

Decarboxylative Protonation of Allyl Ester Catalyzed by Pt and Ru

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After the Tsuji's brilliant contribution in the area of Pd-catalyzed decarboxylative protonation and allylation,¹ many research groups used the reactions in a variety of synthesis.^{2,3} For decarboxylative protonation, the combination of HCOOH/Et₃N was used most frequently as the hydrogen source.^{1,2} Recently Meldrum's acid^{2a} and water³ have been used as the hydrogen donor. Recently we reported an efficient synthesis of 1,5-dicarbonyl compounds from Baylis-Hillman adducts by using Pd-mediated decarboxylative protonation strategy.³ In the reaction we used aqueous CH₃CN as the reaction medium to provide the hydrogen atom.³

Although many transition metals can form the corresponding π -allylmetal complex,⁴ there was no report involving the use of other metals except palladium in the decarboxylative protonation of allyl ester.¹⁻³ Thus, we decided to examine the feasibility of decarboxylative protonation with **1a**, as a model substrate, which was used in our previous paper.³

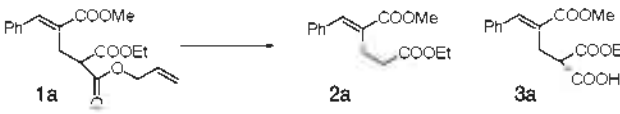
As summarized in Table 1 we examined some metal catalysts which can be easily available commercially. These included four platinum catalysts and two Grubbs catalysts (1st and 2nd generation). Platinum catalysts were all effective in the reactions as in entries 2-4 and 9. However, relatively longer reaction time was required than the Pd-catalyzed reaction (entry 1).³ The use of TPP (triphenylphosphine) was crucial in these reactions.⁵ When we replace TPP into dppe [1,2-bis(diphenylphosphino)ethane], dppp [1,3-bis(diphenylphosphino)propane], *n*-Bu₃P and (*o*-tolyl)₃P, the yield of product was decreased (entries 5-8). The reason is not clear at this moment. It is interesting to note that two Grubbs catalysts were also effective.⁶ However, somewhat elevated temperature was required for the effective reaction in these cases (entries 10 and 11). As in entries 12 and 13, Ni(OAc)₂ and Cu(OAc)₂ were less effective even with 10 mol% of catalyst.

Based on the experimental observations we chose two conditions (entries 4 and 10) as the comparable conditions to the Pd-mediated reaction (entry 1)³ in view of the yield of product and easy availability of the catalyst. Under the selected conditions decarboxylative protonations were examined with **1b** and **1c**, and the results are summarized in Scheme 1. From the reaction of **1b** we isolated decarboxylative protonation product **2b** as the major (75-76%) in all cases. Acid derivative **3b** was isolated in small amounts under Pd- and Pt-catalyzed conditions. Decarboxylative protonation product **2c** was obtained again as the major (74-85%) from the reaction of **1c**. Decarboxylative allylation product **3c** was also obtained in small amounts (5-10%), and compound **4c** was isolated in 11% when we used

Pd as the catalyst. Although the results showed slight differences depending on the catalyst, major products were decarboxylative protonation products in all cases and the yields of them were similar.

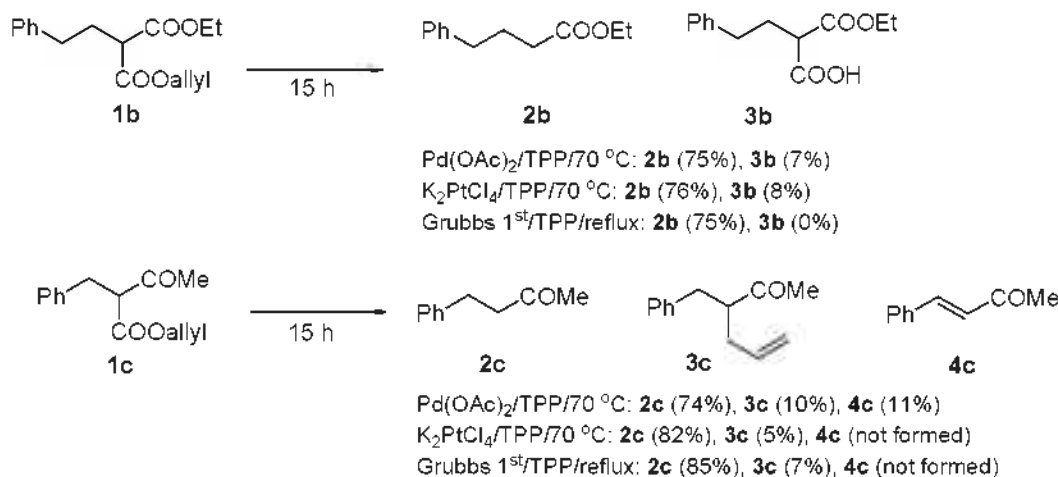
From the comparative studies of **1a-c** with Pd(OAc)₂, K₂PtCl₄, and Grubbs catalyst, decarboxylative protonation reaction could be carried out with either one of the catalysts. Further studies on the application of this condition to different substrates and the synthetic applicability of Grubbs catalyst are currently underway.

Table 1. Decarboxylative protonation of **1a** to **2a** catalyzed by Pt or Ru.^a



Entry	Catalyst (5%)	Ligand (10%)	Time (h)	Yield (%)		
				1a	2a	3a
1 ^{Ref.3}	Pd(OAc) ₂	TPP	2	0	90	0
2	PtO ₂	TPP	13	0	88	0
3	Pt(PPh ₃) ₄	TPP	15	0	90	0
4	K ₂ PtCl ₄	TPP	15	0	90	0
5	K ₂ PtCl ₄	dppe	15	38	53	0
6	K ₂ PtCl ₄	dppp	12	58	31	0
7	K ₂ PtCl ₄	<i>n</i> -Bu ₃ P	12	67	24	0
8	K ₂ PtCl ₄	P(<i>o</i> -tolyl) ₃	15	4	79	10
9	PtCl ₂	TPP	15	6	82	10
10 ^b	Grubbs 1 st	TPP	15	0	80	0
11 ^b	Grubbs 2 nd	TPP	15	0	77	0
12	Ni(OAc) ₂ ^c	TPP	15	36	53	0
13	Cu(OAc) ₂ ^c	TPP	15	34	61	0

^aAll reactions were carried out in the presence of Et₃N (1.2 equiv) in CH₃CN:H₂O (9:1) at 70 °C. ^bReaction was run under refluxing conditions. Grubbs 1st: benzylidene-bis(tricyclohexylphosphine) dichlororuthenium. Grubbs 2nd: 1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolylidene) dichloro(phenylmethylene)(tricyclohexylphosphine) ruthenium. ^cCatalyst 10%.



Scheme 1

References and Notes

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- Without TPP the reactions with PtO_2 , Grubbs catalysts, $\text{Ni}(\text{OAc})_2$ and $\text{Cu}(\text{OAc})_2$ were very sluggish. However, appreciable amounts of product was formed with $\text{Pd}(\text{OAc})_2$, $\text{Pt}(\text{PPh}_3)_4$, K_2PtCl_4 and PtCl_2 without TPP.
- For Ru-catalyzed deallylation, see: (a) Alcaide, B.; Almendros, P.; Alonso, J. M. *Chem. Eur. J.* **2006**, *12*, 2874-2879. (b) Alcaide, B.; Almendros, P.; Alonso, J. M. *Tetrahedron Lett.* **2003**, *44*, 8693-8695. (c) Tanaka, S.; Saburi, H.; Kitamura, M. *Adv. Synth. Catal.* **2006**, *348*, 375-378. (d) Tanaka, S.; Hirakawa, T.; Oishi, K.; Hayakawa, Y.; Kitamura, M. *Tetrahedron Lett.* **2007**, *48*, 7320-7322. (e) Saburi, H.; Tanaka, S.; Kitamura, M. *Angew. Chem. Int. Ed.* **2005**, *44*, 1730-1732. (f) Tanaka, S.; Saburi, H.; Murase, T.; Ishibashi, Y.; Kitamura, M. *J. Organometal Chem.* **2007**, *692*, 295-298.
- Typical procedure for the synthesis of **2a** (entry 4): To a stirred solution of **1a** (173 mg, 0.5 mmol), K_2PtCl_4 (11 mg, 5 mol%), PPh_3 (14 mg, 10 mol%) in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (3 mL, 9:1) was added Et_3N (61 mg, 0.6 mmol) and the reaction mixture was heated to $70\text{ }^\circ\text{C}$ for 15 h. After usual aqueous workup and column chromatographic purification process (hexanes/ether, 95:5) compound **2a** was isolated as colorless oil, 118 mg (90%).³ Other compounds were synthesized similarly and the representative spectroscopic data of **1b**, **1c**, and **3c** are as follows.
 Compound **1b**: colorless oil; IR (film) 2939, 1752, 1734 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 1.27 (t, $J = 7.2$ Hz, 3H), 2.20-2.28 (m, 2H), 2.64-2.69 (m, 2H), 3.38 (t, $J = 7.5$ Hz, 1H), 4.21 (q, $J = 7.2$ Hz, 2H), 4.62-4.65 (m, 2H), 5.22-5.36 (m, 2H), 5.84-5.97 (m, 1H), 7.17-7.34 (m, 5H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 14.07, 30.34, 33.29, 51.20, 61.43, 65.85, 118.58, 126.20, 128.45, 128.52, 131.59, 140.57, 169.00, 169.16.
 Compound **1c**: colorless oil; IR (film) 3030, 1743, 1716 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 2.18 (s, 3H), 3.17 (d, $J = 7.8$ Hz, 2H), 3.86 (t, $J = 7.8$ Hz, 1H), 4.56-4.59 (m, 2H), 5.18-5.27 (m, 2H), 5.75-5.88 (m, 1H), 7.14-7.29 (m, 5H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 29.58, 33.89, 61.10, 65.86, 118.78, 126.60, 128.48, 128.68, 131.29, 137.93, 168.64, 202.13.
 Compound **3c**: colorless oil; IR (film) 2924, 1712 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 1.99 (s, 3H), 2.17-2.26 (m, 1H), 2.31-2.41 (m, 1H), 2.66-2.75 (m, 1H), 2.85-2.95 (m, 2H), 5.02-5.09 (m, 2H), 5.65-5.79 (m, 1H), 7.13-7.30 (m, 5H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 30.48, 35.65, 37.32, 54.14, 117.20, 126.30, 128.45, 128.84, 135.09, 139.37, 211.45.