Pd-catalysed Reaction of Allylic Acetates with Carbonyl Compounds *via* Electrochemical Reduction

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Electroreductive addition of allylic acetates to carbonyl compounds proceeded smoothly at room temperature using zinc chloride and a catalytic amount of $PdCl_2(PPh_3)_2$ to give the corresponding homoallylic alcohols.

The palladium-catalysed displacement of allylic compounds with carbonucleophiles is a well established procedure and a widely used synthetic tool for the formation of C–C bonds.[1] In the displacement, the π-allylic palladium intermediate (**2**) is attacked by nucleophiles. If the π-allylic palladium intermediate gains two electrons, the resultant allylic carbanion can be trapped by electrophiles (Umpolung). Inanaga has reported that the electrophilic substitution of the π-allylic palladium intermediate (**2**) could be induced by SmI_2.[2] It has not yet been reported that such electrochemically derived allylic carbanions have reacted with carboelectrophiles.[3] In this paper, we report a novel electroreductive addition of allylic acetates to carbonyl compounds with palladium catalysis.

A typical procedure is as follows. Electrolysis was carried out in a divided cell fitted with Pt electrodes. A dimethylformamide (DMF) solution of Et_4NOTs (Ts = p-$MeC_6H_4SO_2$) (0.5 g/10 ml) and $ZnCl_2$ (1 g/10 ml) was charged in the cathode chamber and a DMF solution of Et_4NOTs (0.5 g/10 ml) was charged in the anode chamber. Into the cathode chamber were successively added allyl acetate (2.1 mmol), benzaldehyde (3.2 mmol), and $PdCl_2(PPh_3)_2$ (0.1 mmol); a controlled potential was applied at room temperature until most of the

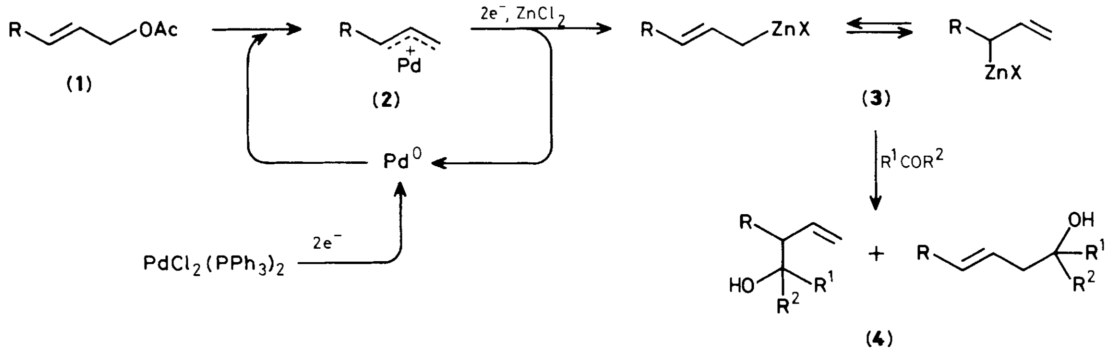
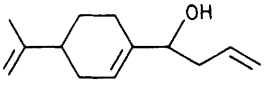


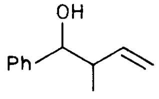
Table 1. Pd-catalysed reaction of allylic acetates with carbonyl compounds *via* electrochemical reduction.

Entry	Acetates	Carbonyl compounds	Products (ratio)	Yield[a] /%
1	$CH_2 = CHCH_2-$	PhCHO	$PhCH(OH)CH_2CH = CH_2$ **(4a)**	77
2		$MeOC_6H_4CHO$	$MeOC_6H_4CH(OH)CH_2CH = CH_2$ **(4b)**	84
3		$n\text{-}C_9H_{19}CHO$	$n\text{-}C_9H_{19}CH(OH)CH_2CH = CH_2$ **(4c)**	79
4		$p\text{-}ClC_6H_4CHO$	$p\text{-}ClC_6H_4CH(OH)CH_2CH = CH_2$ **(4d)**	68
5		$(CH_2)_5C = O$	$(CH_2)_5C(OH)CH_2CH = CH_2$ **(4e)**	40
6		perillaldehyde	**(4f)**	42
7	$CH_2 = CH\underset{\substack{\mid \\ Me}}{C}H-$	PhCHO	**(4g)** : **(4h)** (91 : 9)	62[b]
8	$MeCH = CHCH_2-$	PhCHO	**(4g)** : **(4h)** (91 : 9)	56[b]
9	$PhCH = CHCH_2-$	PhCHO	**(4i)** : **(4j)** (83 : 17)	71[c]
10		PhCHO	—	0[d]
11		PhCHO	β-methylstyrene	32[e]

[a] Isolated total yield. All products gave satisfactory i.r. and ^1H n.m.r. spectra. [b] The ratio of *erythro* : *threo* (57 : 43) of **(4g)** and the regioisomer ratio was determined by ^1H n.m.r. [c] The ratio of *erythro* : *threo* (69 : 31) of **(4i)** was determined by ^1H n.m.r.,[6] and the regioisomers could be separated by column chromatography on silica gel. [d] Carried out in the absence of Pd catalyst. [e] Carried out in the absence of zinc chloride.



(4f)



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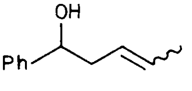
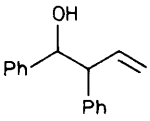
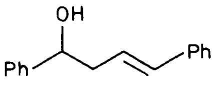


(4h)



(4i)



(4j)

starting material had been consumed (5 F/mol). The usual work-up of the catholytes gave 1-phenylbut-3-en-1-ol **(4a)** in 77% yield (entry 1 in Table 1). When an α,β-unsaturated aldehyde, perillaldehyde, was used, the 1,2-addition product was obtained selectively. Under the same conditions, cinnamyl acetate reacted with carbonyl compound to give two regioisomers **(4i)** and **(4j)** in the ratio 83 : 17 (entry 9). We assume that in the presence of $ZnCl_2$, electrochemical reduction of allylic palladium resulted in two regioisomers of the allylic zinc reagent **(3)**, of which the terminal one may predominate. The intermediate **(3)** was added to carbonyl compounds to form two regioisomers **(4)** after hydrolysis. So **(4i)** was formed as the major product through a 6-centre cyclic mechanism. When crotyl acetate or α-methylallyl acetate was used, **(4g)** and **(4h)** were afforded with the same ratio according to their common intermediates **(2)** and **(3)**. If the reaction was carried out in the absence of the Pd catalyst, most of the acetates were recovered (entry 10). In the absence of $ZnCl_2$, the reaction afforded 32% of β-methylstyrene with minor by-products which were not identified.

We suggest the following mechanism. The π-allylic palladium intermediate **(2)** generated from oxidative addition of allylic acetate to Pd^0,[1] was reduced at the Pt cathode to give the allylic anion and Pd^0,[3] the later could be recycled. The allylic anion was stabilized by zinc chloride forming the allylic zinc reagent **(3)**. Compound **(3)** reacted with carbonyl compounds to provide homoallylic alcohols **(4)**.[4]

This reaction thus provides a novel method for allylic acetates, as the allylic carbanion synthon equivalent, to react with carbonyl compounds to form C–C bonds.†

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References

1 J. Tsuji, 'Organic Synthesis with Palladium Compounds,' Springer-Verlag, Berlin, 1980; B. M. Trost, *Acc. Chem. Res.*, 1980, **13**, 385; J. Tsuji, *Pure Appl. Chem.*, 1982, **54**, 197; R. F. Heck, 'Palladium Reagents in Organic Synthesis' Academic Press, New York, 1985.

2 Aromatic or α,β-unsaturated carbonyl compounds could not be used as substrates since they produced pinacol type products predominantly: T. Tabuchi, J. Inanaga, M. Yamaguchi, *Tetrahedron Lett.*, 1986, **27**, 1195.

3 Electroreductive cleavage of allylic acetates and capture of the allylic carbanion by proton or trimethylsilyl chloride have been reported: S. Torri, H. Kanaka, T. Katoh, and K. Morisaki, *Tetrahedron Lett.*, 1984, **25**, 3207.

4 J. F. Ruppert and J. D. White, *J. Org. Chem.*, 1976, **41**, 550; G. Courtois and L. Miginiac, *J. Organomet. Chem.*, 1974, **69**, 1.

5 T. Hiyama, K. Kimura, and H. Nozaki, *Tetrahedron Lett.*, 1981, **22**, 1037; M. Wada, H. Ohki, and K.-Y. Akiba, *ibid.*, 1986, **27**, 4771.

6 K. Uneyama, H. Nanbu, and S. Torri, *Tetrahedron Lett.*, 1986, **27**, 2395.

7 Charge reversal of π-allylpalladium intermediates: carbonyl allylation by allylic acetates with $Pd(PPh_3)_4$-Zn, Herbert C. Brown, Kristina Bhat, and Ramnarayan Randad, *J. Org. Chem.*, 1987, **52**, 3702.

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† A similar charge reversal of electrophilic π-allylic palladium intermediates by allylic acetates with $Pd(PPh_3)_4$: Zn to serve as nucleophilic allylating agents of aldehydes, has recently been reported by Y. Masuyama, N. Kinugawa, and Y. Kurusu, *J. Org. Chem.*, 1987, **52**, 3702.