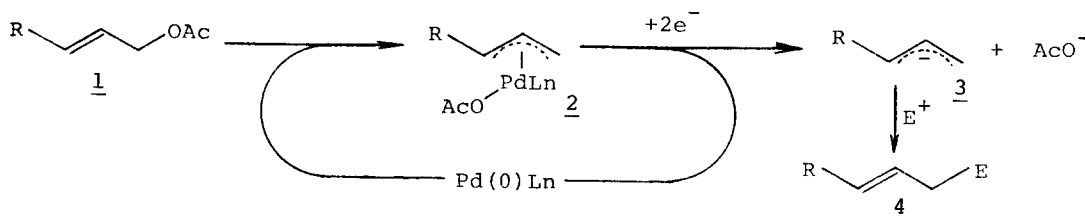


Pd(0)-Catalyzed Electroreductive Cleavage of Allylic Acetates<sup>1</sup>

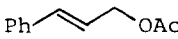
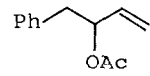
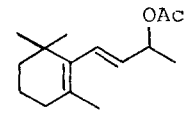
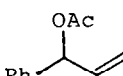
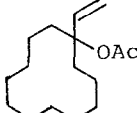
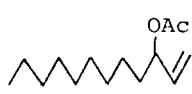
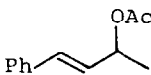
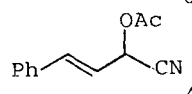
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**ABSTRACT:** Pd(0)-catalyzed electroreductive cleavage of allylic acetates yielding alkenes and/or allyltrimethylsilanes is described. Deprotection of allyl esters can be performed in the same electrolysis system.

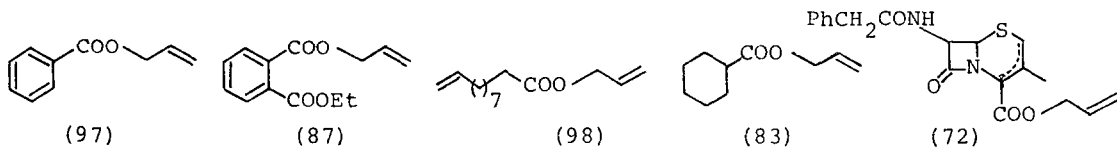
The Pd(0)-catalyzed displacement of allylic acetates with various nucleophiles is a well established procedure.<sup>2</sup> In principle, attack of electrons (+2e<sup>-</sup>) in place of nucleophiles is expected to undergo a reductive cleavage of allylic acetates, providing allylic carbanions and carboxylate along with a Pd(0) complex, former of which can be captured with various electrophiles (dipole inversion). However, this type of conversion has not yet been realized. We investigated these possibilities of the electrochemical procedure and found an electroreductive Pd(0)-recycling system:



Electrolysis was carried out in an H-type divided cell fitted with Pb cathode (3 cm<sup>2</sup>) and Pt anode (3 cm<sup>2</sup>). A mixture of allylic acetates 1 (0.31 mmol) and Pd(0)(PPh<sub>3</sub>)<sub>4</sub> (0.016 mmol, 5 mol %) in CH<sub>3</sub>CN (10 ml) containing Et<sub>4</sub>NOTs (0.5 g) was charged into the cathode chamber and a solution of CH<sub>3</sub>CN (10 ml) - Et<sub>4</sub>NOTs (0.5 g) into the anode chamber. After the cell was purged with argon gas, regulated dc power (3.75 mA/cm<sup>2</sup>) was supplied (2-8 F/mol) until most of starting materials were consumed. Usual work-up of the catholyte afforded the corresponding alkenes 4 (E = H) in good yields. Allyltrimethylsilanes 4 (E = SiMe<sub>3</sub>) were also obtained when the electrolysis was carried out in the presence of excess amounts of trimethylsilyl chloride (0.5 ml) (entries 2, 4, and 6). As illustrated in the Table (entries 1-4, 7, 9, and 10), the major products were inner olefins rather than terminal olefins, presumably due to the preferential attack of H<sup>+</sup> or Me<sub>3</sub>SiCl from the less hindered site of electro-generated allylic carbanions 3.<sup>3</sup>

entry	substrate	F/mol	product (%)	entry	substrate	F/mol	product (%)
1		2.2	E = H (58%)	7		5.8	(69)
2		6.0	E = SiMe <sub>3</sub> (82)	8		6.0	(72)
3		2.2	E = H (45)	9		2.2	(82)
4		8.0	E = SiMe <sub>3</sub> (68)	10		8.0	(63)
5		2.4	E = H (64, 2/1)	11		4.0	(73)
6		6.0	E = SiMe <sub>3</sub> (66, 2/1)				

The electroreduction procedure could be effectively used for deprotection of allyl esters.<sup>4</sup> Following allyl esters were converted to the corresponding carboxylic acids (yields, %):



The idea of the present electroreductive procedure would involve dipole inversion methodology in contrast to the conventional Pd(0)-catalyzed nucleophilic substitution reaction.<sup>2</sup> Further applications of the electrochemical Pd(0) recycling system are in progress.

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