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New Efficient Electrochemical Allylation of Aldehydes and Ketones with a Cadmium-modified Electrode

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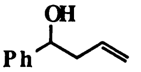
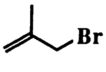
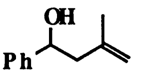
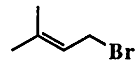
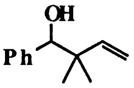
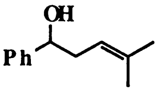
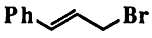
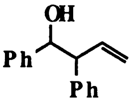
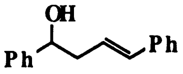
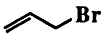
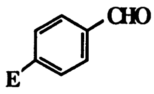
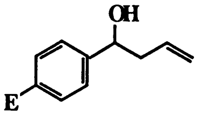
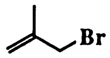
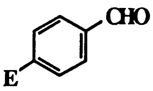
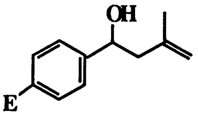
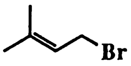
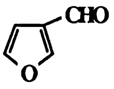
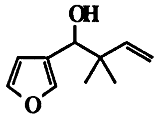
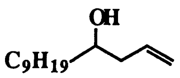
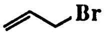
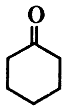
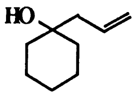
Electrochemical allylation of aldehyde or ketone with allylic halides by the use of a cadmium-modified platinum anode and by alternating the cathode and anode at constant intervals gives high yields of the corresponding homoallyl alcohols.

Preparation of homoallyl alcohols by allylation of carbonyl compounds is of importance in organic synthesis. Electrochemical allylation has recently been reported to be useful by us[1,2] and other investigators.[3] Thus, we have recently reported a new synthesis of egomaketone by a regioselective electrochemical allylation of aldehyde.[2] We now wish to report an efficient electrochemical allylation of aldehydes or ketones by the use of a cadmium-modified electrode.

The present electrochemical allylations have been achieved either by the use of a platinum cathode along with a cadmium anode (method A) or by the use of a platinum cathode and a cadmium-modified platinum anode and by alternating the cathode and anode at ten minutes intervals (method B). The cadmium-modified electrode was made by depositing a cadmium metal dissoluted from a cadmium anode onto a platinum cathode by an electrolysis in N,N-dimethylformamide (DMF) containing 0.1 mol dm^{-3} tetraethylammonium perchlorate (TEAP) using a platinum cathode and a cadmium anode with an electricity of 2 Faradays per mol of the carbonyl compound. Typically, a mixture of aldehydes or ketones and two molar equivalents of allylic halides in DMF containing 0.1 mol dm^{-3} TEAP was electrolyzed at a constant current of 1 A dm^{-2} in a one compartment cell under a nitrogen atmosphere. The electricity passed was 5 Faradays per mol of the carbonyl compound in method A and 2 Faradays in method B. The products and their isolated yields are summarized in Table 1.

Table 1 indicates that while the electrochemical allylation of benzaldehyde with methallyl bromide by the use of platinum plate electrodes as the cathode and anode was found to give only a 22% yield of the homoallyl alcohol in our separate experiment, much higher yields of the homoallyl alcohols (38-100%) can be obtained when a cadmium or a cadmium-modified anode is used in the electrochemical allylations. Moreover, between the two methods A and B, we found that method B was superior since it gave appreciably higher yields (46-90% isolated yield) of the homoallyl alcohols. Also, the loss of a cadmium metal was smaller; 2.6 molar equivalents of cadmium metal were consumed owing to a dissolution in the electrochemical allylation by method A, whereas most of the metal was recovered as a deposit on the surface of the platinum electrode after electrolysis by method B.

Table 1. Electrochemical Allylation of Aldehydes or Ketones with Allylic Halides by the Use of a Cadmium or a Cadmium-modified Platinum Anode

Halide	Carbonyl compound	Method	Product	(Isolated yield / %) a)	Product	(Isolated yield / %) a)
	PhCHO	A B		(53) (80; 100 b))		
	PhCHO	A B		(72; 90 b)) (71)		
	PhCHO	A B		(55) (71)		(9) (0)
	PhCHO	A B		(49) (43)		(32) (45)
	 (E=CO$_2$Me)	A B		(61) (88)		
		A B		(60) (90)		
		A B		(50) (55)		
	C$_9$H$_{19}$CHO	A B		(38) (77)		
		A B		(61; 95 c)) (46; 92 c))		

a) Based on aldehydes or ketone employed.
b) GC yield.
c) Four molar excess of allyl bromide was used.

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References

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