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Palladium(0)-Catalyzed Amination of Allylic Acetate with Methyl Carbamate

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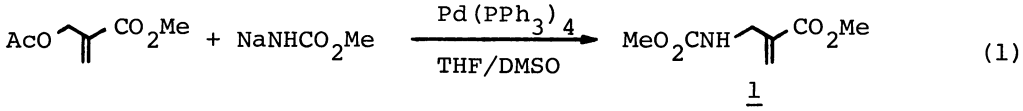
Methyl sodiocarbamate, a recalcitrant nucleophile toward π-allylpalladium intermediate, was found to react with allylic acetates to give allylic carbamates in the presence of a catalytic amount of $Pd(PPh_3)_4$ in THF-DMSO mixed solvent.

Palladium(0)-catalyzed amination of allylic acetates (or phosphates) with secondary amines[1] is an efficient method for the synthesis of tertiary allylamines. The reaction with ammonia or primary amines, however, cannot be applied for the preparation of primary or secondary allylamines, respectively, because the allylamines formed undergo further allylation. Therefore, certain nitrogen nucleophiles[2] toward π-allylpalladium intermediates were proposed to prepare primary or secondary allylamine derivatives, including amides such as p-toluenesulfonamide,[3] phthalimide[4] or di-tert-butyl iminodicarbonate.[5]

In our study of carbamate-directed asymmetric hydrogenation of substituted acrylic esters,[6] we need an α-methylene-β-alanine derivative as a prochiral substrate. In order to prepare methyl 3-(methoxycarbonylamino)-2-methylenepropionate (1),[7] we have found that methyl sodiocarbamate, reportedly unreactive toward π-allylpalladium intermediate,[3b,5] does apply for palladium-catalyzed amination of an allylic acetate in THF-DMSO mixed solvent (Eq. 1).

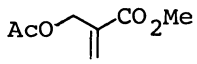
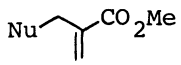
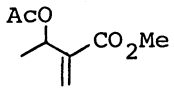
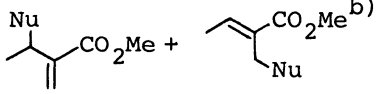
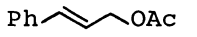
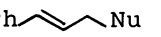
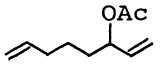
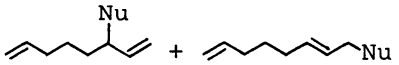
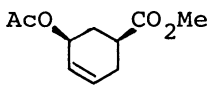
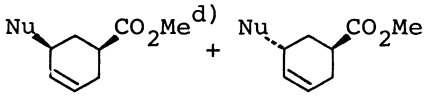


1 (1)

A typical procedure is as follows: To sodium hydride (96 mg, 2 mmol) dispersed in THF (2 mL) and DMSO (2 mL) was added dropwise a THF (2 mL) solution of methyl carbamate (450 mg, 6 mmol) at room temperature and the mixture was stirred for 2 h. The resulting suspension was added to a THF/DMSO (5 mL/2 mL) solution of methyl 3-acetoxy-2-methylenepropionate[8] (316 mg, 2 mmol) and a catalytic amount of $Pd(PPh_3)_4$ (0.1 mmol), and the reaction mixture was stirred under reflux for 30 min. After usual work-up, the product was purified by column chromatography to give 1 in 68% yield (236 mg, 1.36 mmol). Addition of DMSO or HMPA to THF solvent is indispensable presumably because of the solubility of methyl sodiocarbamate.

The reaction was effective for several allylic acetates (Table 1). Thus, methyl sodiocarbamate underwent allylation smoothly at best with mono- or 1,2-disubstituted π-allylpalladium intermediates (entries 1-4), no regioselectivity being observed except for cinnamyl acetate. In entry 5, products were isomeric

Table 1. Palladium(0)-Catalyzed Amination with Methyl Carbamate

Entry	Substrate	Products (Nu=$NHCO_2Me$)	(Ratio)	Yield/%[a]
1				68
2			(56 : 44)	45
3				72
4			(52 : 48)	63
5[c]			(76 : 24)	27[e]

a) Isolated yield after being heated overnight except entry 1. b) Isomerically pure (E) on the basis of NOE of ^1H NMR. C) $Ph_2P(CH_2)_4PPh_2$ (5 mol%) was added. d) Determined by ^1H NMR. e) Major by-product was cyclohexadiene derivatives.

mixture, preferring one with net retention of configuration.

Acetamide anion reacted with cinnamyl acetate to give cinnamyl alcohol, indicating faster attack on the acetate prior to the oxidative addition of the latter to Pd(0). Thus, we observed the borderline nucleophilicity toward π-allylpalladium intermediates with methyl sodiocarbamate.

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