

## SmCl<sub>3</sub>-CATALYZED ELECTROCHEMICAL REDUCTIVE ALLYLATION OF KETONES

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*Abstract* : A series of homoallylic alcohols was prepared in moderate to good yields from allyl chlorides and ketones, through an electrochemical method using SmCl<sub>3</sub> as the catalyst precursor. The electrosyntheses were carried out in undivided cells fitted with a consumable magnesium anode.

The Barbier reaction is receiving recent interest as a one step alternative to the Grignard reaction<sup>2</sup>, owing to the development of several modifications which have expanded its synthetic potential. Particularly, the condensation of aldehydes and ketones with allyl iodides or bromides in the presence of SmI<sub>2</sub><sup>3,4</sup> has been reported to yield the corresponding homoallyl alcohols. Recently, allyl samarium species have been prepared from allylic chlorides and SmCp<sub>2</sub><sup>5</sup>. These reactions require the use of stoichiometric amounts of the reducing Sm(II) species.

We have been interested in the use of Sm(III) salts as catalyst precursors in electrochemical reactions. We have formerly reported the SmCl<sub>3</sub> catalyzed reductive coupling of aromatic esters to  $\alpha$ -diketones<sup>6</sup>, and that of carbonyl compounds to pinacols<sup>7</sup>. In these reactions, the Sm(II) species have been generated and recycled by electrochemical reduction.

Electroreductive Barbier-type allylations of carbonyl compounds have been achieved in nickel-catalyzed processes<sup>8</sup> or other redox systems<sup>9</sup>.

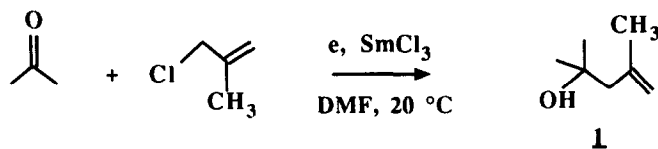
We report here the results of the electrochemical reductive allylation of ketones using a catalytic amount of SmCl<sub>3</sub>. The reactions were carried out in DMF, in a single compartment cell fitted with a consumable magnesium anode. In a typical procedure, after the addition of the halide and the carbonyl compound, the electrolyses were conducted at constant current intensity until complete consumption of the ketone. The electrochemical method offers the advantage of using allyl chlorides, instead of more reactive allyl bromides or iodides generally needed in SmI<sub>2</sub> mediated reactions<sup>3,4</sup>.

The results of the coupling between methallyl chloride and several ketones are collected in Table 1. Both aliphatic and aromatic ketones afforded the corresponding tertiary alcohols in moderate to good yields. The double bond present in 6-methyl-5-hepten-2-one (entry 2) did not interfere in the reaction.

Acetophenone gave 70% of isolated homoallylic alcohol. The yield was 36% in the case of benzophenone, due to the low reduction potential of this ketone and the competitive pinacol formation<sup>7</sup>. The homoallylic alcohol derived from 2-acetylthiophene (entry 5) was formed very selectively, and the moderated yield (40%) is due to the partial polymerization of the starting ketone.

The method was less selective for allyl addition to aldehydes. Meerwein-Ponndorf type side-reactions<sup>10</sup> (including bis-allyl addition) and pinacol coupling were in competition with the formation of the expected secondary alcohols. In the methallyl addition to heptanal, the homoallylic alcohol was isolated in 38% yield.

**Table 1** : SmCl<sub>3</sub>-Catalyzed Electrochemical Coupling of Methallyl Chloride with Ketones<sup>11</sup>).

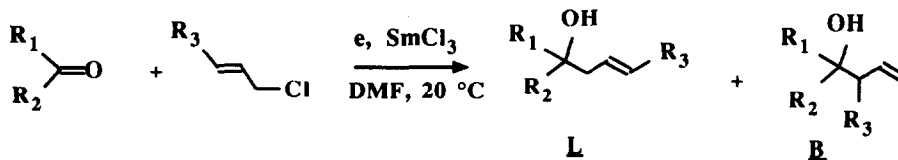


Entry	Ketone	Ratio RCl/ketone	Isolated yield of <b>1</b> (respect to the ketone)
1		4.5	74%
2	Me <sub>2</sub> C=CH(CH <sub>2</sub> ) <sub>2</sub> COMe	4	66%
3	PhCOMe	4	70%
4	PhCOPh	4	36%
5	COMe	3	40%

In the absence of SmCl<sub>3</sub>, the coupling reaction was less effective : the uncatalyzed electrolysis of acetophenone (entry 3) gave the alcohol in 42%. The yield was raised to 70% in the presence of 0.1 equiv. of SmCl<sub>3</sub> (respect to the ketone). In the case of cyclohexanone, the yields went from 74 to 60%, with and without SmCl<sub>3</sub>.

The addition of dissymmetric allyl chlorides to carbonyl compounds is presented in Table 2. The ratio of linear to branched alcohols, **L/B**, was found very dependent on the nature of the substituents. In the addition of crotyl chloride to ketones (R<sub>3</sub>= Me), the formation of the branched alcohol was favored, with a **L/B** ratio of 18/82 in the case of cyclohexanone. In contrast, linear **L**, was the predominant, or the exclusive (entry 4) isomer, in the addition of cinnamyl chloride to ketones.

It is noteworthy that in ketone allylations mediated by SmI<sub>2</sub>, the linear isomer was slightly predominant. For the reaction of cinnamyl or isoprenyl bromides with 2-octanone in THF, **L/B** ratios of 52/31 and 37/27 have been respectively reported<sup>3a</sup>.

**Table 2** : SmCl<sub>3</sub>-Catalyzed Addition of Dissymmetric Allyl Chlorides to Carbonyl Compounds<sup>a)</sup>.

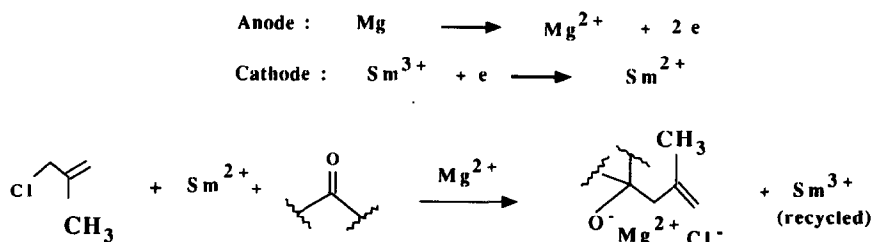
Entry	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	Ratio RCl/ >C=O	Yield (L+B)	Ratio L / B
1		(CH <sub>2</sub> ) <sub>5</sub>	CH <sub>3</sub>	2.7	72%	18 / 82
2	Ph	CH <sub>3</sub>	CH <sub>3</sub>	2.5	61%	47 / 53
3	n-C <sub>3</sub> H <sub>7</sub>	CH <sub>3</sub>	Ph	2.3	60%	69 / 31
4	Ph	CH <sub>3</sub>	Ph	2	50%	100 / -
5	Ph	H	Ph	1.4	85%	35 / 65

a) Experimental procedure : see Ref. 11. Branched alcohols were a mixture of erythro/threo isomers in approx. 1:1 ratio.

In classical allyl Grignard additions to carbonyl compounds, the branched alcohol is generally the predominant isomer<sup>2</sup>.

Some reactions were carried out in the absence of SmCl<sub>3</sub>. Despite the lower yields, the ratio of alcohols issued from the coupling of cinnamyl chloride with benzaldehyde gave identical results (L/B of 35/65), with or without SmCl<sub>3</sub>. The addition of crotyl chloride to cyclohexanone afforded an L/B ratio of 26/74 in the absence of the catalyst, to be compared to a ratio of 18/82 in the SmCl<sub>3</sub> catalyzed process. Thus, the presence of the catalyst did not strongly modify the regioselectivity.

The reactions at the electrodes are shown in Scheme 1: formation of Mg<sup>2+</sup> ions at the anode, and generation and recycling of Sm(II) species at the cathode. Under the electrolysis conditions, the Sm(II) enables the coupling reaction with formation of magnesium alcoholates, which are hydrolyzed at the end of the reaction.

**Scheme 1**

In conclusion, the electrochemical method enables the use of stable  $\text{SmCl}_3$  as the catalyst precursor for the addition of allyl chlorides to ketones, and constitutes an alternative to the use of air sensitive  $\text{SmI}_2$ , employed in similar reactions in stoichiometric amounts. Moreover, less reactive allyl chlorides can be used instead of allyl bromides or iodides.

### References and notes

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11. Electrochemical procedure: In a single compartment cell<sup>12</sup> with a Mg rod anode (diameter 1 cm) and a nickel foam cathode (apparent surface 20 cm<sup>2</sup>) were introduced freshly distilled DMF (40 ml), n-Bu<sub>4</sub>NBF<sub>4</sub> (5.10<sup>-4</sup> M), SmCl<sub>3</sub> (1 mmol), the ketone (10 mmol) and methallyl chloride (10 mmol). The solution was electrolyzed at 20 °C, at constant intensity of 100 mA (apparent current density 0.5 A.dm<sup>-2</sup>), under argon, until disappearance of the starting ketone (4-6 hours). When allyl chloride was consumed (according to GC analysis of aliquots), portions of 5-10 mmol were added during the electrolysis. The faradaic consumption was of 1.5-1.8 F/mol of methallyl chloride. After acidic hydrolysis and ether extraction, the products were purified by column chromatography on silica-gel with pentane-ether mixtures as eluent.
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