Brief Communications

New versions of Pd^0-catalyzed allylation of C-nucleophiles*

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New "one-pot" protocols proposed for Pd^0-catalyzed allylation of C-nucleophiles involve deprotonation of the corresponding CH acids with *in situ* generated dialkylamide and alkoxide anions.

Key words: allylation, C-nucleophiles, Pd^0 complex.

Palladium-catalyzed allylation of C-nucleophiles is an efficient tool for C—C bonding (see Ref. 1). The most commonly used allylating reagents are allylic acetates. The reaction is usually preceded by generation of the carbanion from a CH acid *via* deprotonation with a base (*e.g.*, NaH). The resulting solution is transferred to a reaction vessel with a separately prepared Pd^0 complex. The use of allyl carbonates,[2] which react with Pd^0 to generate *in situ* a (π-allyl)palladium complex and, simultaneously, an alkoxide anion, allows "one pot" reactions. Here we report on a new version of the "one pot" reaction that involves two parallel catalytic cycles for the formation of a C-nucleophile and a (π-allyl)palladium complex. One cycle is based on the known synthesis of lithium dialkylamides from secondary amines and metallic lithium in the presence of electron acceptors,[3] *e.g.*, α-methylstyrene (Scheme 1). According to the proposed procedure, 10 mol.% of the amine is used. This is converted *in situ* into a dialkylamide, which deprotonates a C—H acid, thus ensuring recycling of the amine. Allylation of diethyl malonate with allyl acetate **1** under these conditions gave diethyl allylmalonate **2** in 65% yield.*

To find out whether it is possible to carry out asymmetric synthesis, we performed allylation of diethyl malonate with acetate **3** in the presence of optically active amine **5**. However, the product **4** obtained in 87% yield exhibited no noticeable optical activity.

For the same purpose, we attempted to modify the aforementioned method[2] by replacing achiral allyl carbonate in this process by optically active compound **6** (under the assumption of possible asymmetric induction during the formation of metal complex **7** in the allylation of prochiral CH acid **8** (Scheme 2)).

This reaction smoothly occurred at 30 °C to give allylic derivative **9** in 85% yield. However, compound **9** was optically inactive.

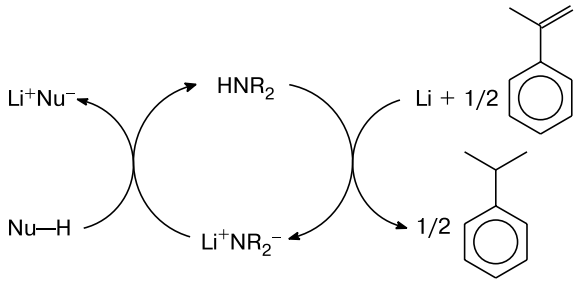
* Dedicated to Academician O. M. Nefedov on the occasion of his 75th birthday.

* In the absence of an amine, diethyl allylmalonate did not form under the conditions studied.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 2024—2026, November, 2006.

1066-5285/06/5511-2103

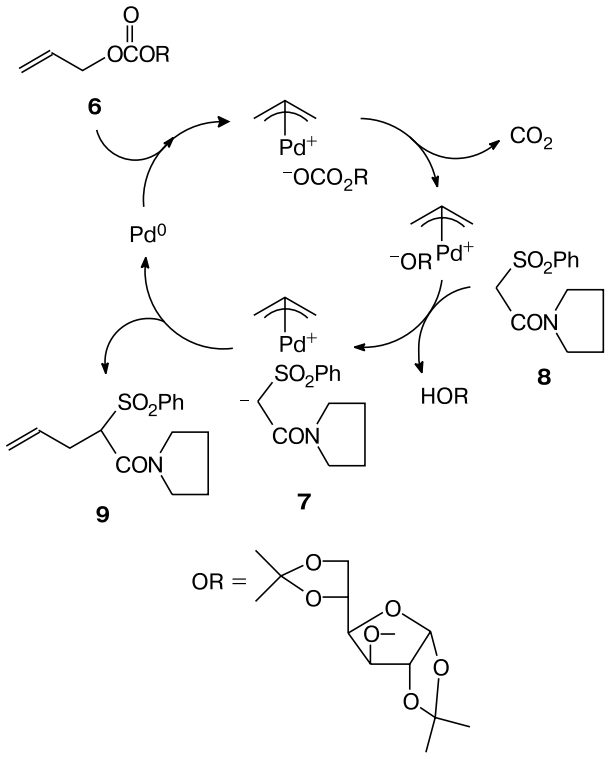
Scheme 1



i. $Pd_2(dba)_3 \cdot CHCl_3$—PPh_3 (1.25 mol.%);
Li — PhC(Me)=CH_2 — HNR_2 (10 mol.%), THF.

Compound	R′	HNR_2
1, **2**	H	$HN(SiMe_3)_2$
3, **4**	Ph	(*R*)-Ph(Me)CHNHSi(Ph)$_2$Bu^t (**5**)

Scheme 2



Experimental

IR spectra were recorded on a Specord M-80 instrument. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-200 spectrometer in $CDCl_3$ with reference to the signals of the solvent. Mass spectra (EI, 70 eV) were recorded on a Finnigan MAT ITD-700 instrument. R_f values were determined on Silufol plates with the fixed SiO_2 layer.

Column chromatography was carried out on Silica gel 60 (0.04—0.06 mm; Fluka).

Solvents were purified and dried according to standard procedures. Light petroleum (b.p. 40—70 °C) was used. The Aldrich chemicals we used were $Pd_2(dba)_3(CHCl_3)$ (dba is dibenzylideneacetone), 1,2,5,6-di-*O*-isopropylidene-α-D-glucofuranose, allyl chloroformate, and TMEDA.

(±)-3-Acetoxy-1,3-diphenylprop-1*E*-ene[4] (**3**) and [*tert*-butyl(diphenyl)silyl][1(*R*)-phenylethyl]amine[5] (**5**) ($[\alpha]_D^{18}$ +70.6 (*c* 1.02, $CHCl_3$)) were prepared according to known procedures.

Diethyl allylmalonate (2). Triphenylphosphine (68 mg, 0.26 mmol) was added at 25 °C to a stirred suspension (argon) of $Pd_2(dba)_3(CHCl_3)$ (27 mg, 0.025 mmol) in THF (4 mL). After 30 min, AllOAc (200 mg, 2 mmol) was added. After 10 min, the following reagents were successively added to the resulting solution in the order of appearance: diethyl malonate (320 mg, 2 mmol), finely sliced Li foil (14 mg, 2 mg-at.), $HN(SiMe_3)_2$ (32 mg, 0.2 mmol), and α-methylstyrene (118 mg, 1 mmol). The reaction mixture was stirred for 5 h, diluted with light petroleum (30 mL), successively washed with water and brine, dried over Na_2SO_4, and concentrated *in vacuo*. Column chromatography of the residue on SiO_2 (10 g) gave 264 mg (65%) diethyl allylmalonate **2** as a colorless oil, R_f 0.44 (light petroleum—EtOAc, 9 : 1). ^1H NMR, δ: 1.28 (t, 6 H, 2 CH_3, J = 7.5 Hz); 2.62 (br.t, 2 H, CH_2, J = 7.2 Hz); 3.38 (t, 1 H, CH, J = 7.2 Hz); 4.20 (q, 4 H, 2 CH_2O, J = 7.5 Hz); 5.00—5.20 (m, 2 H, H_2C=); 5.67 (m, 1 H, HC=) (*cf.* Ref. 6).

(±)-Diethyl (1,3-diphenylprop-2*E*-en-1-yl)malonate (4) was obtained analogously from acetate **3** with the use of amine **5** (5 mol.%). The yield was 87%, a colorless oil, R_f 0.48 (light petroleum—EtOAc, 9 : 1), $[\alpha]_D^{20}$ 0 (*c* 1, $CHCl_3$). ^1H NMR, δ: 1.03, 1.24 (both t, 6 H, 2 CH_3, J = 7.2 Hz); 4.00, 4.21 (both q, 4 H, 2 CH_2O, J = 7.2 Hz); 3.90—4.84 (m, 2 H, CH); 6.30—6.57 (m, 2 H, HC=); 7.30 (m, 5 H, HC_{arom}) (*cf.* Ref. 7).

3-*O*-Allyloxycarbonyl-1,2,5,6-di-*O*-isopropylidene-α-D-glucofuranose (6). A solution of allyl chloroformate (0.53 g, 4.4 mmol) was added at 0 °C for 5 min to a stirred solution (argon) of 1,2,5,6-di-*O*-isopropylidene-α-D-glucofuranose (1.04 g, 4 mmol) and TMEDA (0.28 g, 2.4 mmol) in CH_2Cl_2 (30 mL). The reaction mixture was stirred at 0 °C for 1 h, diluted with CH_2Cl_2, washed with water and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was crystallized from light petroleum to give compound **6** (1.21 g, 88%) as colorless crystals, m.p. 73—75 °C, $[\alpha]_D^{18}$ −36.9 (*c* 2, $CHCl_3$). ^1H NMR, δ: 1.28, 1.32, 1.43, 1.51 (all s, 12 H, 4 CH_3); 4.00—4.30 (m, 4 H); 4.61 (d, 1 H, J = 3.5 Hz); 4.68 (br.d, 2 H, J = 5.1 Hz); 5.14 (d, 1 H, J = 2.6 Hz); 5.30 (br.d, 1 H, H_2C=, J = 9.1 Hz); 5.30 (br.d, 1 H, H_2C=, J = 15.2 Hz); 5.91 (d, 1 H, J = 3.5 Hz); 6.75—6.06 (m, 1 H, HC=) (*cf.* Ref. 8).

***N*-(Phenylsulfonylacetyl)pyrrolidine (8).** Hydrogen peroxide (30%, 5.7 mL, ~50.0 mmol) was added at 20 °C for 5 min to a stirred suspension of *N*-(phenylthioacetyl)pyrrolidine[9] (2.21 g, 10 mmol) in AcOH (15 mL). The reaction mixture was kept at 30 °C for 1 h and at 100 °C for 20 min, cooled to 20 °C, and diluted with water (30 mL). The product was extracted with $CHCl_3$. The extract was washed with water, a saturated solution of $NaHCO_3$, and brine, dried over Na_2SO_4, and concentrated

in vacuo. The residue was chromatographed on SiO_2 with EtOAc as an eluent. The yield of amide **8** was 2.41 g (95%), colorless crystals, m.p. 119—121 °C (EtOAc). Found (%): C, 56.95; H, 6.18; N, 5.55; S, 12.47. $C_{12}H_{15}NO_3S$. Calculated (%): C, 56.90; H, 5.97; N, 5.53; S, 12.66. MS, m/z (I_{rel} (%)): 190 (3), 189 (24), 188 (5), 141 (7), 113 (24), 112 (100), 110 (7), 99 (7), 98 (57), 96 (23), 84 (15), 83 (54), 78 (8), 77 (52), 70 (57), 69 (14), 56 (13), 55 (36). IR (KBr), ν/cm^{-1}: 629, 732, 756, 776, 860, 904—1036, 1084, 1156, 1188, 1232, 1264, 1312, 1324, 1352, 1408, 1440, 1584, 1608, 1648, 2888—2984. ^{1}H NMR, δ: 1.90 (m, 4 H, 2 CH_2); 3.45 (m, 4 H, 2 CH_2N); 3.64 (s, 2 H, CH_2S); 7.25, 7.45 (both m, 5 H, H_{arom}).

***N*-(2-Phenylsulfonylpent-4-enoyl)pyrrolidine (9).** Triphenylphosphine (104 mg, 0.40 mmol) was added at 25 °C to a stirred suspension (argon) of $Pd_2(dba)_3(CHCl_3)$ (52 mg, 0.05 mmol) in THF (3 mL). After 30 min, a solution of allyl carbonate **6** (690 mg, 2 mmol) and sulfone **8** (250 mg, 1 mmol) in THF (4 mL) were added. The reaction mixture was stirred at 30 °C for 1 h, diluted with MeOBu^t (20 mL), and filtered through a short pad of SiO_2. The filtrate was concentrated *in vacuo* and the residue was chromatographed on SiO_2 (25 g) with light petroleum—MeOBu^t (1 : 1) as an eluent. The yield of amide **9** was 250 mg (85%), m.p. 102—104 °C (EtOAc—hexane), $[\alpha]_D^{20}$ 0 (*c* 2, $CHCl_3$). Found (%): C, 61.45; H, 6.74; N, 4.81; S, 10.90. $C_{15}H_{19}NO_3S$. Calculated (%): C, 61.41; H, 6.53; N, 4.77; S, 10.93. MS, m/z (I_{rel} (%)): 293 $[M]^+$ (5), 252 (3), 230 (9), 229 (41), 228 (11), 200 (3), 153 (37), 152 (100), 141 (21), 136 (35), 125 (37), 124 (37), 123 (32), 112 (18), 110 (21), 104 (42), 98 (61), 97 (24), 83 (48), 82 (29), 81 (46), 77 (51), 72 (42), 70 (88), 56 (56), 55 (72). IR (KBr), ν/cm^{-1}: 692, 724, 772, 836, 916, 988, 1040, 1084, 1148, 1288, 1316, 1348, 1440, 1472, 1584, 1648, 2888, 2984. ^{1}H NMR, δ: 1.80—2.04 (m, 4 H, 2 CH_2); 2.60—2.72 (m, 2 H, HC(3)); 3.40, 3.73 (both m, 2 H, CH_2N); 3.73 (t, 2 H, CH_2N, J = 6.7 Hz); 4.16 (dd, 1 H, CHS, J = 5.4 Hz, J = 9.3 Hz); 5.05 (ddd, 1 H, H_2C=C, J = 1.3 Hz, J = 2.5 Hz, J = 10.0 Hz); 5.10 (ddd, 1 H, H_2C=C, J = 1.3 Hz, J = 2.5 Hz, J = 17.0 Hz); 5.64 (dddd, 1 H, HC=C, J = 6.9 Hz, J = 6.9 Hz, J = 10.0 Hz, J = 17.0 Hz); 7.50—7.95 (m, 5 H, H_{arom}).

This work was financially supported by the Russian Foundation for Basic Research (Project No. 06-03-32238).

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Received July 11, 2006