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Effective activation of allylic ethers by boron oxide in palladium catalyzed allylic alkylation

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Abstract

In the presence of boron oxide, allylic ethers react smoothly with carbonucleophiles to afford the allylation products by catalysis with $Pd(PPh_3)_4$ under neutral conditions.

Introduction

Allylic ethers are seldom used as allylation reagents in carbon–carbon bond-forming reactions, because it is difficult to activate allylic ethers for reaction with carbonucleophiles. Recently, Mukaiyama reported the activation of allyl methyl ethers by trityl perchlorate, but only methyl ethers could be activated [1,2]. In palladium-catalyzed allylic alkylations, many functional groups could be employed as leaving groups [3], but, for the allylic ethers, only allylic phenyl ethers are successful allylation agents [4–6]. Thus an efficient method to activate the allylic alkyl ethers of synthetic value was sought.

A systematic study of the reactions of low valence transition metal complexes with the compounds containing C–O bond [7–12] resulted in our recent report of the activation of allylic alcohols by boron oxide in palladium-catalyzed reactions [13]. We report here the activation of allylic alkyl ethers by boron oxide in a palladium-catalyzed allylic alkylation.

Results and discussion

The allylic alkyl ethers **1–8** react with the carbonucleophiles **9–12** in the presence of an equimolar quantity of boron oxide and a catalytic amount of $Pd(PPh_3)_4$ to give the expected allylated products **13–20**. The results are shown in Table 1.

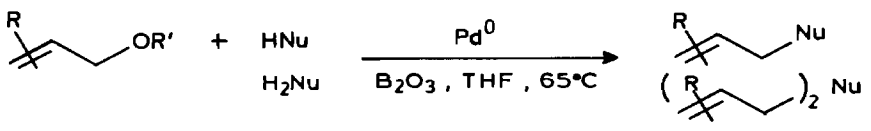

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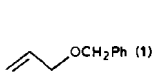
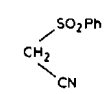
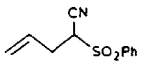
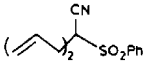
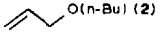
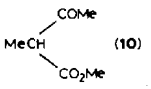
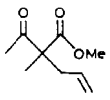
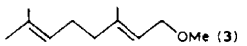
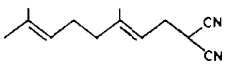
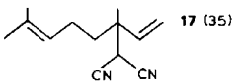
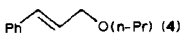
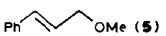
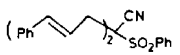
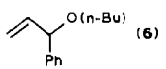
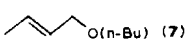
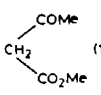
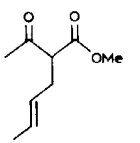
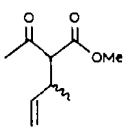
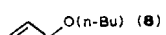
Table 1

Palladium(0) catalyzed reaction of allylic alkyl ethers with nucleophiles in the presence of boron oxide

Allylic ether	Nucleophile	Time (h)	Yield[a] (%)	Products[b] (yield, %)
 (1)	 (9)	11	88	 **13** (26)  **14** (74)
 (2)	(9)	11	91	**13** (20) **14** (80)
2	 (10)	24	60	 **15** (100)
 (3)	$CH_2(CN)_2$ (11)	21	61	 **16** (65)  **17** (35)
 (4)	(9)	24	0	
 (5)	(9)	19	92	 **18** (100)
 (6)	(9)	16	97	**18** (100)
 (7)	 (12)	19	42	 **19** (50)  **20** (50)
 (8)	(12)	19	61	**19** (50) **20** (50)

[a] Isolated yield based on the nucleophile. [b] Figures in parentheses represent the ratio of products determined by ^1H NMR spectra.

The reaction proceeds at 65 °C in THF for several hours under palladium catalysis without any base and the boric acid can be readily removed by washing the reaction mixture with water. The reaction does not occur without boron oxide. From Table 1, it can be seen that of the allylic ethers bearing various kinds of alkyl groups which enter the reaction, the methyl ether is the most reactive (compare compounds **4** and **5**).

The reaction mechanism is not clear at present. It is possible that boron oxide may play a role as a Lewis acid to coordinate with the ether oxygen atom and make the C–O bond labile to cleavage under catalysis by Pd^0. The alkoxy group or borate ion formed can abstract a proton from the nucleophiles to form the carbanions which then attack the π-allyl group to yield the allylated products.

It is noted that boron oxide does effectively activate allylic alkyl ethers. The mild conditions, simple operation and high yields, thus provide a convenient procedure for the palladium-catalyzed allylic alkylations. Further studies on the applications of boron oxide as the activator of alkyl ethers are now in progress.

Experimental

All reactions were carried out under prepurified nitrogen using Schlenk techniques. ^{1}H NMR spectra were recorded on an EM-360A (60 MHz) or a Varian XL-200 (200 MHz) spectrometer, the solvents used were CCl_4 or $CDCl_3$ containing tetramethylsilane as internal standard. Infrared spectra were recorded as liquid film or KCl disc on a Shimadzu IR-440 spectrometer. Mass spectra were obtained on a Finnigan 4021 GC/MS/DC instrument. GLC was performed on a 2 m column (10% OV-101 supported on a 102 silanized white support (60–80 mesh).

General procedure for the reaction of allylic ethers with nucleophiles

To a mixture of $Pd(PPh_3)_4$ (0.05 mmol), PPh_3 (0.2 mmol) and boron oxide (1.0 mmol) in THF (3 ml), an allylic alkyl ether (1–2 mmol) was added by syringe and the carbonucleophile (1 mmol) was added. The reaction mixture was refluxed and monitored by gas chromatography or TLC (silica gel/petroleum ether : ethyl acetate 8 : 1) until the starting materials had disappeared. After the solvent had been removed, ether (5 ml) and water (2 ml) were added. The organic layer was separated and the aqueous layer was extracted with ether three times (3 × 3 ml). The combined ether extract was dried over magnesium sulfate and concentrated. The crude product was purified either by distillation in vacuum followed by flash chromatography or by preparative TLC followed by recrystallization (from ether/hexane). All the products were characterized by ^{1}H NMR, IR and MS.

2-Benzenesulfonyl-4-pentenonitrile (***13***) [14]. B.p. 145 °C (bath temperature)/0.3–1.0 Torr; ^{1}H NMR (δ, 200 MHz, $CDCl_3$): 2.62 (ddd, *J* 14.1 Hz, *J* 10.7 Hz, *J* 7.1 Hz, 1H), 2.88–3.03 (m, 1H), 3.98 (dd, *J* 10.7 Hz, *J* 4.4 Hz, 1H), 5.25–5.35 (m, 2H), 5.60–5.89 (m, 1H), 7.60–7.83 (m, 3H), 8.00–8.05 (m, 2H); IR (neat, cm^{-1}): 2250 (m, C≡N), 1640 (m, C=C), 1585 (m), 1450 (s), 1330 (s, SO_2), 1155 (s, SO_2); MS: 222 ($M^+ + 1$), 157, 141, 77.

2-Allyl-2-benzenesulfonyl-4-pentenonitrile (***14***) [13]. M.p. 45–46.5 °C; ^{1}H NMR (δ, 60 MHz, CCl_4): 2.68 (d, *J* 7 Hz, 4H), 4.98–6.15(m, 6H), 7.48–7.75 (m, 3H),

7.75–7.85 (m, 2H); IR (KCl, cm^{-1}): 2250 (m, C≡N), 1640 (m, C=C), 1330 (s, SO_2), 1155 (s, SO_2); MS: 262 ($M^+ + 1$), 141, 120, 93, 77.

Methyl 2-acetyl-2-methyl-4-pentenoate (***15***) [15]. B.p. 85 °C (bath temperature)/ 0.7–1.5 Torr; ^1H NMR (δ, 60 MHz, CCl_4): 1.25 (s, 3H), 2.15 (s, 3H), 2.47 (d, *J* 6 Hz, 2H), 3.66 (s, 3H), 4.81–5.95 (m, 3H): IR (neat, cm^{-1}): 1745 (s, C=O), 1715 (s, C=O), 1640 (m, C=C); MS: 171 ($M^+ + 1$), 139, 128, 11, 96, 69, 43.

2-Cyano-5,9-dimethyl-4,8-decadienonitrile (***16***) [16]. B.p. 100 °C (bath temperature)/1–2 Torr; ^1H NMR (δ, 60 MHz, CCl_4): 1.46–1.56 (m, 9H), 1.96 (bs, 4H), 2.55 (t, *J* 7 Hz, 2H), 3.50 (t, *J* 7 Hz, 1H), 4.90–5.26 (m, 2H); IR (neat, cm^{-1}): 2250 (m, C≡N), 1665 (m, C=C), 1445 (m), 1380 (m); MS: 202 (M^+), 187, 159, 137, 81, 69.

2-Cyano-3,7-dimethyl-3-vinyl-octenonitrile (***17***) [16]. B.p. 95 °C (bath temperature)/1–2 Torr; ^1H NMR (δ, 60 MHz, CCl_4): 1.35 (s, 3H), 1.50–2.16 (m, 10H), 3.55 (s, 1H), 4.88–6.03 (m, 4H); IR (neat, cm^{-1}): 2250 (m, C≡N), 1640 (m, C=C), 1450 (m), 1380 (m); MS: 203 ($M^+ + 1$), 202 (M^+), 187, 137, 121, 109, 94, 81, 69.

2-Cinnamyl-2-benzenesulfonyl-5-phenyl-4-pentenonitrile (***18***) *[7].* M.p. 111–112.5 °C; ^1H NMR (δ, 200 MHz, $CDCl_3$): 2.88 (d, *J* 7 Hz, 4H), 6.03 (dt, *J* 16 Hz, *J* 7 Hz, 2H), 6.53 (d, *J* 16 Hz, 2H), 7.20 (s, 10H), 7.50–7.76 (m, 3H), 7.93–8.10 (m, 2H); IR (KCl, cm^{-1}): 2225 (m, C≡N), 1580 (m, C=C), 1495 (m), 1325 (s, SO_2), 1155 (s, SO_2); MS: 414 ($M^+ + 1$), 336, 271, 205, 180, 117, 91, 77.

Mixture of methyl 2-acetyl-4-hexenoate (***19***) *and methyl 2-acetyl-3-methyl-4-pentenoate* (***20***) [15]. B.p. 85 °C (bath temperature)/1–1.5 Torr; ^1H NMR (δ, 60 MHz, CCl_4): 1.05 (t, *J* 7 Hz, 3H), 1.61–1.66 (m, 3H), 2.18–2.24 (m, 6H), 2.49–2.56 (m, 2H), 2.92–3.04 (m, 1H), 3.38–3.53 (m, 2H), 3.73 (bs, 6H), 4.98–5.83 (m, 5H); IR (neat, cm^{-1}): 1740 (s, C=O), 1715 (s, C=O), 1640 (m, C=C), 1440 (m), 1360 (m); MS: 171 ($M^+ + 1$), 139, 127, 111, 95, 43.

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