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Palladium-Catalyzed Reaction of Propargylic Acetates with Carbonyl Compounds by SmI_2(1)

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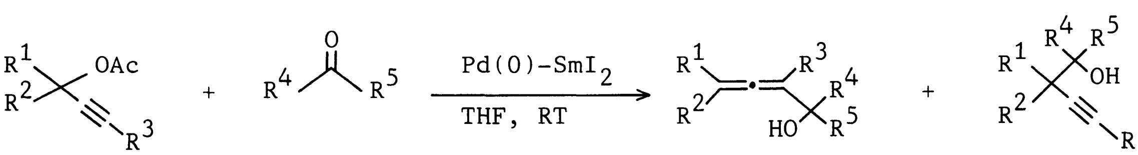
Reductive addition of propargylic acetates to carbonyl compounds proceeded smoothly at room temperature by using SmI_2 and a catalytic amount of $Pd(PPh_3)_4$ to give the corresponding acetylenic and/or allenic alcohols with appreciable selectivity. The method is useful especially for the preparation of tri- and tetrasubstituted allenic alcohols.

Palladium-catalyzed displacement of allylic compounds with carbonucleophiles is a well-established procedure and a widely used synthetic tool for the formation of C-C bonds.(2) In contrast to the extensive studies on the allylic systems, very few studies have been carried out on the palladium-catalyzed reactions of propargylic compounds.(3) Although the oxidative addition of propargylic acetates to Pd(0) is known to occur equally well as that of allylic acetates, the resulting allenyl palladium intermediates do not react with stabilized carbanions such as sodium dimethyl malonate, and have only a limited usefulness as electrophilic allenylating agents.(3b,4) We recently found that successive transfer of two electrons from SmI_2 to allenyl palladium species can easily convert them into the corresponding nucleophilic organosamarium derivatives under mild conditions.(5,6)

In this paper we wish to report a novel reductive addition of propargylic acetates to carbonyl compounds. (Scheme 1)



Scheme 1.

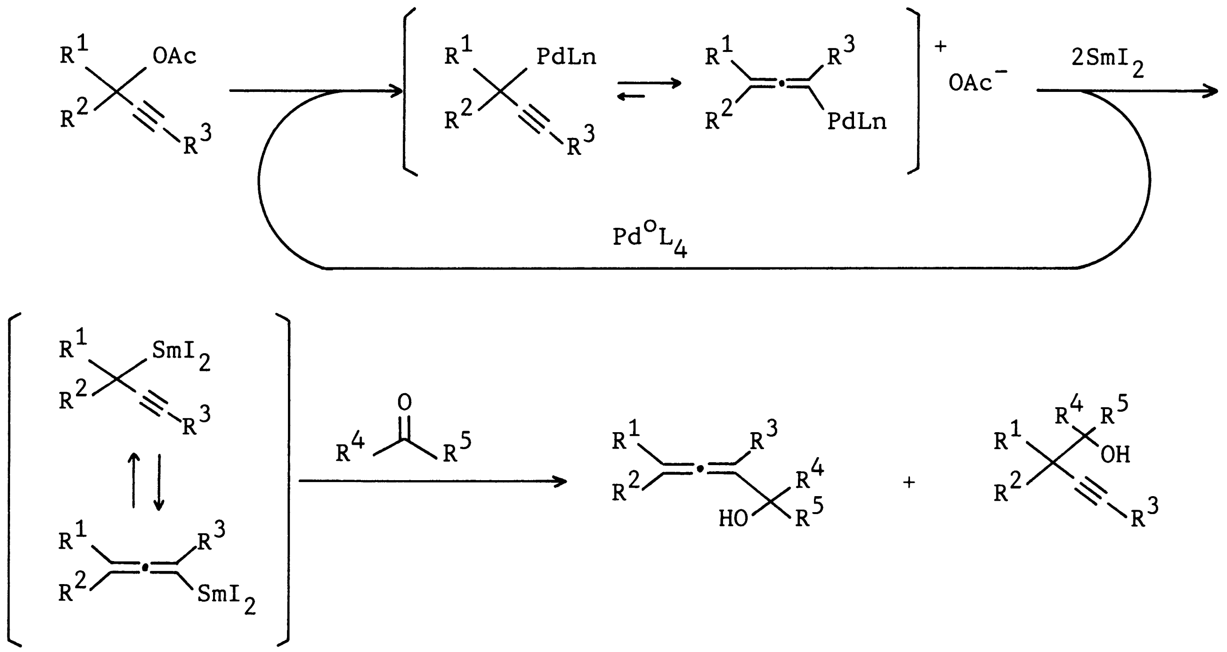
For a typical experiment: To a mixture of 3-butyn-2-yl acetate (12.3 mg, 0.11 mmol), cyclododecanone (18.2 mg, 0.1 mmol), and 5 mol% of $Pd(PPh_3)_4$ in THF (2 ml) was added a SmI_2-THF solution(7) (0.1 mol dm^{-3}, 2 ml) and the mixture was stirred at room temperature for 6 h under an atmosphere of nitrogen. Usual workup followed by chromatographic purification (silica gel) gave 1-(1,2-butadienyl)-

cyclododecanol (18.4 mg, 78%) as an oil. (Run 5 in Table 1)

Other examples are also shown in Table 1. Similar to the allene-acetylene selectivity observed on the palladium-catalyzed reduction of propargylic acetates by SmI_2,[5] the present C-C bond formation also took place at sterically less hindered site thus affording only allenic alcohols from sec-acetates with terminal acetylene (Runs 5 and 6) or tert-acetates (Runs 7 - 9), and a mixture of allenic and homopropargylic alcohols in varing ratios in primary cases. Aldehydes could be used only for relatively reactive propargylic acetates (e.g., Run 10) because of their tendency to form pinacols rapidly.[8]

Interestingly, Pd(II), Ni(II), or even Co(II) salts were found to be effective as a catalyst, though the yields were not always satisfactory.[9]

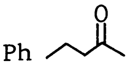
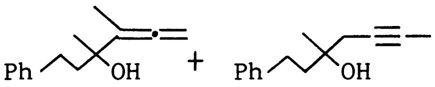
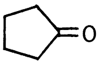
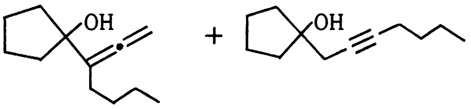
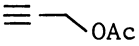
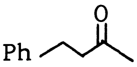
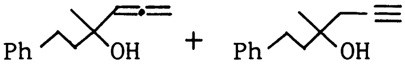
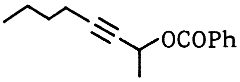
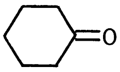
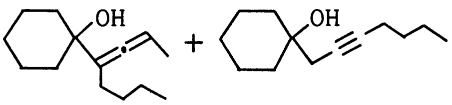
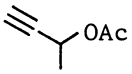
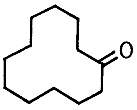
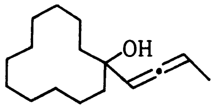
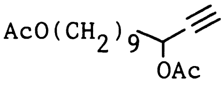
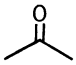
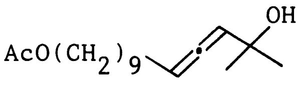
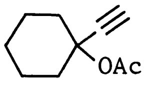
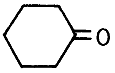
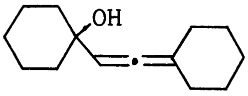
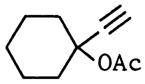
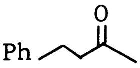
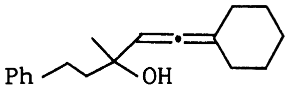
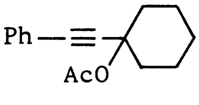
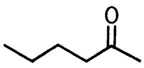
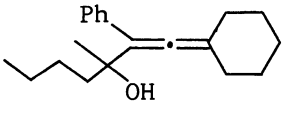
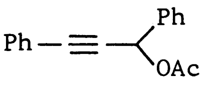
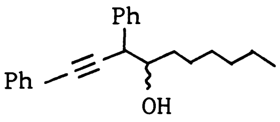
Mechanistically, as discussed in the previous paper,[5] "allenic carbanion" generated by Pd(0)-SmI_2 system is assumed to exist as an equilibrating mixture of allenic and propargylic samarium, which combine with carbonyl compounds via S_E2' (or S_E2) pathways to afford homopropargylic and allenic alcohols (Scheme 2). As such the equilibration is considered to be very rapid, the product distribution is consequently determined by relative rates of their additions to carbonyl compounds. Both the steric bulk of the electrophile and substitution pattern on the organosamarium species have thus been found to influence the regiochemical outcome of the present reaction.



Scheme 2.

Although a number of allenic and propargylic organometal derivatives, such as Li, Mg, Al, Si, Ti, Zn, or Cd have been known,[10] addition reaction of these organometallics to carbonyl compounds usually gives a mixture of regioisomeric alcohols in low to moderate selectivity except for titanium[11] and silicon derivatives.[12] Furthermore, such organometallic derivatives had usually been

Table 1. Palladium-Catalyzed Reaction of Propargylic Esters with Carbonyl Compounds by SmI$_2$$^{a)}$

Run	Proparbylic ester	Carbonyl compound	Reaction time/h	Product (ratio)$^{b)}$	Yield/%$^{c)}$
1			6	 (25 : 75)	83
2			6	 (25 : 75)	51
3			6	 (45 : 55)	85
4			6	 (85 : 15)	53
5			6		78
6			6		46
7			6		56
8			6		82
9			3		61
10			2 d)	 e)	62

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a) Reactions were carried out by using propargylic esters (0.11 – 0.22 mmol), carbonyl compounds (0.1 – 0.2 mmol), 5 mol% of Pd(PPh$_3$)$_4$, and a SmI$_2$-THF solution (0.1 mol dm^{-3}, 2.5 – 5 ml) at room temperature, unless otherwise stated. b) Determined by ^{1}H NMR (400 MHz) analysis. c) Isolated total yield. Regioisomers could be separated by column chromatography on silica gel. d) 1 mol% of catalyst was used. e) Isomeric ratio was not determined.

prepared from allenes or acetylenes by using strong bases or from propargyl halides which are less conveniently prepared and handled than the corresponding acetates because of their instability.

The present mild and convenient one-pot C-C bond-formation accompanied with high allene-selectivity seems to be practically useful for the synthesis of tri- and tetrasubstituted allenic alcohols, which are not easily accessible by the conventional methods.[10)]

References

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2) For recent reviews, see: J. Tsuji, "Organic Synthesis with Palladium Compounds," Springer-Verlag, Berlin (1980); B. M. Trost, Acc. Chem. Res., 13, 385 (1980); J. Tsuji, Pure Appl. Chem., 54, 197 (1982); R. F. Heck, "Palladium Reagents in Organic Synthesis," Academic Press (1985).
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4) It has also been reported that proparglic carbonates undergo palladium-catalyzed nucleophilic substitution by 1,3-dicarbonyl compounds at 60-80 °C; see Ref. 3a.
5) T. Tabuchi, J. Inanaga, and M. Yamaguchi, Tetrahedron Lett., 27, 5237 (1986).
6) For applications of the Pd(0)-SmI_2 system to allylic acetates, see: T. Tabuchi, J. Inanaga, and M. Yamaguchi, Tetrahedron Lett., 27, 601, 1195 (1986), and 28, 215 (1987).
7) P. Girard, J. L. Namy, and H. B. Kagan, J. Am. Chem. Soc., 102, 2693 (1980).
8) Aldehydes and α,β-unsaturated ketones usually gave self-coupling products predominantly. See J. L. Namy, J. Souppe, and H. B. Kagan, Tetrahedron Lett., 24, 765 (1983).
9) For example, SmI_2-induced coupling reaction of 3-butyn-2-yl acetate with cyclododecanone was carried out at room temperature in the presence of 5 mol% of $PdCl_2$ (6 h), $NiCl_2$ (6 h), or $CoCl_2$ (10 min) with the combination of 4 equiv. of PPh_3 to give the corresponding allenic alcohol in 63, 45, or 26% yield, respectively. (Cf. Run 5 in Table 1)
10) R.Epsztein, "The Formation and Transformations of Allenic-acetylenic Carbanions," in "Comprehensive Carbanion Chemistry," ed by E. Buncel and T. Durst, Elsevier Science, New York (1984), Part B, Chap. 3, p. 107.
11) Regio- and stereocontrolled synthesis of allenic and acetylenic alcohols using propargylic titanium reagents has been reported, though the allene-selectivity was observed only in such cases that alcohols having terminal allene moiety were produced: See M. Ishiguro, N. Ikeda, and H. Yamamoto, J. Org. Chem., 47, 2225 (1982).
12) A regiocontrolled synthesis of homopropargylic alcohols was realized by using (trimethylsilyl)allenes in the presence of $TiCl_4$: See R. L. Danheiser, D. J. Carini, and C. A. Kwasigroch, J. Org. Chem., 51, 3870 (1986).

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