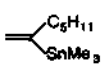
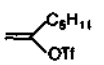
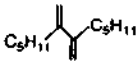
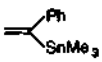
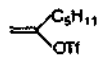
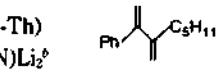
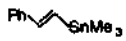
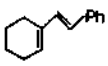
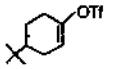
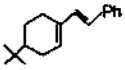
Table 1. Synthesis of Substituted 1,3-Butadienes from Vinyl Triflates and Trimethylstannyl Alkenes

Vinyl stannane	Vinyl triflate	Cyanocuprate	Product	Yield, %[c]
		$Me_2Cu(CN)Li_2$[d]		80
		Me(2-Th) $Cu(CN)Li_2$[b]		76
		$Me_2Cu(CN)Li_2$		62
		Me(2-Th) $Cu(CN)Li_2$		74
		$Me_2Cu(CN)Li_2$		65[d]
		Me(2-Th) $Cu(CN)Li_2$		73[d]
		$Me_2Cu(CN)Li_2$		60[d]

[a] 0.55 equiv was used. [b] The transmetalation was carried out between 0 ℃ and room temperature for 1.5 h. [c] Isolated, chromatographically pure and all the compounds gave satisfactory spectral data. [d] Stereochemically pure by ^1H NMR analysis.

only (1*E*)-1-styryl-4-*tert*-butylcyclohexene.

The typical experimental procedure is as follows. To a solution of copper cyanide (89.6 mg, 1.0 mmol) in THF (2 mL) was added methyllithium (1.40 mL, 1.50 M in diethyl ether, 2.1 mmol) at −20 ℃ under argon. After the reaction mixture was stirred for 20 min between −20° and 0 ℃, the resultant colorless solution was cooled at −78 ℃ and 2-trimethylstannyl-1-heptene (474.2 mg, 1.82 mmol) in THF (2 mL) was added. The temperature rose to 0 ℃ for 0.5 h and 2-trifluoromethanesulfonyloxy-1-heptene (334.7 mg, 1.36 mmol) in THF (2 mL) was added. After 0.5 h, the reaction mixture was quenched with 10% NH_4OH/sat. NH_4Cl (30 mL) and the product was extracted with hexane (3×20 mL). The organic phase was dried over anhydrous $MgSO_4$, filtered, and evaporated to dryness under vacuum. The crude product was purified by silica gel column chromatography (hexane eluent) to give 211.3 mg (80%) of 2,3-dipentyl-1,3-butadiene. bp 85-90 ℃/5.5 mm Hg (Kugelrohr distillation) [lit.[10] 135 ℃/45 mm Hg]; ^1H NMR ($CDCl_3$) δ 4.90 (br s, $2H_{olefin}$), 4.77 (br s, $2H_{olefin}$), 2.10 (t, 4H, J=7 Hz), 1.70-0.95 (m, 12H), 0.80 (t, 6H, J=7 Hz); IR (film) 3030 (=C-H), 2960, 2930, 2865, 1595 (C=C), 890 (1,1-disubstituted), 765 cm^{-1}.

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Aromatization of Hantzsch 1,4-Dihydropyridines with Pyridinium Dichromate

Kwang-Youn Ko* and Jong Yek Park

Department of Chemistry, Ajou University, Suwon 441-749, Korea

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Calcium channel blockers of the 3,5-bis(alkoxycarbonyl)-2,6-dimethyl-1,4-dihydropyridines (**1**, Hantzsch 1,4-DHP) are currently used for the treatment of cardiovascular disease. These compounds undergo oxidative metabolism in the liver to form the pyridine derivatives, which become biologically inactive.[1] In this respect, the convenient preparation of pyridines from 1,4-dihydropyridines is important for the identification of metabolites.

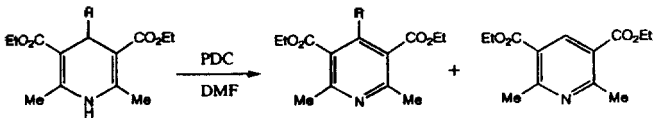
Aromatization of 1,4-DHP has been achieved using various oxidants[2] such as nitric acid,[3] oxygen,[4] HNO_3/bentonite,[5] CrO_3/AcOH,[6] pyridinium chlorochromate (PCC) adsorbed on a solid support,[7] clay-supported cupric nitrate,[8] cerium ammonium nitrate,[9] MnO_2/bentonite[10] or $KMnO_4$.[11] Previously, we reported that pyridinium dichromate (PDC) can be used as an oxidant for the aromatization of 2-pyrrolines.[12] To further illustrate the use of PDC-induced aromatization, the oxidation of Hantzsch 1,4-DHP was investigated in this work.

We found that Hantzsch 1,4-DHP **1**, prepared according to the known procedure,[13] can be oxidized to pyridines **2**

Table 1. Aromatization of 1,4-Dihydropyridines with PDC in DMF[a]

1,4-DHP	R	Pyridines	Yield (%)[b]
1a	phenyl	**2a**	80
1b	3-nitrophenyl	**2b**	79
1c	2-chlorophenyl	**2c**	89
1d	methyl	**2d**	77
1e	*n*-propyl	**2e**	81
1f	isopropyl	**3**	85

[a]molar ratio of 1,4-DHP to PDC=1, DMF, room temperature, 1 hour. [b]yield of isolated, pure product.



1a-f **2a-e** **3**

Scheme 1.

or **3** in good yields by PDC in *N,N*-dimethylformamide (DMF), as shown in Scheme 1.[14,15] The result is summarized in Table 1.[16] As previously noticed by other research groups,[5,7] 1,4-DHP bearing a secondary alkyl group at the 4-position such as **1f** underwent simultaneous dealkylation to give **3**.

Oxidation of 4-aryl-1,4-DHP with solid-supported PCC is reported to take several hours or one day.[7] However, oxidation with PDC was complete within one hour. In conclusion, PDC in DMF solvent can be used as a mild and neutral oxidant for the oxidation of 1,4-DHP.[17]

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14. Oxidation in dichloromethane solvent was sluggish.
15. In a typical experiment, a solution of 330 mg (1.0 mmol) of **1a** (R=phenyl) in 5 mL of dry DMF was treated with 380 mg (1.0 mmol) of PDC under the nitrogen atmosphere and the mixture was stirred at room temperature until TLC showed the absence of **1a** (1 hour). On TLC the product was less polar than **1a**. The mixture was diluted with 50 mL of water and the product was extracted with ethyl acetate (10 mL×3). The combined extract was washed with water, dried and concentrated to give a crude product. Finally, the purification by silica gel column chromatography (hexanes : ethyl acetate=2 : 1) gave 260 mg (80%) of product as a solid, mp 60-61 ℃.
16. **2a**: 60-61 ℃ (Lit.[3] 61-62 ℃), ^{1}H NMR ($CDCl_3$): δ 7.39-7.26 (m, 5H), 4.01 (q, 4H, *J*=7 Hz), 2.61 (s, 6 H), 0.90 (t, 6H, *J*=7 Hz); **2b**: 61-62 ℃ (in *Beilstein* **22** II 127, 63 ℃), ^{1}H NMR ($CDCl_3$): 8.30-8.17 (m, 2H), 7.61-7.52 (m, 2H), 4.05 (q, 4H, *J*=7 Hz), 2.63 (s, 6H), 0.99 (t, 6H, *J*=7 Hz); **2c**: 60-62 ℃ (in *Beilstein* **22** II 127, 62 ℃), ^{1}H NMR ($CDCl_3$): δ 7.44-7.16 (m, 5H), 4.01 (q, 4 H, *J*=7 Hz), 2.65 (s, 6H), 0.91 (t, 6H, *J*=7 Hz); **2d**: oil, ^{1}H NMR ($CDCl_3$): δ 4.40 (q, 4H, *J*=7 Hz), 2.51 (s, 6H), 2.26 (s, 3H), 1.38 (t, 6H, *J*=7 Hz); **2e**: oil, ^{1}H NMR ($CDCl_3$): δ 4.42 (q, 4H, *J*=7 Hz), 2.60-2.54 (m, 2H), 2.52 (s, 6H), 1.64-1.52 (m, 2H), 1.40 (t, 6H, *J*=7 Hz), 0.93 (t, 3H, *J*=7 Hz); **3**: 72-73 ℃ (Lit.[3] 69-69.5 ℃), ^{1}H NMR ($CDCl_3$): δ 8.70 (s, 1H), 4.39 (q, 4H, *J*=7 Hz), 2.85 (s, 6H), 1.41 (t, 6H, *J*=7 Hz).
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