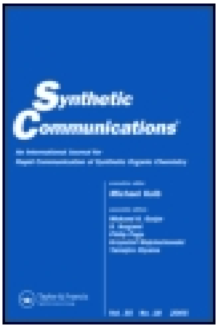

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TTMPP-Catalyzed Addition of Alkynes Using Trimethylsilylacetylenes

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TTMPP-Catalyzed Addition of Alkynes Using Trimethylsilylacetylenes

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Abstract: A highly basic phosphine, tris(2,4,6-trimethoxyphenyl)phosphine (TTMPP), catalyzes alkynylation using trimethylsilylalkyne to give the corresponding products in good to high yields.

Keywords: Alkynylation, base catalyst, organosilicon compounds

INTRODUCTION

Tris(2,4,6-trimethoxyphenyl)phosphine (TTMPP) is known as a highly basic phosphine because of its multiple methoxy substitutions.[1] Many unique reactions have been reported using TTMPP as an organocatalyst by authors such as Yoshimoto, Kawabata, and Chuprakor.[2] We have previously demonstrated that TTMPP catalyzes aldol and imine–aldol reactions via O-Si bond activation[3] and also reported the catalytic reaction via C-Si bond activation.[3] To apply the underlying mechanisms to other useful reactions, catalytic alkynylation was examined.

Alkynylation of carbonyl compounds is one of the most important carbon–carbon bond-forming reactions in organic synthesis. Although several Lewis acid catalytic reactions are known, examples of base-catalyzed alkynylation remain scarce.[4] We report herein the TTMPP-catalyzed alkynylation of carbonyl compounds using trimethylsilylacetylenes.

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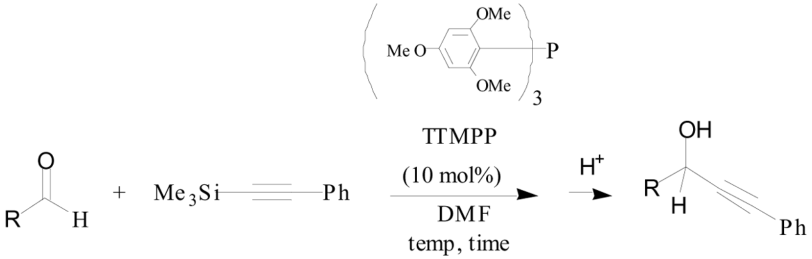
RESULTS AND DISCUSSION

Initially, alkynylation of benzaldehyde with 1-phenyl-2-(trimethylsilyl)-acetylene was examined in the presence of 10 mol% TTMPP in dimethylformamide (DMF) at room temperature. However, the reaction was very slow. The reaction was then performed at elevated temperature. The desired product was obtained in 95% yield in 8 h at 100°C. The product was obtained in low yield when other phosphines were used instead of TTMPP. These results indicate that TTMPP effectively activates the C-Si bond of 1-phenyl-2-(trimethylsilyl)acetylene.

To clarify the scope of this reaction, several aldehydes were examined in the presence of 10 mol% TTMPP (Table 1). Good results were obtained

Table 1. TTMPP-catalyzed alkynylation of carbonyl compounds



Entry	R	Temperature (°C)	Time (h)	Yield (%)
1	C_6H_5	rt	24	Trace
2		100	8	95
3[a]		100	24	12
4[b]		100	24	Trace
5	4-$CH_3OC_6H_4$	100	16	85
6	4-ClC_6H_4	120	8	98
7	4-$NO_2C_6H_4$	120	8	80
8	1-Naphthyl	120	16	74
9	2-Naphthyl	120	8	80
10	(*E*)-PhCH=CH	100	16	90
11	$PhCH_2CH_2$	120	8	95
12	*n*-C_8H_{17}	100	8	96
13	*c*-C_6H_{11}	100	16	88
14[c]	C_6H_5	120	24	n.r.

[a] $P(nBu)_3$ was used instead of TTMPP.

[b] PPh_3 was used instead of TTMPP.

[c] 1-Trimethylsilyl-1-hexyne was used instead of 1-phenyl-2-(trimethylsilyl) acetylene.

for aromatics having either electron-donating or electron-withdrawing group aldehydes. 1,2-Adducts were obtained in good yields when α,β-unsaturated aldehydes were employed. In addition, aliphatic aldehydes also worked well.

In summary, we demonstrated TTMPP-catalyzed alkynylation of aldehydes using trimethylsilylacethylene. Although hotter temperatures were needed, TTMPP effectively activated the C-Si bond of trimethylsilylacethylene, and the reaction proceeded smoothly to afford the corresponding product.

Representative Experimental Procedure

Aldehyde (0.5 mmol) and 1-phenyl-2-trimethylsilylacetylene (0.75 mmol) were added to a solution of TTMPP (0.05 mmol) in DMF (1 mL) at 100°C. After stirring for 8 h, the resultant mixture was quenched with 5% HCl-MeOH. The mixture was extracted with EtOAc, and the organic layer was washed with brine, dried over anhydrous Na_2SO_4, and evaporated. The crude mixture was purified by column chromatography on silica gel (AcOEt–hexane = 1:3) to give the corresponding product.

Selected Data

1,3-Diphenyl-2-propyn-1-ol

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.45 (br, 1H), 5.65 (s, 1H), 7.22–7.30 (m, 6H), 7.36 (m, 2H), 7.60 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 64.6, 84.2, 122.3, 126.6, 128.1, 131.6, 137.5, 140.5.

1-(4′-Methoxyphenyl)-3-phenyl-2-propyn-1-ol

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.35 (br, 1H), 3.83 (s, 3H), 5.62 (s, 1H), 6.90 (d, J = 8.0 Hz, 2H), 7.31 (m, 3H), 7.45 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.2, 64.6, 86.4, 113.9, 122.6, 128.2, 131.6, 133.0, 139.7.

1-Cyclohexyl-3-phenyl-2-propyn-1-ol

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.10–1.42 (m, 5H), 1.50–2.00 (m, 7H), 4.38 (m, 1H), 7.27–7.46 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.8, 26.3, 28.1, 28.5, 44.3, 67.5, 85.5, 89.3, 122.7, 128.1, 131.5.

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