First Samarium-catalysed Coupling of Aldehydes and Ketones

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The $SmCl_3$ catalysed electrochemical coupling of carbonyl compounds affords 1,2-diols in good yields.

A considerable interest in the use of lanthanide compounds as new reagents in organic transformations has developed in the last decade.[1] Among them, low-valent lanthanide derivatives, mainly Sm(II) compounds, have been used as promoters for various coupling reactions between carbonyl compounds and/or organic halides.[2] Sm(II) derivatives have strong reducing properties and react as one-electron transfer reagents in the C–C bond forming reactions. These coupling reactions require the use of stoicheiometric amounts of Sm(II)† which is transformed into Sm(III) and no further recycling of these last complexes has been described.

We report here the first samarium-catalysed coupling reaction of aldehydes and ketones (pinacol condensation[2a—c,7,11], involving the recycling of the active Sm(II) species by electrochemical reduction.

Our one-compartment cell electrolysis procedure, based on the use of sacrificial anodes of magnesium or aluminium,[8] allows the use of only 5—10% of $SmCl_3$ as catalyst precursor. A further advantage of the electrochemical method is the use of $SmCl_3$ (a stable and commercially available compound) as starting material, with no need to prepare the air and water sensitive Sm(II) derivatives [usually SmI_2[9] or $(C_5H_5)_2Sm$[10]].

The carbonyl condensations take place in dimethylformamide (DMF) or *N*-methylpyrrolidone (NMP) as solvents, under mild conditions. The results of the pinacol coupling for several aldehydes and ketones are presented in Table 1.

Aromatic, as well as aliphatic aldehydes afford good yields of the corresponding 1,2-diols. The competition between the reduction of an aromatic chloride and that of an aldehyde is shown in example 2, where the chloro group remains unchanged in the diol adduct.

Several examples of ketone condensation (entries 5—9) demonstrate the general applicability of the method. Intramolecular coupling of ketones is presented in examples 8 and 9. The strained diphenyl-substituted cyclopropanediol ring (entry 9) is formed quantitatively.

Table 1. Electrochemically mediated $SmCl_3$-catalysed carbonyl condensation to 1,2-diols.[a]

$$2\ R^1\text{–C(:O)–}R^2 \rightarrow R^1\text{–C(OH)}R^2\text{–C(OH)}R^2\text{–}R^1$$

Conditions: i, $SmCl_3$ (5—10%) +e, then H_3O^+.

Entry	R^1	R^2	Solvent, *T*/°C	Anode	Isolated yield/%[c]
1	Ph	H	DMF, 20	Mg	80
2	*p*-ClC_6H_4	H	NMP, 20	Al	73
3	Me_3C	H	NMP, 20	Al	72
4	n-C_6H_{13}	H	NMP,[b] 20	Al	75
5	Ph	Me	DMF, 20	Mg	90
6	Ph	Ph	NMP, 20	Al	85
7	n-C_5H_{11}	Me	NMP,[b] 50	Al	40
8	$PhC(O)(CH_2)_4$	Ph	NMP, 20	Al	90
9	$PhC(O)\text{-}CH_2$	Ph	NMP, 50	Al	98

[a] Electrolysis: cathode was nickel or stainless steel; solvent, 30 ml; R^1COR^2, 10^{-2} mol; apparent current densities 0.4—0.5 A dm^{-2} Faradaic yield: 60—100%; reaction time: 5—18 h. Entries 1,5,8,9: 5% $SmCl_3$; entries 2—4, 6,7: 10% $SmCl_3$ (Alfa, anhydrous). [b] 6 ml Et_2O were added to the NMP solution during electrolysis. [c] Work up: Acid hydrolysis and diethyl ether extraction. The crude product chromatographed on silica gel or alumina(III) column, with pentane–Et_2O mixtures as eluent. Pinacols recovered as a mixture of *meso*/(±) diastereoisomers.

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† The samarium-catalysed examples concern hydrogenation,[3] polymerization,[4] isomerization,[5] or redox[6] type processes.

Samarium ions are essential in our experiments for an effective pinacol condensation; in the absence of the catalyst, heptan-2-one yielded heptan-2-ol and mixtures of aldol-type condensation products and no 1,2-diol was formed. The alcohol reduction is an important side-reaction in other reported electrochemical mediated pinacol condensations (applied only to aromatic derivatives).[11]

From a mechanistic point of view, we propose that $SmCl_3$ is electrochemically reduced to Sm(II) species [E°_{aq}Sm(III)/Sm(II) = 1.55 *vs.* standard calomel electrode (S.C.E.)[12]]. This reacts with the carbonyl compound to form a Sm(III)-pinacolate after the coupling of two ketyl radical ions.[11,13] Evidence that Sm(II) is effectively formed in solution was obtained from the electrolysis of a $SmCl_3$ solution (NMP, Al anode, 1.1 F mol^{-1}), followed by the addition of excess acetophenone. After stirring for 3 h the expected stoicheiometric amount of pinacol was isolated.

The originality of the present method lies in the possibility of the Sm(III) alcoholates being involved in a transmetallation reaction Sm(III)/Mg(II) [or Sm(III)/Al(III)], the magnesium (or aluminium) ions being formed *in situ* by anodic oxidation. By metal-exchange, Mg(II) [or Al(III)] alcoholates are formed, liberating the Sm(III) ion, able to undergo a further electrochemical reduction and thus to re-enter the catalytic cycle.

In conclusion, the samarium-catalysed pinacol condensation demonstrates that electrosynthesis can be an interesting alternative for adapting Sm(II) promoted stoicheiometric processes to catalytic reactions, by the *in situ* regeneration of the low-valent active species.

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