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PALLADIUM-CATALYZED REDUCTION OF PROPARGYLIC ACETATES WITH SmI_2. A MILD AND CONVENIENT METHOD FOR THE PREPARATION OF ALLENES[1)]

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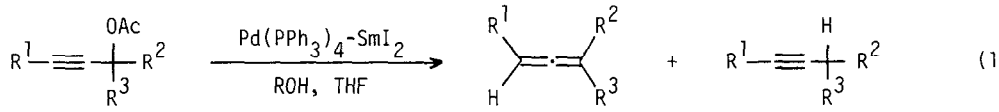
Summary: A highly regioselective reduction of propargylic acetates has been attained by using SmI_2 and catalytic Pd(0) in the presence of 2,4-dimethyl-3-pentanol affording various types of allenes in high yields.

Allenes not only constitute an important class of natural products but also serve as useful intermediates in organic synthesis.[2a-c)] Although numerous methods have been known for the synthesis of allenes, reduction of propargylic halides, ethers, or esters with the conventional reducing agents such as $LiAlH_4$,[3)] Mg,[4)] Zn,[5)] $CrCl_2$,[6)] or organocuprates[7)] usually affords a mixture of allenes and acetylenes in varying ratios, except for the selective formation of terminal allenes from propargylic compounds having terminal triple bonds,[8)] and only a few methods, including nucleophilic addition to propargylic compounds, have so far been reported to obtain internal allenes with high regioselectivity.[2a,b),9)]

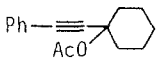
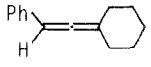
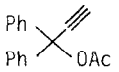
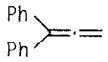
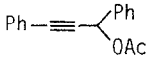
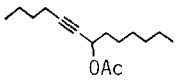
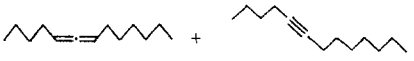
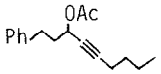
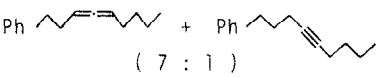


Recently, we reported that allylic acetates could be reduced by SmI_2 in the presence of alcohol and catalytic Pd(0).[10)] In the present study, it is shown that the same Pd(0)-SmI_2-alcohol system is also effective in reducing propargylic acetates through polarity inversion of cationic allenylpalladium intermediates,[11)] thus providing a mild and convenient method for the preparation of mono-, di-, and trisubstituted allenes (eq 1).

In Table 1 is shown the reduction of various propargylic acetates to allenes and acetylenes in high yield, with propanol as a proton source. Allene-acetylene ratios were greatly dependent on the substitution pattern of the substrates: tert-Acetates yielded allenes exclusively (Run 1 and 2), whereas the allene-selectivity was decreased in cases of sec-acetates (Runs 3-5) and was even reversed in the case of prim-acetate (Run 6).

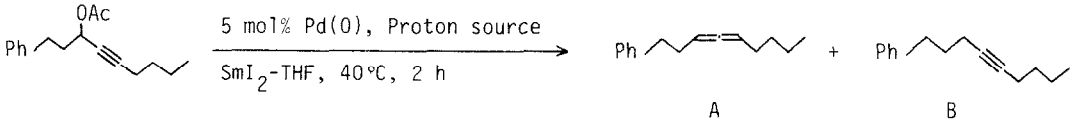
In Table 2 is shown the effect of proton source on allene-acetylene selectivity in the reduction of a sec-acetate. Interestingly, the more sterically crowded alcohols gave the higher allene-selectivity. Thus, a highly selective synthesis of disubstituted internal allene was attained by using 2,4-dimethyl-3-pentanol as a proton source (Run 8). Additional examples of the reduction under the conditions are summarized in Table 3. A terminal allene could also be obtained with satisfactory selectivity when an acetate with a terminal acetylene was employed (Run 2). On the other hand, acetylene-selectivity was rather promoted in the case of prim-acetate (cf. Run 3 of the Table with Run 6 in Table 1). (Trimethylsilyl)allenes which have recently been shown to be useful intermediates especially for the synthesis of 5-membered carbocycles[12)], could be prepared by the present method, but

Table 1. Reduction of Propargylic Acetates in the Presence of 2-Propanol[a)]

Run	Propargylic acetate	$Pd(PPh_3)_4$	Temp, Time	Product[b)] (ratio)[c)]	Yield (%)[d)]
1		2 mol%	rt, 2 h		90
2		1 mol%	rt, 2 min		95
3		2 mol%	rt, 0.5 h	 (16 : 1)	93
4		5 mol%	40°C, 2 h	 (11 : 1)	90
5		5 mol%	40°C, 2 h	 (7 : 1)	85
6	$CH_3(CH_2)_{17}C{\equiv}CCH_2OAc$	5 mol%	65°C, 1 h	$CH_3(CH_2)_{17}CH{=}C{=}CH_2$ + $CH_3(CH_2)_{17}C{\equiv}CCH_3$ (1 : 1.3)	88

a) To a solution of propargylic acetates (0.1 mmol), 2-propanol (0.11 mmol), and a catalytic amount of $Pd(PPh_3)_4$ in THF (1 ml) was added a SmI_2-THF solution (0.1 mol dm^{-3}, 2.5 ml, 0.25 mmol) under an atmosphere of nitrogen. b) Satisfactory ^1H NMR, IR, and analytical data were obtained. c) Determined by GLC and/or ^1H NMR analyses. d) Isolated yield.

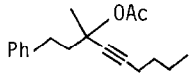
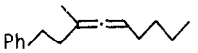
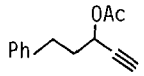
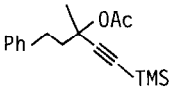
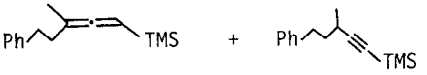
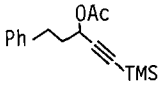
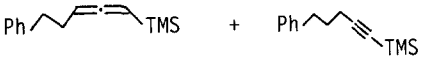
Table 2. Effect of Proton Source on the Allene-Acetylene Selectivity[a)]



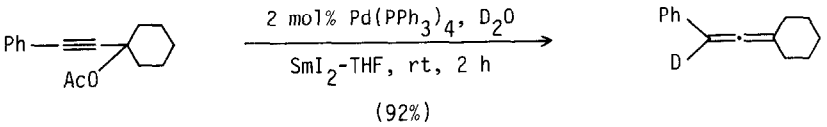
Run	Proton source	A : B	Run	Proton source	A : B
1	H_2O	1 : 1.5	5	PhOH	9 : 1
2	CH_3OH	2 : 1	6	$(CH_3)_3COH$	15 : 1
3	$(CH_3)_2CHCO_2H$	3 : 1	7	Ph_3COH	17 : 1
4	$(CH_3)_2CHOH$	7 : 1	8	$(CH_3)_2CHCH(OH)CH(CH_3)_2$	20 : 1

a) Ratios were determined by GLC analysis.

Table 3. Reduction Using 2,4-Dimethyl-3-pentanol as a Proton Source[a)]

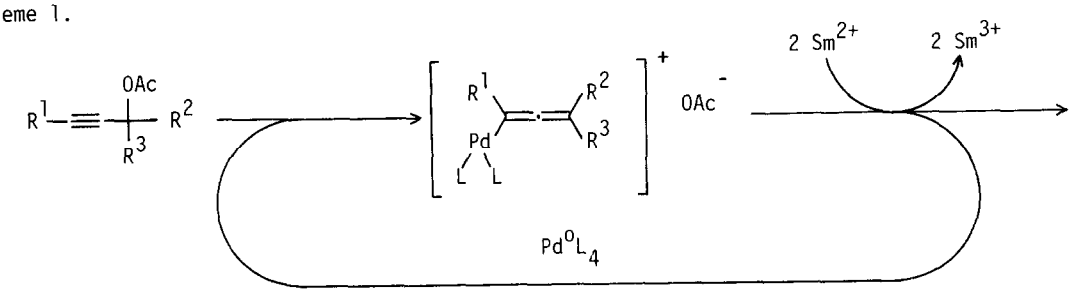
Run	Propargylic acetate	Product (ratio)[b)]	Yield (%)[c)]
1			96
2		 (17 : 1)	75
3	$CH_3(CH_2)_{17}C{\equiv}CCH_2OAc$	$CH_3(CH_2)_{17}C{=}C{=}CH_2$ + $CH_3(CH_2)_{17}C{\equiv}CCH_3$ (1 : 3)	88
4		 (6 : 1)	82
5		 (5 : 2)	76

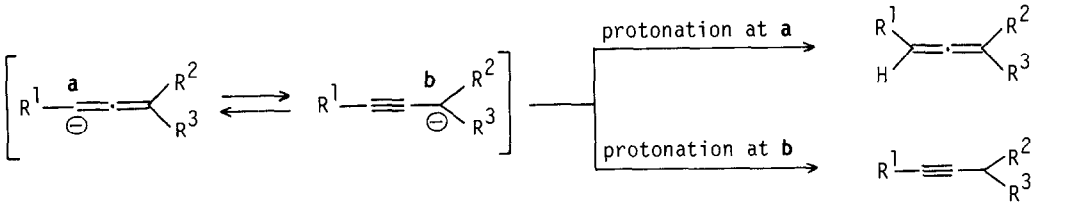
a) The reactions were carried out by using propargylic acetates (0.1 mmol), $Pd(PPh_3)_4$ (5 mol%), 2,4-dimethyl-3-pentanol (0.11 mmol), and a SmI_2-THF solution (0.1 mol dm^{-3}, 2.5 ml) at 40°C for 2 h. b) Determined by GLC and/or ^1H NMR analysis. c) Isolated yield.



(2)

Scheme 1.



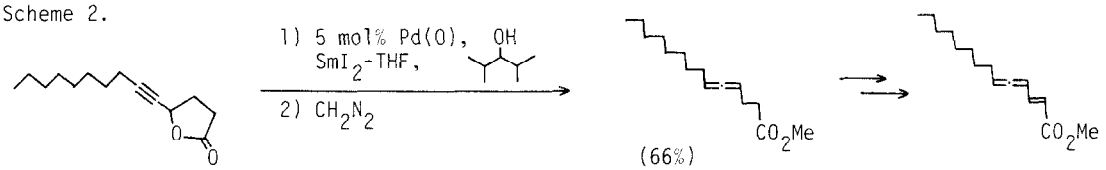


with moderate selectivity.

When D_2O was used as a proton source, only a deuterated allene was obtained (eq 2), the fact indicating an intervention of anion species. A possible mechanism for the present reduction is proposed in scheme 1, which may explain all the experimental results including the allene-acetylene selectivity: Oxydative addition of Pd(0) to a propargylic acetate forms a 1,2-propadienylpalladium acetate[11] which accepts two electrons from SmI_2 releasing Pd(0) to be recycled and an allenic anion.[8] Thus, in cases of sec- or tert-acetates (R^2=alkyl, R^3=H or R^2=R^3=alkyl, respectively), the protonation occurs at the sterically less-hindered carbon atom **a** to give allenes, while prim-acetates (R^2=R^3=H) produce acetylenes preferably through the protonation at the carbon atom **b**.

An application of the present method to a pheromone synthesis is demonstrated in Scheme 2. A propargylic γ-lactone[13] was reduced at 40°C for 2 h and then methylated

Scheme 2.



affording 66% yield of the allenic ester as a single product, which had already been converted to the pheromone of the male dried bean beetle by Mori et al.[14]

References and Notes

1) Presented at the 52th National Meeting of the Chemical Society of Japan, Kyoto, Apr 1986. 2) Reviews for syntheses and reactions of allenes: a) H.F.Schuster and G.M.Coppola, "Allenes in Organic Synthesis", Wiley-Interscience, New York (1984); b) D.J.Pasto, Tetrahedron, **39**, 2805 (1983); c) W.Smadja, Chem. Rev., **83**, 263 (1983). 3) A.Claesson and L-I.Olsson, J. Am. Chem. Soc., **101**, 7302 (1979). The reduction of propargylic quaternary ammonium salts was reported to produce allenes exclusively. 4) J.H.Ford, C.D.Thompson, and C.S.Marvel, ibid., **57**, 2619 (1935). 5) M.Biollaz, W.Haefliger, E.Velarde, P.Crabbe, and J.H.Fried, J. Chem. Soc., Chem. Commun., **1971**, 1322. 6) B.Cazes, C.Verniere, and J.Gore, Tetrahedron Lett., **23**, 3501 (1982). 7) C.Sahlberg and A.Claesson, J. Org. Chem., **49**, 4120 (1984) and references cited therein. 8) Protonation of internal "allenic carbanions" has been known to produce allenes and acetylenes in varying ratios (mainly allenes) depending on the mode of substitution, counter cations, and proton sources: See R.Epsztein, "The Formation and Transformations of Allenic-α-acetylenic Carbanions," in "Comprehensive Carbanion Chemistry," ed by E.Buncel and T.Durst, Elsevier Science, New York (1984), Part B, Chap. 3, p. 107. 9) T.Takeda, K.Suzuki, H.Ohshima, and T.Fujiwara, Chem. Lett., **1985**, 1249 and references cited therein. 10) T.Tabuchi, J.Inanaga, and M.Yamaguchi, Tetrahedron Lett., **27**, 601 and 1195 (1986). 11) For recent studies of palladium-catalyzed reactions of propargyl compounds: See C.J.Elsevier, H.Kleijn, J.Boersma, and P.Vermeer, Organomet., **5**, 716 (1986); J.Tsuji, H.Watanabe, I.Minami, and I.Shimizu, J. Am. Chem. Soc., **107**, 2196 (1985). 12) R.L.Danheiser, D.J.Carini, D.M.Fink, and A.Basak, Tetrahedron, **39**, 935 (1983). 13) R.E.Doolittle, J.H.Tumlinson, A.T.Proveaux, and R.R.Heath, J. Chem. Ecol., **6**, 473 (1980). 14) K.Mori, T.Nukada, and T.Ebata, Tetrahedron, **37**, 1343 (1981).

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