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REDUCTIVE COUPLING OF ALLYLIC ACETATES WITH CARBONYL COMPOUNDS BY USING Pd(0)-SmI_2 SYSTEM

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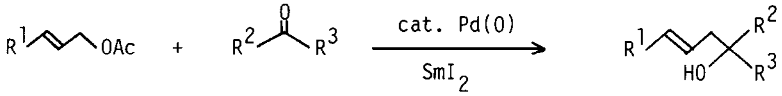
Summary: Reductive coupling of allylic acetates with carbonyl compounds proceeded by SmI_2 in the presence of catalytic Pd(0) to yield homoallylic alcohols.

In a previous paper we reported the Pd(0)-catalyzed reduction of allylic acetates with SmI_2 and 2-propanol.1) Now we found that allylic acetates can be coupled with carbonyl compounds to give homoallylic alcohols in good yields by the same combination of SmI_2 and catalytic Pd(0).



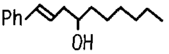
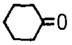
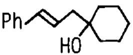
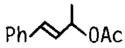
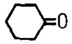
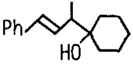
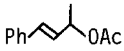
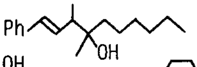
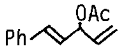
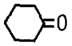
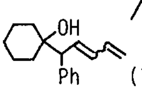
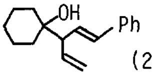
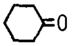
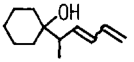
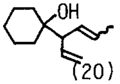
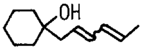
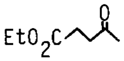
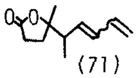
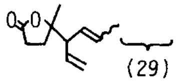
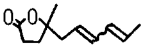
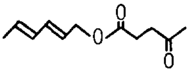
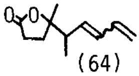
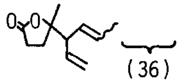
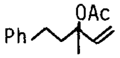
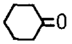
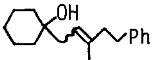
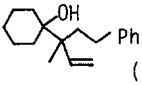
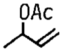
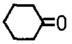
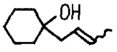
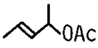
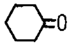
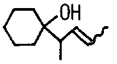
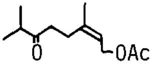
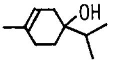
In a typical experiment, a SmI_2-THF solution2) (0.1 mol cm^{-3}, 2 ml) was added to a mixture of cinnamyl acetate (17.6 mg, 0.1 mmol), cyclohexanone (9.8 mg, 0.1 mmol), and 1 mol% of $Pd(PPh_3)_4$3) in oxygen-free dry THF (2 ml) during 30 min at 0^oC and the mixture was stirred at this temperature for 2 h, in which time the blue-green color (Sm^{2+}) turned into yellow (Sm^{3+}). Usual workup followed by chromatographic purification (silica gel) gave 1-(3-phenyl-2-propenyl)cyclohexanol (16.1 mg, 75 %) (entry 2).

As can be seen in the Table, C-C bond formation occurred, in most cases, at less hindered site. In the case of dienyl acetates, however, the reaction occurred mainly at the ε-carbon (entry 6 and 7) and a similar regiochemical trend was observed when dienyl levulinate was subjected to the same reaction conditions (entry 8). Aromatic or α,β-unsaturated carbonyl compounds could not be used as substrates of the present reaction since they produced pinacol type self-coupling products, predominantly.4)

The Barbier-type coupling of allyl halides and carbonyl compounds by using SmI_2 has been carried out by Kagan et al.,5) most effectively with allyl iodides. However, these halides are not always easily accessible and sometimes unstable and toxic. Therefore, the use of easily preparable allylic acetates and fairly mild reaction conditions seem to be synthetically very advantageous. As an example, terpinen-4-ol (1-p-menthen-4-ol)6) was synthesized in a straightforward fashion from neryl acetate via intramolecular cyclization (entry 12).

It is interesting to note that the present reductive coupling process formally involves SmI_2-induced electrophilic substitution of π-allyl palladium complexes in contrast to the conventional Pd(0)-catalyzed nucleophilic substitutions.7)

Table. Reductive Coupling of Allylic Acetates with Carbonyl Compounds.[a)]

Entry	Allylic acetate	Carbonyl compound	Conditions Temp/Time	Product[b)] (ratio)[c)]	Yield[d)] (%)
1			0°C/2.5h[e)]		63
2			0°C/2.5h[e)]		75
3			RT/3h[e)]		71
4			RT/3h[e)]		84[f)]
5			-78°C/10min[e)]	 (73)  (27)	61
6			RT/4h[g)]	 (60)  (20)  (20)	97
7			RT/4h[g)]	 (71)  (29) 	57[h)]
8			RT/4h[g)]	 (64)  (36) 	53[h)]
9			Refl/1h[i)]	 (70)  (30)	76
10			Refl/3h[i)]		59
11			Refl/3h[i)]		52
12	 [j)]		Refl/3h[g)]	 (terpinen-4-ol)[k)]	62

a) Reaction conditions, see the text. b) Satisfactory ^{1}H NMR data were obtained. c) From ^{1}H NMR. A wavy line indicates that the E/Z or the diastereomeric ratio was not determined. d) Isolated yield. e) 1 mol% of $Pd(PPh_3)_4$ was used. f) Erythro/Threo≈1/1. g) 5 mol% of $Pd(PPh_3)_4$. h) The isomers could not be separated and their structures are tentatively assigned. i) 10 mol% of $Pd(PPh_3)_4$. j) Prepared from neryl acetate in two steps (9-BBN/H_2O_2, NaOH; PDC). k) Identified by the comparison of the ^{1}H NMR spectrum with the authentic one.

References and Note

1) T.Tabuchi, J.Inanaga, and M.Yamaguchi, Tetrahedron Lett., in press. 2) P.Girard, J.L.Namy, and H.B.Kagan, J. Chem. Soc., **102**, 2693 (1980). 3) Either $PdCl_2$ or $Pd(OAc)_2$ could be used with PPh_3 in place of $Pd(PPh_3)_4$. Furthermore, Ni(0) was also found to be effective. For example, cinnamyl acetate was coupled with cyclohexanone by SmI_2 at 0°C for 2.5h in the presence of 5 mol% of $NiCl_2$ and 20 mol% of PPh_3 affording the corresponding homoallylic alcohol in 69% yield. (Cf. entry 2 in the Table) 4) J.L.Namy, J.Souppe, and H.B.Kagan, Tetrahedron Lett., **24**, 765 (1983). 5) J.Souppe, J.L.Namy, and H.B.Kagan, Tetrahedron Lett., **23**, 3497 (1982). 6) L.H.Briggs and M.D.Sutherland, J. Org. Chem., **7**, 397 (1942). 7) For reviews: J.Tsuji, Organic Synthesis with Palladium Compounds, Springer-Verlag, Heidelberg (1980); R.F.Heck, Palladium Reagents in Organic Syntheses, Academic Press, P.117 (1985).

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