CHEMISTRY LETTERS, pp. 1035 - 1038, 1984. © The Chemical Society of Japan 1984

ELECTROCHEMICAL REDUCTIVE COUPLING OF ALLYL AND BENZYL HALIDES IN THE PRESENCE OF $Cu(acac)_2$

Masao TOKUDA,* Kuniaki SATOH, and Hiroshi SUGINOME
Organic Synthesis Division, Department of Chemical Process Engineering,
Faculty of Engineering, Hokkaido University, Sapporo 060

The electroreduction of allyl and benzyl bromides takes place at a reduction potential less negative than that of the bromides to give coupling products with enhanced yields if $Cu(acac)_2$ is added to the solution, while the yields of the couplings of allyl- and benzyl chlorides and allyl iodide are unaffected by the addition of $Cu(acac)_2$.

Lower valent metals generated by an electrochemical reduction of nickel,[1-3] iron,[4] or cobalt complex[5] have been reported to induce a coupling reaction of alkyl halide[1,2,4,5] or aryl halide.[3] In our continuing study on the carbon-carbon bond formation by electrochemical reductions of organic halides,[6] we have studied the effects of several metal complexes on this reaction in order to find a new effective metal. We report here that the addition of bis(2,4-pentanedionato)-copper(II), $Cu(acac)_2$, in the electrochemical reduction of allyl and benzyl bromides leads to appreciably higher yields of the coupling products and that the coupling reaction occurs at a potential less negative than that of the bromides. We also wish to report some interesting results found in the voltammetric study of the effect of the copper complex.

Electrolysis of allyl bromide (1a) in N,N-dimethylformamide (DMF) containing 0.1 M[†] tetraethylammonium perchlorate (TEAP) at a constant current of 20 mA/cm^2 gave 1,5-hexadiene (3) in a 22% yield. Two platinum plates were used as electrodes and the electricity passed was 2.0 Faraday per mol of 1a. When the electrolysis was

$$CH_2{=}CHCH_2X \xrightarrow[Cu(acac)_2]{Pt-Pt} CH_2{=}CHCH_2CH_2CH{=}CH_2$$

1a: X=Br 3
1b: X=Cl
1c: X=I

$$C_6H_5CH_2X \xrightarrow[Cu(acac)_2]{Pt-Pt} C_6H_5CH_2CH_2C_6H_5 \quad + \quad C_6H_5CH_3$$

2a: X=Br 4 5
2b: X=Cl

[†] 1 M = 1 mol dm^{-3}.

Table 1. Electrochemical reductive coupling of allyl and benzyl halides in the presence of Cu(acac)$_2$

substrate RX	Molar ratio Cu(acac)$_2$/RX	Curr. dens. mA cm^{-2}	Electricity F mol^{-1}	Conv. of RX %	Yield of R-Ra) %
1a	0	20	2	82	22
	1	20	2	94	88
	1	15	1.5	91	84
	0.4	15	1.5	67	84
	0.2	15	1.5	72	50
1b	0	20	3	85	trace
	1	20	3	90	0
1c	0	20	2	98	46
	1	20	2	95	40
2a	0	20	2	83	6b)
	1	20	2	85	34b)
2b	0	15	4	70	traceb)
	1	15	4	70	1b)

a) Based on reacted RX. b) Toluene (5) was obtained as a by-product in 20-50% yield.

carried out in the presence of Cu(acac)$_2$, the yield of coupling product 3 was found to be enhanced to 88%. In this electrolysis, a part of the copper complex remained undissolved in DMF and the electrolysis was therefore carried out with stirring. Table 1 summarizes the effects of the addition of Cu(acac)$_2$ to the solution under various electrolytic conditions. The results show that even the addition of 0.2 equivalents of Cu(acac)$_2$ to 1a gives 3 in the yield approximately twofold higher than that achieved in the absence of the complex. A similar effect of the copper complex was observed in the electrochemical reductive coupling of benzyl bromide (2a) to give bibenzyl (4). On the other hand, the addition of the copper complex in the coupling reaction of allyl chloride (1b), allyl iodide (1c), or benzyl chloride (2b) was found to have no effect on the yield of the coupling products (Table 1).

The cyclic voltammogram7) of Cu(acac)$_2$ is shown in Fig. 1 which demonstrates reduction waves with no coupled anodic waves on the reverse scan. When 1a was added to the solution of Cu(acac)$_2$, an increase of the reduction current which indicates some electrocatalytic property of the complex was observed (curves b, c, d, and e in Fig. 1). When a more than twofold excess of 1a was added to the solution of the copper complex, the increase of the reduction current could not be seen at -0.85 V and instead the peaks at -1.3 and -1.7 V grew linearly with the concentration of 1a. Nearly the same was true in the cyclic voltammogram of Cu(acac)$_2$ in the presence of 2a (Fig. 2). When 2a was added to the solution of the copper complex, the new reduction peak at -1.02 V became larger at the expense of the reduction peak of 2a at -1.43 V. In the cyclic voltammogram of Cu(acac)$_2$ in the presence of 1b, 1c, and 2b, however, the reduction peak of Cu(acac)$_2$ at -0.8--1.0 V did not change appreciably by the addition of those halides and the reduction peaks of 1b, 1c, and 2b at -1.90, -0.78, and -1.92 V, respectively, were linearly enhanced with the concentration of the added halides (Figs. 3,4).

The potential of the working electrode in a constant current electrolysis of 1a at 20 mA/cm^2 was -1.7 V, which corresponded to the reduction potential of 1a. When the electrolysis was carried out in the presence of one equivalent of Cu(acac)$_2$, the potential rose to -0.8 V, which corresponded to the enhanced reduction peak in Fig. 1. Lower valent copper may play an important role in this reaction. However, when the copper complex was electrolyzed at -0.8 V or 20 mA/cm^2 with the electricity ranging from 1.2 to 3.5 Faraday per mol of the complex and the resulting solution was allowed to react with 1a, none of 3 was produced. This result indicates that both the presence of lower valent coppers and the passage of the electricity are necessary for the formation of 3. On the bases of the above results, we propose the probable pathways for the electrochemical reductive coupling of allyl and benzyl bromides in the presence of Cu(acac)$_2$ as shown in Scheme 1. Two electron reduction of

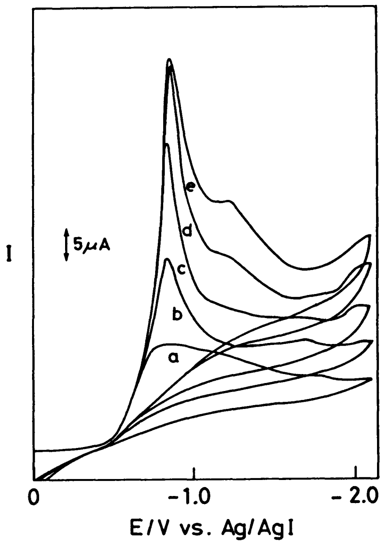


Fig. 1. Cyclic voltammograms of 1.0x10^{-2} M Cu(acac)$_2$ in the presence of allyl bromide (1a).

Concentration of 1a: (a) 0 M; (b) 5.0x10^{-3} M; (c) 1.0x10^{-2} M; (d) 1.5x10^{-2} M; (e) 2.0x10^{-2} M.

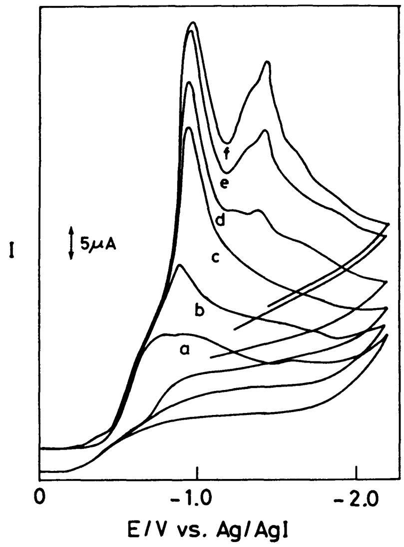


Fig. 2. Cyclic voltammograms of 1.0x10^{-2} M Cu(acac)$_2$ in the presence of benzyl bromide (2a).

Concentration of 2a: (a) 0 M; (b) 5.0x10^{-3} M; (c) 1.0x10^{-2} M; (d) 1.5x10^{-2} M; (e) 2.0x10^{-2} M; (f) 2.5x10^{-2} M.

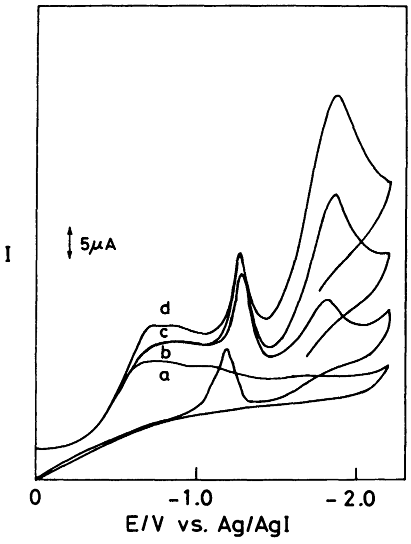


Fig. 3. Cyclic voltammograms of 1.0x10^{-2} M Cu(acac)$_2$ in the presence of allyl chloride (1b).

Concentration of 1b: (a) 0 M; (b) 5.0x10^{-3} M; (c) 1.0x10^{-2} M; (d) 1.5x10^{-2} M.

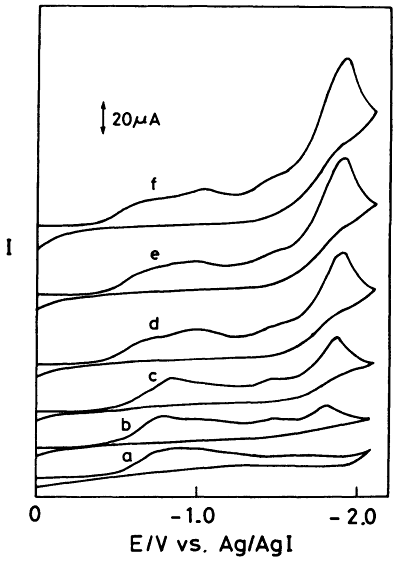


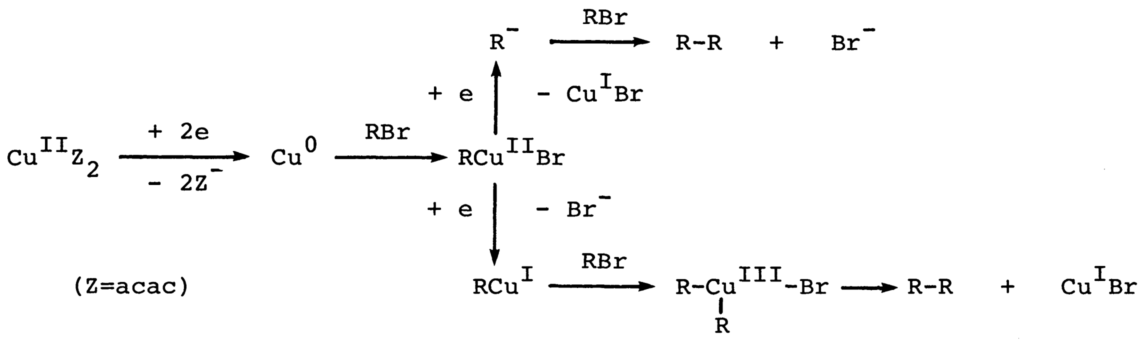
Fig. 4. Cyclic voltammograms of 1.0x10^{-2} M Cu(acac)$_2$ in the presence of benzyl chloride (2b).

Concentration of 2b: (a) 0 M; (b) 5.0x10^{-3} M; (c) 1.0x10^{-2} M; (d) 1.5x10^{-2} M; (e) 2.0x10^{-2} M; (f) 2.5x10^{-2} M.

Cu(II) gives Cu(0) and an oxidative addition of RBr to Cu(0) would give an unstable organocopper compound which was shown by the following experiment. Thus an equimolar amount of 1a was added to the solution containing lower valent coppers which were obtained by electrolysis of 1.0×10^{-2} M $Cu(acac)_2$ at -0.75 V and the resulting solution was immediately studied by cyclic voltammetry. The reduction peak of 1a at -1.75 V did not appear at all and instead a peak at -0.8 V, which may be attributable to the unstable organocopper species, was observed. The new peak, however, did not arise when the voltammetry was carried out after 1.5 h.

Copper(I) bromide formed *via* the pathways in Scheme 1 can be further reduced to give Cu(0), but the catalytic effect of this metal is small since it was confirmed that the electrolysis of 1a in the presence of CuBr gave 3 in only an 11% yield.

The lower efficiency of the copper complex on the coupling reaction of chlorides 1b and 2b may be due to a lower reactivity of those chlorides towards Cu(0). The results of the cyclic voltammetry of $Cu(acac)_2$ in the presence of 1b or 2b are consistent with this. In the reduction of iodide 1c, the reduction of 1c competes with that of $Cu(acac)_2$ and the formation of the lower valent copper may perhaps be inefficient.



Scheme 1.

References

1) P. W. Jennings, G. D. Pillsbury, J. L. Hall, and V. T. Brice, J. Org. Chem., 41, 719 (1976).
2) C. Gosden, K. P. Healy, and D. Pletcher, J. Chem. Soc., Dalton Trans., 1978, 972.
3) M. Mori, Y. Hashimoto, and Y. Ban, Tetrahedron Lett., 21, 631 (1980).
4) J. L. Hall, R. D. Geer, and P. W. Jennings, J. Org. Chem., 43, 4364 (1978).
5) S. Margel and F. C. Anson, J. Electrochem. Soc., 125, 1232 (1978).
6) S. Satoh, H. Suginome, and M. Tokuda, Bull. Chem. Soc. Japan, 56, 1791 (1983) and the references cited therein.
7) Cyclic voltammetry was carried out at a sweep rate of 0.2 V s^{-1} using a platinum disc electrode (1 mm dia.) in DMF solution containing 0.1 M TEAP. A potential was measured in V *vs.* Ag/AgI.

(Received March 15, 1984)