

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

Weiming Qiu and Zhiqin Wang*

Shanghai Institute of Organic Chemistry, Academia Sinica, 345 Lingling Lu, Shanghai, People's Republic of China

Electroreductive addition of allylic acetates to carbonyl compounds proceeded smoothly at room temperature using zinc chloride and a catalytic amount of $\text{PdCl}_2(\text{PPh}_3)_2$ 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 ($\text{Ts} = p\text{-MeC}_6\text{H}_4\text{SO}_2$) (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 $\text{PdCl}_2(\text{PPh}_3)_2$ (0.1 mmol); a controlled potential was applied at room temperature until most of the

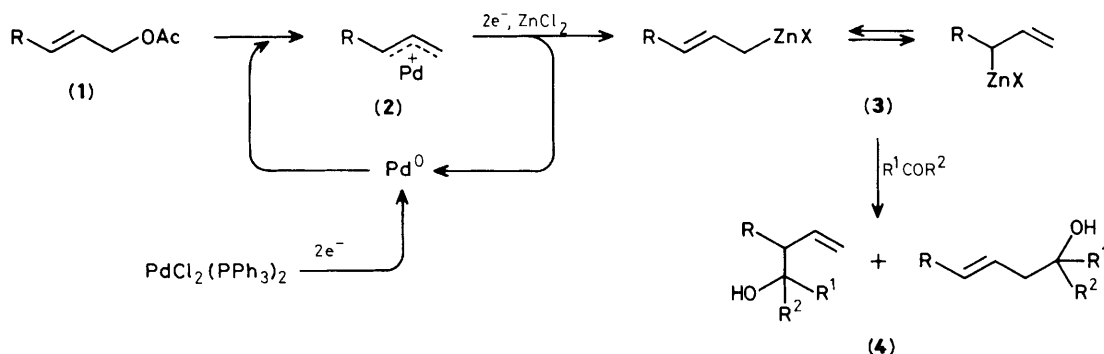
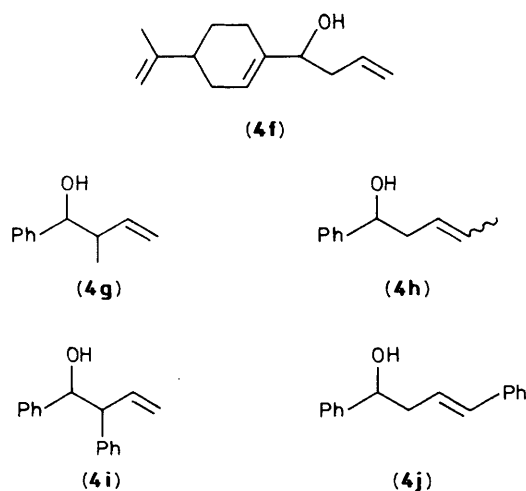


Table 1. Pd-catalysed reaction of allylic acetates with carbonyl compounds *via* electrochemical reduction.

Entry	Acetates	Carbonyl compounds	Products (ratio)	Yield ^a /%
1	CH ₂ =CHCH ₂ -	PhCHO	PhCH(OH)CH ₂ CH=CH ₂ (4a)	77
2		MeOC ₆ H ₄ CHO	MeOC ₆ H ₄ CH(OH)CH ₂ CH=CH ₂ (4b)	84
3		<i>n</i> -C ₉ H ₁₉ CHO	<i>n</i> -C ₉ H ₁₉ CH(OH)CH ₂ CH=CH ₂ (4c)	79
4		<i>p</i> -ClC ₆ H ₄ CHO	<i>p</i> -ClC ₆ H ₄ CH(OH)CH ₂ CH=CH ₂ (4d)	68
5		(CH ₂) ₅ C=O	(CH ₂) ₅ C(OH)CH ₂ CH=CH ₂ (4e)	40
6		perillaldehyde	(4f)	42
7	CH ₂ =CHCH-	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.



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 ZnCl₂, 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 ZnCl₂, 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 Pd⁰,¹ was reduced at the Pt cathode to give the allylic anion and Pd⁰,³ 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.[†]

Received, 29th July 1988; Com. 8/03108H

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(PPh₃)₄-Zn, Herbert C. Brown, Kristina Bhat, and Ramnarayan Randad, *J. Org. Chem.*, 1987, **52**, 3702.

[†] A similar charge reversal of electrophilic π-allylic palladium intermediates by allylic acetates with Pd(PPh₃)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.