Nickel(0)-catalyzed Reaction of *O,O*-Dialkyl Phosphonates with Allyl Acetates or Carbonates. A Novel Method of Preparing Allyl Phosphonates

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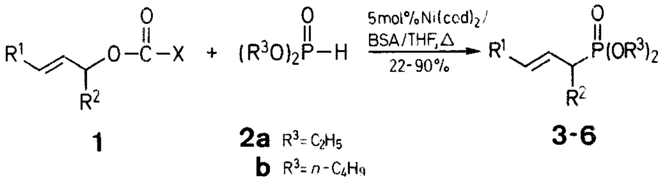
Allyl phosphonates are synthesized in good yield by the reaction of allyl acetates or carbonates with *O,O*-dialkyl phosphonates under the catalysis of Ni(cod)$_2$ in the presence of *O,N*-bis(trimethylsilyl)acetamide (BSA).

Palladium-catalyzed reactions leading to C—P bond formation have recently been described producing vinyl, aryl and allyl phosphonates, phosphinates and phosphine oxides by the reaction of compounds of the type HP(O)R^{1}R^2 (R^1,R^2 = alkyl, aryl or alkoxyl group) with alkenyl bromides, aryl bromides and 1,3-dienes[1-4]. Fiaud reported the palladium catalyzed reaction of phosphides and thiophosphides with allyl acetates but only limited yields were obtained from the former[5]. However, to our knowledge, the transition metal catalyzed reaction of allyl carboxylates with HP(O)R^{1}R^2 (R^1, R^2 = alkyl or alkoxy group) has not been reported. Here, we wish to report a novel method of preparing allyl phosphonates from allyl acetates or carbonates and *O,O*-dialkyl phosphonates through a nickel(0) catalyzed reaction.

Instead of the ubiquitous catalyst palladium(0), Ni(cod)$_2$ is known[6] to catalyze the rearrangement of allyl phosphites to the corresponding phosphonates. Therefore, Ni(cod)$_2$ was tried as a catalyst for the reaction of allyl acetates with sodium *O,O*-dialkylphosphonates or *O,O*-dialkyl phosphonates and triethylamine in refluxing tetrahydrofuran, but only a low yield of allyl phosphonates was obtained[7]. We have now found that the use of an equivalent amount of *O,N*-bis(trimethylsilyl)acetamide (BSA) instead of triethylamine increase the yield of the expected allyl phosphonates both from allyl acetates and allyl carbonates (Table 1).

Allyl carbonates could react with nucleophiles under neutral conditions using palladium(0)[11] as catalyst. The alkoxide ion formed in situ may be strong enough to abstract the proton from *O,O*-dialkyl phosphonates to form the phosphonate anions. However, it is surprising that allyl carbonates failed



1	R^1	R^2	X
a	H	H	CH$_3$
b	H	C$_6$H$_5$	CH$_3$
c	C$_6$H$_5$	H	CH$_3$
d	H	H	OC$_2$H$_5$
e	H	C$_6$H$_5$	OC$_2$H$_5$
f	C$_6$H$_5$	H	OC$_2$H$_5$

	R^1	R^2	R^3
3	H	H	C$_2$H$_5$
4	C$_6$H$_5$	H	C$_2$H$_5$
5	H	H	*n*-C$_4$H$_9$
6	C$_6$H$_5$	H	*n*-C$_4$H$_9$

Table 1. Allyl phosphonates **3–6** prepared

Entry	Reactants	Time [h]	Product No.	Yield [%]	b.p. [°C]/torr[a]	Molecular Formula or Lit. b.p. [°C]/torr
1	**1a + 2a**	14	**3**	80	80°/2	97–98°/16[8]
2	**1b + 2a**	11	**4**	87	140°/1	130°/0.3[9]
3	**1c + 2a**	70	**4**	22[b]		
4	**1a + 2b**	36	**5**	65	140°/2	110°/0.4[10]
5	**1b + 2b**	15	**6**	90	143°/0.1	$C_{17}H_{27}O_3P$ (310.4)[c]
6	**1d + 2a**	7	**3**	75	80°/2	97–98°/16[8]
7	**1e + 2a**	12	**4**	85	140°/1	130°/0.3[9]
8	**1f + 2a**	25	**4**	80		

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

[b] A large amount of starting material is recovered.

[c]

calc.	C 65.78	H 8.77	P 9.98
found	65.88	8.87	10.00

Table 2. Spectral Data of Allyl Phosphonates **3–6**

Product	^{1}H-N.M.R. (CCl$_4$/TMS)[a] δ [ppm]	I.R. (neat)[b] ν [cm^{-1}]	M.S.[c] (*m/e*)
3	1.33 (t, 6H, $^3J_{HH}$ = 7 Hz); 2.58 (dd, 2H, $^3J_{HH}$ = 7 Hz, $^2J_{PH}$ = 22 Hz); 3.90–4.60 (m, 4H); 5.10–6.21 (m, 3H)	1615 (m, C=C); 1235 (s, P=O); 1010 (s, P—O—C)	179 (M$^+$ + 1)
4	1.32 (t, 6H, $^3J_{HH}$ = 7 Hz); 2.58 (dd, 2H, $^3J_{HH}$ = 7 Hz, $^2J_{PH}$ = 23 Hz); 3.86–4.42 (m, 4H); 5.98–6.86 (m, 2H); 7.21–7.72 (m, 5H)	1640 (m, C=C); 1240 (s, P=O); 1030 (s, P—O—C)	255 (M$^+$ + 1), 254 (M$^+$), 226, 198, 117
5	0.8–1.89 (m, 14H); 2.54 (dd, 2H, $^3J_{HH}$ = 7 Hz, $^3J_{PH}$ = 22 Hz); 3.8–4.23 (m, 4H); 4.93–6.13 (m, 3H)	1625 (m, C=C); 1230 (s, P=O); 1005 (s, P—O—C)	235 (M$^+$ + 1), 179, 123
6	0.73–1.87 (m, 14H); 2.61 (dd, 2H, $^3J_{HH}$ = 7 Hz, $^3J_{PH}$ = 21 Hz); 3.74–4.07 (m, 4H); 5.81–6.60 (m, 2H); 7.03–7.34 (m, 5H)	1235 (s, P=O); 1010 (s, P—O—C)	311 (M$^+$ + 1), 310 (M$^+$), 254, 198, 117

[a] The ^{1}H-N.M.R. spectra were recorded on an EM 360 spectrometer.

[b] The IR spectra were taken using a SPECORP 75-IR spectrometer.

[c] The mass spectra were recorded on a Finigan 4021 GC/MS/DC instruments.

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to react with *O,O*-dialkyl phosphonates to yield allyl phosphonates without the use of BSA as a base. In additon, it seems that both nickel(0) catalyst and BSA are necessary for this reaction, because tetrakis(triphenylphosphine)palladium, iron pentacarbonyl and molybdenum hexacarbonyl are ineffective for this reaction under the same condition. The details and mechanism of this reaction are currently under investigation in our laboratory.

Allyl Phosphonates; General Procedure:

To a solution of *O,O*-dialkyl phosphonate (2 mmol), BAS (2 mmol) and Ni(cod)$_2$ (0.1 mmol) in tetrahydrofuran (5 ml), allyl acetate or carbonate (2 mmol) is added with a syringe under a prepurified nitrogen atmosphere. The solution is refluxed to the disappearance of *O,O*-dialkyl phosphonate as monitored by G.L.C. The crude product obtained after the removal of solvent is purified by column chromatography (silica gel/petroleum ether-ethyl acetate) and distilled under vacuum. All the allyl phosphonates obtained gave satisfactory I.R., ^{1}H-N.M.R. and M.S. data (Table 2).

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