcinogenic solvent (g), or obtaining lower yield (h). The present method has the advantages of easy availability of starting materials, mild reaction conditions, simple workup and better yields.

Arylphosphonates 3; General Procedure:

NaH (0.072 g, 3 mmol) was added to a stirred solution of dialkyl phosphite (3 mmol) in DMF (15 mL) under an N_2 atmosphere. When H_2 evolution had ceased, diaryliodonium salt[17] (1.5 mmol) was added. The mixture was heated at 70–80 °C with stirring for the time given in the Table. After being cooled, the mixture was diluted with water (80 mL) and the product was extracted with CH_2Cl_2 (3 × 50 mL). The extract was washed with water (2 × 80 mL) and dried ($MgSO_4$). The solvent was removed in vacuo and the residue was chromatographed on a column of silica gel first using cyclohexane then $CHCl_3$ as eluent to give the arylphosphonate. All relevant data are summarized in the Table.

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