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Tin-Promoted Electrochemical Hydrodimerization of Ionones

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Synopsis. Electrochemical hydrodimerization of α and β-ionones in the presence of metal tin provides the corresponding hydrodimers in 77 and 60% yields, respectively.

Reductive hydrodimerization of carbonyl compounds is important for the carbon–carbon bond formation. Especially, hydrodimerization of polyenyl carbonyl compounds is useful for the carotenoid synthesis. The electrochemical hydrodimerization would be usable for the purpose. In fact, the electroreductive hydrodimerization is successfully employed for the saturated carbonyl compounds.[1] On the other hand, the hydrodimerization of α, β-unsaturated carbonyl compounds has not been studied in details. 3-Methyl-2-butenal,[2] citral,[3] ionone,[4] and retinal[4] have been electrochemically hydrodimerized by the use of a mercury electrode, but the isolated yields are unsatisfactory. Moreover, the electrolysis has been mostly conducted by the use of a mercury electrode and very few electrodes have been examined for the purpose. On these backgrounds and in connection with our recent study on the electrochemical generation and recycle of the reactive tin reagent,[5] this paper describes a tin-promoted electroreductive hydrodimerization of ionones by the use of platinum electrodes.

Results and Discussion

The electrolysis of α-ionone **1a** was conducted in a methanol-acetic acid-water-1 M (1 M=1 mol dm^{-3}) sulfuric acid solution containing metal tin. Constant current was supplied using two platinum foils as electrodes in a beaker type undivided cell. The result is summarized in Table 1. The reaction at around 40 °C gave the hydrodimer **2a**[6] in more than 70% yield. The reaction at the lower temperature resulted in the increase of the recovered **1** (**2a**; 46% and **1a**; 33%).

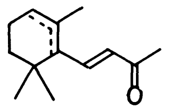
Table 1. Electrochemical Hydrodimerization of Ionones

Substrate	Sn/mol%	F mol^{-1}	**2a** or (**2b**)/%
1a[a]	5	8.6	69
	10	7.5	73
	50	6.6	74
	100	5.8	77
	0	2.5	46
1b[b]	20	3.0	(60)

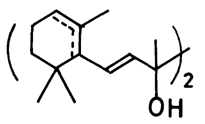
a) **1a** (1 mmol), MeOH (1.5 cm^3), AcOH (0.5 cm^3), H_2O (0.5 cm^3), 1 M H_2SO_4 (0.03 cm^3). b) **1b** (1 mmol), MeOH (2.0 cm^3), H_2O (1.0 cm^3), Et_4NOTs (0.1 mmol).

The increase of metal tin amount led to a slight increase of the yield of **2a**. On the other hand, only 46% of **2a** was obtained in the absence of metal tin after 2.5 F mol^{-1} (1F=96480 C) of current passage. The prolonged electrolysis in the absence of metal tin lost the product **2a** since **2a** was in part converted into the pinacolone **3a**[6] via the pinacol-pinacolone rearrangement in the electrolysis conditions.

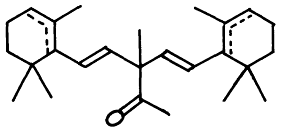
The action of metal tin in the same electrolysis solution under no current passage did not induce the hydrodimerization, clearly suggesting that the metal tin is not a reducing agent. Presumably, di- or tetravalent tin generated in situ would chelate the 1,2-diol to suppress the rearrangement. Another role of tin ion would associate the reductively generated anion radical from **1a** as proposed for chromium(III)[7] to promote an effective dimerization of the metal-associated anion radical **4**. In fact, **2a**(54%) and **3a**(36%) were obtained by the electrolysis in the presence of tin(II) sulfate ($SnSO_4$). The electrolysis of **1b** in a methanol-acetic acid-water-1 M sulfuric acid solution containing metal tin as employed for **1a** provided a trace of **2b**.[4] The pinacol **2b** is so acid-sensitive that it smoothly undergoes the pinacol-pinacolone rearrangement. The electrolysis at −7 °C gave **2b** in 46% yield. Therefore, the electrolysis was conducted in a neutral solution such as in an MeOH-H_2O-Et_4NOTs system, affording **2b** in 60% yield.



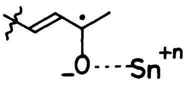
1a α-isomer
b β-isomer



2a α-isomer
b β-isomer



3a α-isomer
b β-isomer



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Experimental

Electrolysis of 1a. A mixture of **1a** (1.0 mmol) and tin powder (0.1 mmol) dissolved in methanol (1.5 cm^3), water (0.5 cm^3), acetic acid (0.5 cm^3), and 1 M sulfuric acid (0.03 cm^3) was electrolyzed in an undivided beaker type cell at 40 °C using platinum foil electrodes (1×1.5 cm^2) under a constant current (20 mA for 10.5 h, 7.5 F mol^{-1}, Metronix

543B DC power supply). After neutralization with saturated sodium hydrogencarbonate, methanol was removed under reduced pressure. Then, the mixture was extracted with ethyl acetate several times. The combined extracts were washed with brine, dried over sodium sulfate, and concentrated in vacuo. The residue was chromatographed on silica gel (hexane–AcOEt) to give **2a**[6] in 73% yield (141 mg).

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