

GRIGNARD-TYPE ALLYLATION OF CARBONYL COMPOUNDS IN METHANOL

BY THE ELECTROCHEMICALLY RECYCLED ALLYL TIN REAGENT.

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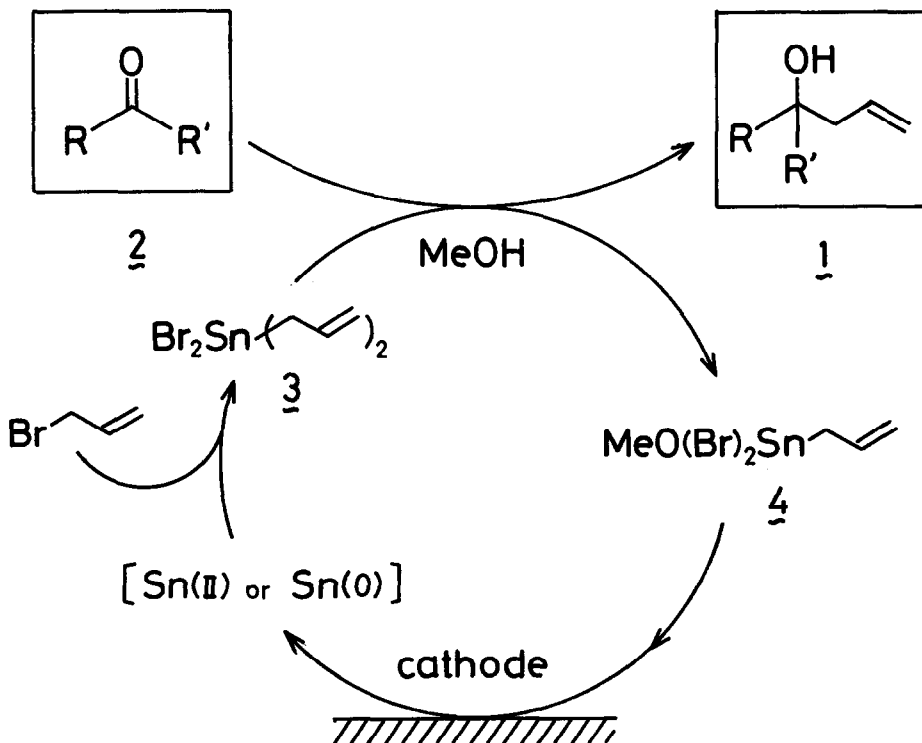
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Abstract : An electrochemical allylation of aldehydes and ketones in methanol was achieved by the electroreductive regeneration of diallyl tin reagent in the presence of a catalytic amount of tin, affording the corresponding homoallyl alcohols in 72 - 91% yields.

Because of the potential usefulness of allylation of carbonyl compounds, a variety of metals such as magnesium, lithium, zinc, boron, aluminium, silicon, manganese, titanium, chromium, zirconium, and tin has been employed for metallic allyl reagents.¹⁾ However, no study on the recycle use of these metallic reagents in situ has appeared presumably because the reaction conditions where three different reactions; generation of the organometallic reagents, allylation of carbonyl compounds, and reductive regeneration of zero or low valent metal have to be conducted in one batch system are not feasible. Here we describe the first example on the electrochemical allylation of aldehydes and ketones in methanol by the use of a catalytic amount of tin. In order to recycle the tin reagent, tetravalent tin produced after allylation must be reduced to di or zero valent tin so that it becomes active enough to react with allyl bromide for regeneration of the allyl tin reagent.²⁾

Electroreduction in an acidic methanol is an adequate choice for the purpose.

A typical electrolysis procedure is as follows: A mixture of benzaldehyde (7.5 mmol), allyl bromide (15 mmol), tin powder (0.75 mmol), and cyclohexene (30 mmol)³⁾ dissolved in methanol (3 ml) and acetic acid (0.75 ml) was stirred at room temperature for 2 h and then was electrolyzed in an undivided beaker type cell at 50 - 55 °C using platinum foil electrodes (2 x 1.5 cm²) under a constant current (50 mA for 16 h, 3.9 F/mol), affording $\underline{\underline{1}}$ (R=Ph, R'=H, 91%). On the other hand, only 11% of $\underline{\underline{1}}$ was obtained when no current was passed. Another interesting feature of this reaction is that after extraction of $\underline{\underline{1}}$ with hexane, the residual methanol solution was used additional nine times for the allylation to provide $\underline{\underline{1}}$ in 90 - 95% yields by repeating extraction and electrolysis, demonstrating that the tin reagent is satisfactorily



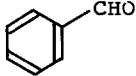
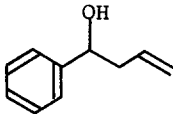
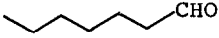
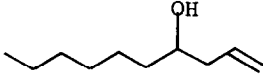
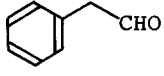
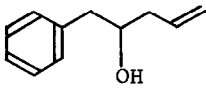

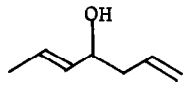
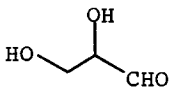
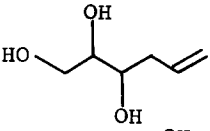
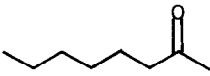
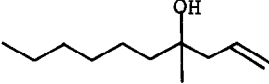
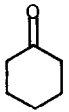
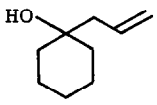
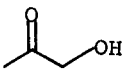
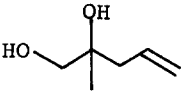
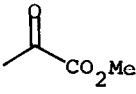
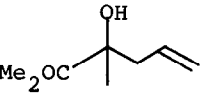
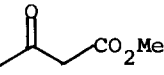
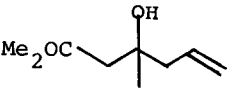
recycled on this electrolysis system.

A simplified overall reaction process is illustrated in scheme 1. Diallyl tin dibromide 3 produced from a metallic tin and allyl bromide in methanol reacts immediately with benzaldehyde ⁴⁾ to provide the corresponding adduct, allyldibromotin monoalkoxide which undergoes alkoxy exchange with methanol, affording the desired homoallyl alcohols 1 and the monomethoxide 4. In contrast to the reaction in THF, ^{2a)} the reaction rate of allyl tin dibromide with benzaldehyde in methanol is so fast as to avoid loss of the tin reagent by electroreduction. ⁵⁾ Meanwhile, 4 is susceptible to electroreduction so that it can be converted electrochemically to di and/or zero valent tin, ⁶⁾ which reacts smoothly with allyl bromide to regenerate diallyl tin dibromide.

Cyclic voltammogram of 3 in methanol clearly shows a reduction peak (ca -1.0 V vs. Ag/AgNO₃), which upon adding benzaldehyde, disappears and shifts to a new peak (ca -0.8 V). ⁷⁾ The newly appeared peak would correspond to a reduction peak for 4 or its related alkoxide and is less negative than the original, suggesting 4 is more easily reducible than 3.

The result of the allylation of aldehydes and ketones with the electrochemically recycled diallyl tin dibromide is shown in Table 1. Both aliphatic and aromatic aldehydes can be converted to the corresponding homoallyl alcohols in excellent yields with 10 mol % of tin. α,β -Unsaturated aldehydes gave cleanly 1,2 adduct (entry 4) by the use of a divided cell. Ketones also gave the desired homoallyl alcohols in reasonable yields. Particularly noteworthy

Table I. Homoallylation of Aldehydes and Ketones by the Electrochemically Recycled Allyltin Reagent in Methanol.^a

entry	substrate	F/mol	product 1	yield (%)
1		3.9		91 ^b
2		4.0		87 ^b
3		2.2		91 ^{b,e}
4		4.5		85 ^{b,d,f}
5		3.3		81 ^{b,d,g}
6		3.0		73 ^c
7		3.6		77 ^c
8		5.0		73 ^c
9		2.8		78 ^c
10		2.8		72 ^c

^a Substrate (7.5 mmol) in 4.5 - 3.75 ml of solvent at 50 - 55 °C. ^b 10 mol % of Sn to substrate in MeOH (3 ml) - AcOH (0.75 ml). ^c 20 mol % of Sn to sub-

strate in MeOH (3 ml) - AcOH (1.5 ml). ^d A two compartment cell divided with a sintered glass was employed. ^e MeOH (3 ml) - H₂O (0.3 ml). ^f In MeOH (4 ml) - AcOH (0.2 ml) - H₂O (0.2 ml) at 20 °C.

is the fact that (1) hydroxyketone provides diol in a good yield without protection of the hydroxyl group (entry 8), (2) glyceraldehyde for which allyl Grignard reagent is not usable because of its insolubility in ether and THF can be converted to the desired triol (entry 5), (3) an enolizable ketone (entry 10) is reactive, and (4) the allylation proceeds chemoselectively (entries 9 and 10).

The present electrochemical allylation is characterized by (a) an in situ recycled use of allyltin reagent, (b) reaction in methanol under an open air, and (c) the wide applicability to any substrates bearing hydroxyl, carbomethoxyl, and enolizable methylene groups.

References and Notes

- 1) (a) Y. Yamamoto and K. Maruyama, Heterocycles, 18, 357 (1982). (b) Y. Yamamoto, H. Yatagai, Y. Naruta, and K. Maruyama, J. Am. Chem. Soc., 102, 7107 (1980) and references cited therein.
- 2) Generation of diallyltin dibromide from metallic tin and allyl bromide; (a) T. Mukaiyama and T. Harada, Chem. Lett., 1527 (1981). (b) J. Nokami, J. Otera, T. Sudo, and R. Okawara, Organometallics, 2, 191 (1983).
- 3) Cyclohexene was employed for trapping bromine formed at the anode. When a divided cell with a glass filter was used, no cyclohexene was necessary and the yield of 1 (R=Ph, R'=H) was 88%.
- 4) The reaction of 3 with benzaldehyde was found to be very fast. The ¹H-NMR signal of the formyl proton of benzaldehyde was completely disappeared and the methyne proton of 1 appeared within one minute on mixing 3 and benzaldehyde in the electrolysis methanol solution at room temperature.
- 5) On electrolyzing diallyltin dibromide in methanol (4 F/mol) and then adding benzaldehyde, a trace of 1 was obtained and benzaldehyde was recovered, suggesting 3 is also electroreducible.
- 6) Although a structure of Sn(II) compound in this electrolysis is not clear at this moment, it is known allylic reagent produced from stannous halides and allyl bromide reacts with carbonyl compounds, providing the corresponding homoallyl alcohols. (a) T. Mukaiyama, T. Harada, and S. Shoda, Chem. Lett., 1507 (1980). (b) A. Gambaro, V. Peruzzo, G. Plazzogna, and G. Tagliavini, J. Organomet. Chem., 197, 45 (1980).
- 7) Cyclic voltammogram was measured in 0.1 M TEAP-MeOH solution using platinum electrode vs. Ag/AgNO₃ (0.01 m) in 0.1 M TEAP-MeCN. Scan rate (0.2 V/sec).
- 8) The authors are grateful to the Ministry of Education, Science, and Culture for a financial support by a Grant-in-Aid (No 57118002 and 59550596).

(Received in Japan 18 September 1984)