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REDUCTION OF ALLYLIC ACETATES BY USING A NOVEL Pd(0)-SmI_2 SYSTEM

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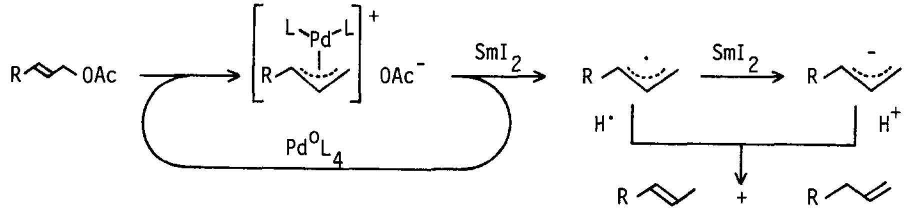
Summary: Allylic acetates were reduced to alkenes in high yields with SmI_2 and 2-propanol in the presence of a catalytic amount of palladium(0) complex.

Reduction of π-allyl palladium complexes have been known to produce C-H bond by using (1) ammonium formate in refluxing dioxane,1) (2) hydride reagent such as $NaBH_4$, $NaBH_3CN$,2a) or $LiBHEt_3$,2b) (3) tributyltin hydride,3) (4) alkylzinc derivatives bearing β-hydrogens,4) (5) NAD(P)H model,5) (6) polymethylhydrosiloxane,6) or (7) Pb cathode and Pt anode.7)

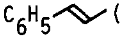
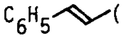
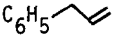
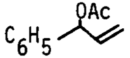
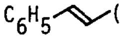
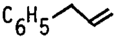
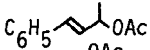
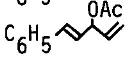
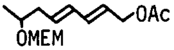
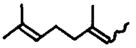
Here we wish to report a new entry for the reduction of allylic acetates by using a novel system containing a Pd(0) complex and SmI_2, the latter having been reported to be a one electron transfer agent.8) Various kinds of allylic acetates could be reduced cleanly to alkenes with 1 eq of 2-propanol and 2 eq of SmI_2 in the presence of 1-5 mol% of $Pd(PPh_3)_4$. The results are listed in the Table. No reaction occurred in the absence of Pd(0). It is noteworthy that $PdCl_2$ or $Pd(OAc)_2$ can be used with PPh_3 instead of $Pd(PPh_3)_4$, indicating that SmI_2 produces Pd(0) species in situ (entry 2). The regiochemistry of the double bonds produced by this reaction appears to depend greatly on the substrates used. Thus, in one example, terminal diene was isolated exclusively (entry 7) and geranyl acetate produced (E)-2-olefin with high regio- and stereoselectivity9) (entry 8), whereas modest selectivity was observed on other systems studied. As expected, optical activity in carvyl acetate (p-mentha-6,8-dien-2-yl acetate) was completely lost in the product (entry 6).

The mechanism of the reaction is not clear, but it is likely that both allylic radical and anion species are involved in the present reduction as schematized below.10)



Thus, in this study the polarity inversion of the electrophilic π-allyl palladium complexes11) to nucleophilic species was realized with the aid of SmI_2. Further applications of this system to other reactions are in progress.

Table. Reduction of Allylic Acetates by Using Pd(0)-SmI_2 System.[a)]

Entry	Allylic acetate	Reaction time (h)	Product[b)] (ratio)[c)]	Yield[d)] (%)
1	cinnamyl acetate	1	 (20),  (80)	quant.
2[e)]	cinnamyl acetate	1	 (20),  (80)	quant.
3		1	 (20),  (80)	quant.
4		1	 (83),  (17)	(81)
5		1	 (43),  (7),  (50)	(88)
6[f)]	(-)-carvyl acetate[g)]	8[h)]	(±)-limonene[i)]	81
7[f)]		2	 j)	(79)
8[f)]	geranyl acetate	2[h)]	 (93),(E/Z=95/5)[k)],  (7)	92
9[f)]	neryl acetate	2[h)]	 (85),(E/Z=11/89)[k)],  (15)	95

a) *Unless otherwise mentioned, the reaction was carried out at room temperature in THF with* allylic acetate-SmI_2-2-propanol (1:2:1) in the presence of 1 mol% of $Pd(PPh_3)_4$. b) All products gave satisfactry ^1H NMR spectra and/or the same retention times as those of the authentic samples. c) Determined by GLC and/or ^1H NMR analyses. A wavy line indicates that the E/Z ratio was not determined. d) Determined by GLC. Isolated yields are given in parentheses. e) 1 mol% of $PdCl_2$ and 4 mol% of PPh_3 was used in place of $Pd(PPh_3)_4$. f) 5 mol% of $Pd(PPh_3)_4$ was used. g) $[\alpha]_D^{25}$ -52.8° (c 1.00, MeOH). h) At refluxing temperature. i) $[\alpha]_D^{25}$ 0°. j) No other regioisomer was detected. k) Determined by ^{13}C NMR (see ref. 4).

References and Notes

1) J.Tsuji and T.Yamakawa, Tetrahedron Lett., **1979**, 613. 2) a) R.O.Hutchins, K.Learn, and R.P.Fulton, Tetrahedron Lett., **21**, 27 (1980). b) R.O.Hutchins and K.Learn, J. Org. Chem., **47**, 4380 (1982). 3) E.Keinan and N.Greenspoon, Tetrahedron Lett., **23**, 241 (1982).
4) H.Matsushita and E.Negishi, J. Org. Chem., **47**, 4161 (1982). 5) K.Nakamura, A.Ohno, and S.Oka, Tetrahedron Lett., **24**, 3335 (1983). 6) E.Keinan and N.Greenspoon, J. Org. Chem., **48**, 3545 (1983). 7) S.Torii, H.Tanaka, T.Katoh, and K.Morisaki, Tetrahedron Lett., **25**, 3207 (1984). 8) a) For examples of the reducing ability of SmI_2 and its application to organic syntheses, see: P.Girard, J.L.Namy, and H.B.Kagan, J. Am. Chem. Soc., **102**, 2693 (1980); J.Souppe, J.L.Namy, and H.B.Kagan, Tetrahedron Lett., **25**, 2869 (1984) and references cited therein; T.Imamoto, T.Takayama, and M.Yokoyama, Tetrahedron Lett. **25**, 3225 (1984). b) For a mechanistic study, see: H.B.Kagan, J.L.Namy, and P.Girard, Tetrahedron, **37**, Suppl. No 1, 175 (1981). 9) The reported ratios of 1- : 2-olefin in the reduction of geranyl acetate are 94:6 (ref. 1), 58:42 (ref. 2a), 3:97 (ref. 4), and 48:52 (ref. 6). 10) A reduction of cinnamyl bromide with SmI_2 in the presence of methanol gave a mixture of β-methylstyrene and 3-phenyl-1-propene in 1:9 ratio. In the absence of methanol, this reaction has been known to afford radical coupling products, exclusively (Girard et al. in ref. 8a). On the other hand, in the present reduction (entry 1 in the Table) a similar ratio (2:8) was obtained, but almost no coupling products were produced in the absence of 2-propanol. Protonation of cinnamyl Grignard reagent also gave a mixture of β-methylstyrene and 3-phenyl-1-propene (4:3). In electroreduction system, two electron transfer process to form allylic anion has been proposed (ref. 5). For the mechanistic discussion of the Pd(0) catalized reductions of allylic acetates; see ref. 2b. 11) For a review: J.Tsuji, Organic Synthesis with Palladium Compounds, Springer-Verlag, Heidelberg (1980).

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