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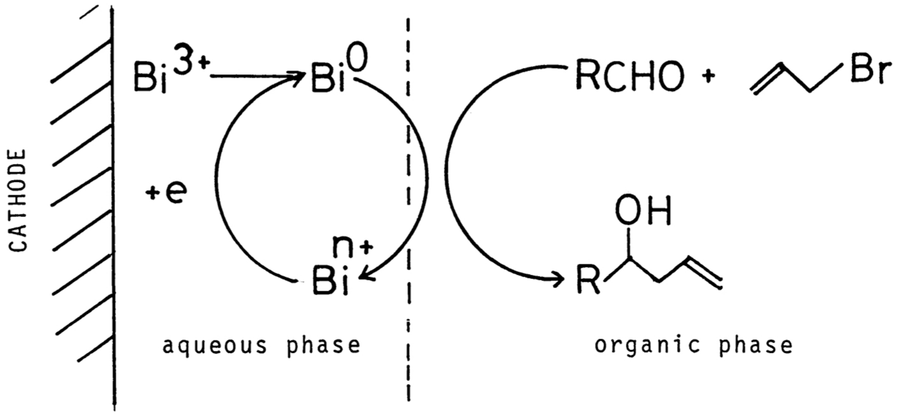
# Allylation of Aldehydes in an Aqueous Two-phase System by Electrochemically Regenerated Bismuth Metal

Makoto MINATO and Jiro TSUJI*
Department of Chemical Engineering, Tokyo Institute of Technology,
Meguro, Tokyo 152

Aldehydes are allylated efficiently by the catalysis of $BiCl_3$ in a two-phase electroreductive system.

Various kinds of metals are utilized in a wide variety of organic synthetic processes based on their characteristic properties. Among them noble metals, such as Pd, Ru, Rh, and Pt are so expensive that they must be used only as a catalyst. On the other hand, base metals, such as Sn, Mn, Cd, Zn, Mg, and Bi are utilized stoichiometrically because they are relatively cheap and their catalytic processes have not been investigated, except a few cases.1) Apparently in view of environmental contamination and natural resources, it is preferable to use these base metals catalytically. In many cases, reactions of these metals involve redox steps. Therefore, if one combine these redox steps with other redox systems, it is possible to achieve catalytic processes. In this sense, electrochemical redox processes seem to be of current interest.2) This prompted us to attempt the allylation of aldehydes with a catalytic amount of $BiCl_3$, which is reduced to a low valent state by an electrochemical reduction as expressed by the following diagram and the results are presented in this communication. The allylation reactions using stoichiometric and catalytic amounts of bismuth have been reported recently by Wada and coworkers.3,4)



We explored the electrolysis in a two-phase system, which has seldom been utilized in allylation reactions. The two-phase electrolysis, in which the electrolyte is made up from emulsion of an aqueous electrolyte and an immiscible organic solvent, has many advantages in practical organic electrosyntheses, in view of high selectivity, higher current density, and simplified extraction procedures.[5)]

At first, we carried out a reaction of benzaldehyde with allyl bromide in order to find out optimum conditions. Three different aqueous solutions, namely neutral, slightly acidic, and strongly acidic solutions, were tested. The reaction proceeded smoothly in the neutral solution (Run 1), but the best result was obtained in the acidic solutions (Runs 3 and 4) as shown in Table 1. And the presence of acetate ion might interfere with the reaction (Run 2).

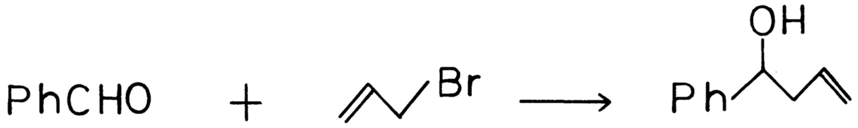


Table 1. Influence of the supporting electrolyte on the allylation of benzaldehyde

| Run | Supporting electrolyte | Yield/% |
|---|---|---|
| 1 | $NaBF_4$ (0.12 mol $dm^{-3}$) | 74 |
| 2 | $CH_3COONa$-HCl (pH=4) | N. R. |
| 3 | $H_2SO_4$ (0.06 mol $dm^{-3}$) | 83 |
| 4 | HCl (0.12 mol $dm^{-3}$) | 86 |

A typical procedure is as follows: an aqueous cathodic mixture (60 ml) containing dichloromethane (10 ml), $BiCl_3$ (1 mmol), benzaldehyde (5 mmol), allyl bromide (10 mmol), and the supporting electrolyte ($NaBF_4$ 0.12 mol $dm^{-3}$) was electrolyzed using a Pt cathode at 0.83 A $dm^{-2}$ of constant current density in a divided cell at a room temperature under argon. After passage of 5 F/mol of electricity, usual work-up provided 1-phenyl-3-buten-1-ol as a single product from the organic layer. Then we investigated the influence of current density and found that yields became higher with an increase of current density and reached maximum at 1.0 A $dm^{-2}$ as shown in Fig. 1.

Subsequently, based on these results we carried out the allylation of several aldehydes and the results are shown in Table 2. The allylation proceeded smoothly in all cases.[6)]

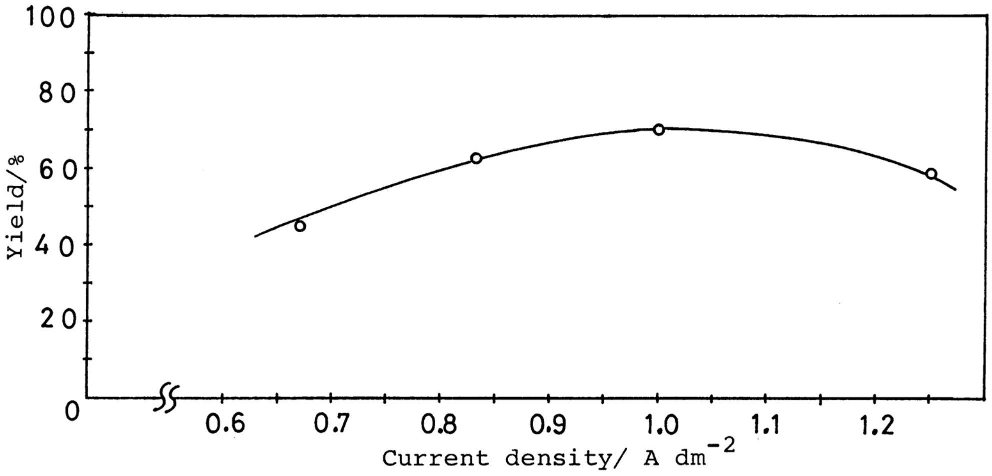
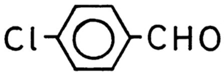
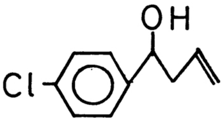
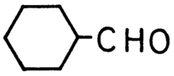
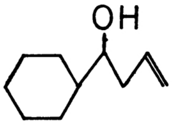
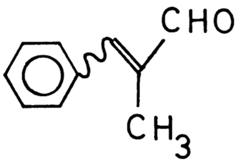
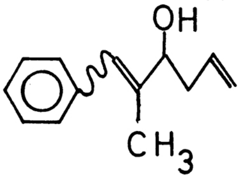


Fig. 1. Influence of current density.

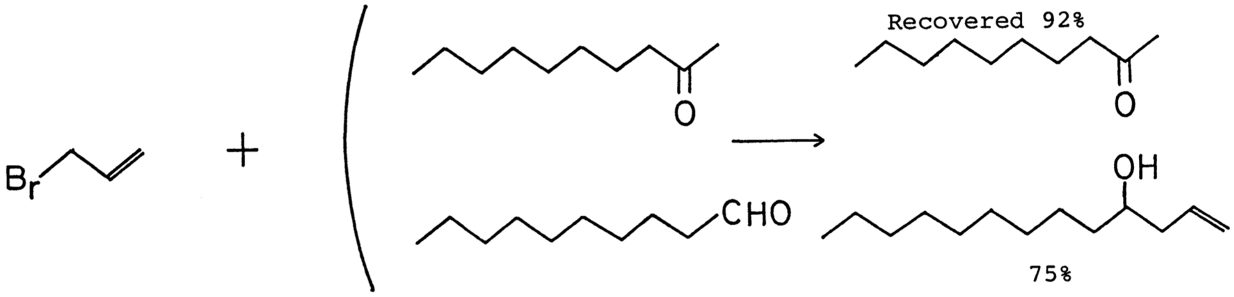
Table 2. Allylation of aldehydes using electrochemically regenerated bismuth metal[a)]

| Substrates | Products | Isolated yield/% |
|---|---|---|
|  b) |  | 88 |
|  |  | 55 |
|  |  | 71 |
|  b) |  | 78 |

a) Electrolysis was carried out in the presence of $BiCl_3$ (30 mol%) and the supporting electrolyte was $HBF_4$ (0.12 mol $dm^{-3}$).

b) Organic phase consisted of dichloromethane (5 ml) and 1-butanol (5 ml).

Wada reported that the allyl-bismuth reagents prepared in situ react with aldehydes without attacking ketones.$^{3)}$ Thus, we examined the allylation of decanal in the presence of 2-decanone in our system and confirmed that only decanal was allylated and 2-decanone (92%) was recovered.



References

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2) For review, S. Torii, Synthesis, 1986, 873.
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5) S. R. Forsyth and D. Pletcher, International Symposium on Electroorganic Synthesis, Kurashiki, October 1986, Abstr. p.35.
6) Recently, Torii and coworkers reported allylation of carbonyl compounds by the electrochemical recycling of allyl tin and lead reagents. K. Uneyama, H. Matsuda, and S. Torii, Tetrahedron Lett., 1984, 6017; H. Tanaka, S. Yamashita, T. Hamatani, T. Nakahara, and S. Torii, Stud. Org. Chem. (Amsterdam), 30, 307 (1987): Chem. Abstr., 107, 143590f (1987).

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