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An Efficient Electrochemical Coupling of Allylic Halides by Using a Copper Anode

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A new electrolytic method for an efficient coupling of allylic halides by the use of a copper anode and a platinum cathode in the presence of sodium iodide is described. A method which avoids a loss of the copper anode owing to dissolution is also described.

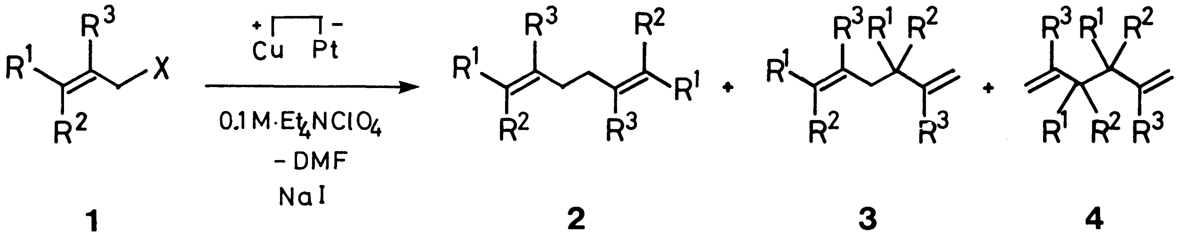
Lower valent metals generated by an electrochemical reduction of nickel,[1-4) iron,[5) cobalt,[6) or palladium complex[7,8) have been reported to induce a coupling reaction of alkyl,[1,2,5) allyl,[6,8) or aryl halide.[3,4,7) We have recently reported that an electrochemical reduction of allyl and benzyl bromides takes place at a reduction potential less negative than that of the bromides to give the coupling products with enhanced yields if bis(2,4-pentanedionato)copper(II), $Cu(acac)_2$, is added to the solution, while an addition of the copper complex is no more effective in a coupling of allyl chloride or allyl iodide.[9) We have suggested that an organocopper species may be involved in this coupling reaction as an intermediate in the presence of $Cu(acac)_2$.[9)

We now wish to report that the electrochemical coupling of allylic halides can be achieved more efficiently when the electrolysis is carried out with a copper anode and a platinum cathode in the presence of sodium iodide in an undivided cell. This new electrolytic method was found to be quite efficient for the coupling of allylic halides compared with other electrolytic methods. Thus, we carried out the electrochemical couplings under four different conditions (A)-(D): (A) an electrolysis by the use of a platinum (Pt) anode and a Pt cathode; (B) an electrolysis by the use of a Pt anode and a Pt cathode in the presence of 0.5 equivalent of $Cu(acac)_2$; (C) an electrolysis by the use of a copper (Cu) anode and a Pt cathode; and (D) an electrolysis by the use of a Cu anode and a Pt cathode in the presence of sodium iodide (one equivalent). In case of (D), a solution containing sodium iodide was stirred for 30 minutes at room temperature before the electrolysis. In each electrolysis (A) to (D), allylic halides **1a**-**1i** (2 mmol, 0.1 mol dm^{-3}) in N,N-dimethylformamide (DMF) containing 0.1 mol dm^{-3} tetraethylammonium perchlorate (TEAP) were electrolyzed at a constant current of 7.5 mA/cm^2 under a nitrogen atmosphere using an undivided cell. The electricity passed was 3 Faradays per mol of the allylic halide. The yields of the three types of the coupling products (**2**, **3**, **4**) under the above four different conditions are summarized in Table 1.

Table 1 indicates that while the electrolysis of the allylic halides with a Pt anode and a Pt cathode [condition (A)] gave only a low yield of the coupling products, the addition of $Cu(acac)_2$ [condition (B)] or the replacement of the Pt anode by a Cu anode [condition (C)] clearly enhanced the yields of the products of the coupling and the enhancement of the yields under the condition (C) is particularly appreciable in the electrolysis of methallyl bromide (**1c**), cinnamyl chloride (**1h**), and cinnamyl bromide (**1i**).

Table 1 also shows a dramatic enhancement of the yields of the coupling products when a new electrolytic method using a Cu anode with an addition of sodium iodide [condition (D)] was employed and the coupling of the allylic bromides was achieved in 72-100% yields.

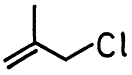
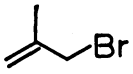
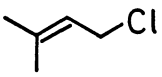
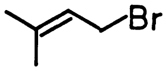
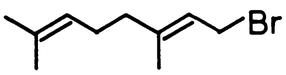
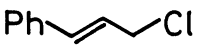
In the electrolysis of allylic halides **1d**-**1i**, the three isomers **2**, **3**, and **4** are formed in different ratios for each substrate (footnotes d-j in Table 1). The ratio of the three isomeric products from each allylic halide remains almost the same under any of the above four conditions of electrolysis. Moreover, while the product **2** which arose from the coupling between the carbons bearing a halogen atom was the major isomer in crotyl (**1d**), prenyl (**1e** and **1f**) and geranyl halide (**1g**), the major isomer from the cinnamyl halides (**1h** and **1i**) was product **3**, which stemmed from the coupling between the carbon bearing a halogen atom and the allylic carbon.



During electrolysis under the conditions (C) and (D), we found that 1.8-3.1 equivalents of the copper anode per mol of allylic halides was lost and the most of the dissolved copper was deposited on the surface of the Pt cathode and that these copper-deposited platinum electrodes obtained after the electrolysis can be used again as anodes by combining them with a platinum cathode; this leads to the enhancement of the yields of the coupling products. Thus, the electrolysis of cinnamyl chloride (**1h**) with a copper-deposited platinum anode and a platinum cathode under the condition (C) gave a 41:59 ratio of the coupling products **2h** and **3h** in 67% yield. We also found that the coupling products are only formed when the dissolved copper and allylic halides are in the same compartment of the electrolysis, since, although the loss of the copper anode can still be observed, none of the products of the coupling is formed in the electrolysis when a divided cell is used.

The foregoing results indicate that both the coppers dissolved from the electrode and the sodium iodide as additives play an important role in enhancing

Table 1. The Electrochemical Coupling of Allylic Halides under the Four Electrolytic Conditions (A)-(D)[a]

Substrate		Yield of coupling products / %[b]			
		(A)	(B)	(C)	(D)
	**1a**	12	88	20	80
	**1b**	trace	14	13	73
	**1c**	2	48	27	100
	**1d**	6	—	12	47[c]
	**1e**	1	15	4	53[d]
	**1f**	trace	28[e]	45[f]	93[g]
	**1g**	7	—	33	72[h]
	**1h**	1	17	75	62[i]
	**1i**	trace	—	68	95[j]

a) Electrolysis was carried out in a DMF solution containig 0.1 mol dm^{-3} Et_4NClO_4 at a constant current of 7.5 mA/cm^2. Electricity passed was 3 F/mol of **1a**-**1i**. The electrolytic conditions of (A)-(D) are given in the text.

b) Determined by GLC using an internal standard.

c) The isomer ratio was not determined.

d-j) The isomer ratios of **2**:**3**:**4** were as follows: d, 57:26:17; e, 45:17:38; f, 55:23:22; g, 58:26:16; h, 76:24:0; i, 30:70:0; j, 36:58:6.

the yield of the coupling products.

The sodium iodide probably acts as a nucleophile to transform the starting allylic halides into the corresponding iodides which are more reactive than the starting halides. Actually, when **1c** was stirred for 30 minutes at room temperature in the presence of sodium iodide, 30% of **1c** was found to be converted to methallyl iodide. Furthermore, it was shown that the yield of the product **2c** was raised from 2% to 36% by the addition of sodium iodide even in the electrolysis of allylic halide **1c** when a Pt anode and a Pt cathode [condition (A)] were used.

While the copper dissolved from the electrode thus leads to the enhancement of the yields of the products arising from the coupling in the electrolysis of allylic halides, the loss of a part of the copper anode simultaneously becomes a drawback when we wish to carry out the electrolysis on a large scale. We therefore devised a new method to overcome this disadvantage during a large scale electrolysis: a high yield of the coupling products could be attained by exchanging between the copper-deposited platinum electrode obtained by the electrolysis under the condition (D) and a platinum cathode at ten minutes intervals. The products **2h** and **3h** (a 42:58 ratio) in an yield of 63% were obtained when cinnamyl chloride (**1h**) was subjected to electrolysis by this electrode exchange method. In this case, most of the copper metal was not lost and it was deposited on the one platinum electrode after the electrolysis. That is, this new electrochemical method allows a circulating use of the copper metal.

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