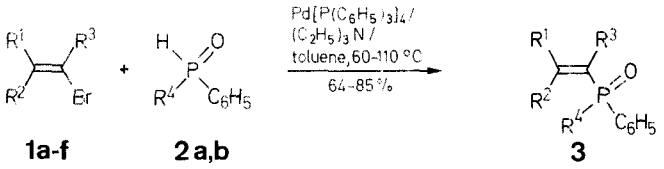
Palladium-Catalysed Synthesis of Alkenyldiphenyl- and Alkenylbenzylphenylphosphine Oxides

Yuanyao XU*, Jiazhi XIA, Huiju GUO

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

Alkenyldiphenyl- and Alkenylbenzylphenyl phosphine oxides **3** were prepared by the palladium catalysed reaction of alkenyl bromides **1** with phosphine oxides **2a** or **2b**.

Tertiary phosphine oxides containing an alkenyl substituent are useful synthetic intermediates. They undergo addition reaction readily with amines, alcohols and compounds containing a P-H bond[1-3]; and the adducts from alkenyldiphenylphosphine oxides and secondary amines could react with carbonyl compounds via Horner-Wittig reaction, giving rise to a variety of allylic amines[4]. However, only few methods on the preparation of alkenyl derivatives of tertiary phosphine oxides are known, but these are concerned mainly with Grignard[5,6] and elimination[1,7] reactions. A method based on the direct deoxygenation of 1,2-epoxyethyldiphenylphosphine oxides with diphosphorus tetraiodide has been recently described[8]. As a continuation of our studies on palladium-catalyzed formation of carbon-phosphorus bond[9], we now wish to report on the synthesis of alkenyldiphenyl- and alkenylbenzylphenylphosphine oxides **3** by the palladium catalysed reaction of an alkenyl bromide **1** with diphenylphosphine oxide (**2a**) or benzylphenylphosphine oxide (**2b**), respectively, in the presence of triethylamine and a catalytic amount of tetrakis[triphenylphosphine]palladium.



1a-f **2a,b** **3**

1	R^1	R^2	R^3
a	H	H	H
b	H	CH_3	H
c	CH_3	CH_3	H
d	H	C_6H_5	H
e	C_6H_5	H	H
f	$COOCH_3$	CH_3	H

2	R^4
a	C_6H_5
b	$C_6H_5CH_2$

The yields of products **3** are moderate to good as shown in Table 1. When (*Z*)-1-bromopropene, methyl (*E*)-3-bromo-2-methyl propenoate, (*Z*)- or (*E*)-β-bromostyrenes was used as the starting material, the present reaction proceeded with retention of configuration at the double bond and the corresponding alkenyl derivatives of tertiary phosphine oxides were obtained without any contamination of the isomer, as evidenced by both ^{1}H-NMR (Table 2) and TLC. Thus, the present reaction provides a convenient and stereospecific synthesis of alkenyldiphenyl- and alkenylbenzylphenylphosphine oxides.

It is of interest to point out that although use of dichlorobis[triphenylphosphine]palladium also gave good yields of alkylphenylphosphinates[10] and alkenyl derivatives of phosphinates[9] via palladium-catalysed formation of C-P bond, it is ineffective for the formation of alkenyl derivatives of tertiary phosphine oxides, indicating that the secondary phosphine oxides **2a** and **2b** failed to reduce dichlorobis[triphenylphosphine]palladium in situ to the Pd(O) species under the present condition.

Alkenyldiphenyl- and Alkenylbenzylphenylphosphine Oxides 3; General Procedure:

In a capped thick-wall tube are placed the alkenyl bromide **1** (2 mmol), diphenyl- or benzylphenylphosphine oxide **2** (2.2 mmol), triethylamine (1 ml, 7.2 mmol), dry toluene (8 ml) and tetrakis[triphenylphosphine]palladium (231 mg, 0.2 mmol). The tube is flushed with nitrogen, capped and heated in an oil bath at 60–110 °C for 4–38 h. After the mixture has been cooled, ethyl acetate (20 ml) is added and the solid is removed by filtration. The filtrate is concentrated on a rotary evaporator and the residue is purified by column chromatography on silica gel eluating with petroleum ether (b.p. 60–90 °C)/ethyl acetate (1:1–4). The product **3** thus obtained shows uniformly no impurities by TLC. For microanalysis, the sample is further purified by recrystallization.

Table 1. Alkenyldiphenyl- and Alkenylbenzylphenylphosphine Oxides **3** Prepared

Educts	Product No.	Reaction Conditions Time [h]/Temp [°C]	Yield [%]	m.p. [°C][a]	Molecular Formula[b] or Lit. m.p. [°C]
1a + **2a**	**3aa**	8/60	85	15–117	116–117[1]
1b + **2a**	**3ba**	8/80	76	116–118	113–116[5]
1c + **2a**	**3ca**	8/100	69	147–148	149–150[11]
1d + **2a**	**3da**	4/90	76	106–107	$C_{20}H_{17}OP$ (304.3)
1e + **2a**	**3ea**	8/80	78	167–167.5	168–169[6]
1a + **2b**	**3ab**	8/80	79	137–138	$C_{15}H_{15}OP$ (242.3)
1b + **2b**	**3bb**	8.5/110	64	125–127	$C_{16}H_{17}OP$ (256.3)
1c + **2b**	**3cb**	38/110	76	136–137	$C_{17}H_{19}OP$ (270.3)
1d + **2b**	**3db**	6/110	78	149–150	$C_{21}H_{19}OP$ (318.3)
1f + **2b**	**3fb**	30/110	80	129–130	$C_{18}H_{19}O_3P$ (314.3)

[a] Determined on a Kofler melting point apparatus.
[b] Satisfactory microanalyses obtained: C ±0.40, H ±0.11, P ±0.15.

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

Product No.	IR (KCl)[a] ν [cm^{-1}]	MS[b] *m/e*	^{1}H-NMR ($CDCl_3$/TMS)[c] δ [ppm]
3aa	1185 (P=O) 1600 (C=C)	228 (M^+) 229 ($M^+ + 1$)	6.40 (m, 3H$_{olefin}$); 7.60 (m, 10H$_{arom}$)
3ba	1180 (P=O) 1615 (C=C)	242 (M^+) 243 ($M^+ + 1$)	2.03 (m, 3H, CH_3); 6.10 (m, 1H, =CHP, $J_{H,H}$ = 13 Hz); $J_{P,H}$ = 27 Hz); 6.82 (m, 1H. CH=CP, $J_{H,H}$ = 13 Hz, $J_{P,H}$ = 40 Hz); 7.71 (m, 10H$_{arom}$)
3ca	1190 (P=O) 1630 (C=C)	256 (M^+) 257 ($M^+ + 1$)	2.08 (m, 6H, CH_3); 5.90 (d, 1H, =CHP, $J_{P,H}$ = 26 Hz); 7.52 (m, 10H$_{arom}$)
3da	1180 (P=O) 1610 (C=C)	304 (M^+) 305 ($M^+ + 1$)	6.27 (dd, 1H, =CHP, $J_{H,H}$ = 14 Hz, $J_{P,H}$ = 21 Hz); 7.65 (m, 16H, H$_{arom}$ + =CH)
3ea	1190 (P=O) 1610 (C=C)	304 (M^+) 305 ($M^+ + 1$)	6.78 (dd, 1H, =CHP, $J_{H,H}$ = 18 Hz, $J_{P,H}$ = 22 Hz); 7.80 (m, 16H, H$_{arom}$ + =CH)
3ab	1185 (P=O) 1600 (C=C)	242 (M^+) 243 ($M^+ + 1$)	3.35 (d, 2H, Ar—CH_2, $J_{P,H}$ = 14 Hz); 6.10 (m, 3H$_{olefin}$); 7.35 (m, 10H$_{arom}$)
3bb	1180 (P=O) 1610 (C=C)	256 (M^+) 257 ($M^+ + 1$)	1.94 (m, 3H, CH_3); 3.30 (d, 2H, Ar—CH_2, $J_{P,H}$ = 14 Hz); 5.90 (m, 1H, =CHP, $J_{H,H}$ = 12 Hz, $J_{P,H}$ = 28 Hz); 6.64 (m, 1H, CH=CP, $J_{H,H}$ = 12 Hz, $J_{P,H}$ = 40 Hz); 7.35 (m, 10H$_{arom}$)
3cb	1180 (P=O) 1630 (C=C)	270 (M^+) 271 ($M^+ + 1$)	1.90 (s, 6H, CH_3); 3.24 (d, 2H, Ar—CH_2, $J_{P,H}$ = 14 Hz); 5.67 (d, 1H, =CHP, $J_{P,H}$ = 26 Hz); 7.38 (m, 10H$_{arom}$)
3db	1175 (P=O) 1600 (C=C)	318 (M^+) 319 ($M^+ + 1$)	3.25 (d, 2H, Ar—CH_2, $J_{P,H}$ = 14 Hz); 6.15 (dd, 1H, =CHP, $J_{H,H}$ = 14 Hz, $J_{P,H}$ = 21 Hz); 7.25 (m, 16H, H$_{arom}$ + =CH)
3fb	1180 (P=O) 1610 (C=C) 1720 (C=O)	314 (M^+) 315 ($M^+ + 1$)	2.10 (d, 3H, CH_3, $J_{H,H}$ = 3 Hz); 3.38 (d, 2H, Ar—CH_2, $J_{P,H}$ = 14 Hz); 3.76 (S, 3H, OCH_3); 7.30 (m, 11H, 10H$_{arom}$ + =CH)

[a] The I.R. spectra were recorded on 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 or a 200 MHz Varian XL-200 spectrometer.

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