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ELECTROCATALYTIC TRANSESTERIFICATION

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Summary: Transesterification took place electrocatalytically at mild conditions in cathodic compartment, on glassy carbon electrode, in acetonitrile solution of the mixture of ester and alcohol.

For the purpose of changing the properties of fat, Falkovich et al.[1] tried to ester-exchange by passing electricity into a mixture of linseed refined oil and polyhydric alcohols. Their reaction was carried out in anodic compartment at remarkablly high temperature of 160°C to 220°C. They reported that the reaction did not occur at cathodic, and also at the anodic compartment if they used the electrodes except those metals such as Pb, Mn or their alloys which had been generally used as the catalysts for the chemical transesterification procedure in oil industry. Since then, there were no reports published on catalytic electrochemical transesterification until the very recent issuance of the work[2] by Torii et al., who changed tripalmitin into alkyl palmitates in anodic compartment.

We are now reporting that the transesterification reactions of several acid esters and alcohols proceeded electrocatalytically at mild conditions smoothly not in anodic but in cathodic compartment at room temperature (Table 1). Electrolyses were performed in an ordinary two compartment H-type cell attached with a glassy carbon cathode and a Pt anode, containing an acetonitrile[3] solution (10 ml) of substrate ester (1 mmol), alcohol (20 mmol) and supporting electrolyte (1 mmol), either Et_4NClO_4 or $LiClO_4$, at constant potential of -1.7 V or -1.0 V vs. SCE, respectively. After passing current to 0.5 F mol^{-1}, a maximum yield of transesterification was attained, as checked by gas-liquid chromatography. After usual work-up, a mixture of the product and the starting material was obtained, which was separated into components by use of a low pressure liquid chromatography on silica-gel in hexane-benzene mixture.

The attempts of transesterification with phenolic substances instead of alcohols were unsuccessful.

TABLE 1. Electrocatalytic Transesterification

$$\mathrm{RCOOR'} \longrightarrow \mathrm{RCOOR''}$$

Compound R	 R′	Condition[a)]	Product R″	Yield[b)] (%)	Recovered[b)] (%)
Benzyl	Methyl	A	(-)-2-Methylbutyl	47	33
Benzyl	Methyl	A	Benzyl	46	34
Benzyl	Benzyl	A	Methyl	45	32
Benzyl	(-)-2-Methylbutyl	A	Methyl	43	32
Cinnamyl	Methyl	A	(-)-2-Methylbutyl	50	32
Cinnamyl	Methyl	A	Benzyl	48	35
Cinnamyl	(-)-2-Methylbutyl	A	Methyl	45	34
Cinnamyl	Benzyl	A	Methyl	48	33
Benzoyl	Methyl	B	(-)-2-Methylbutyl	52	34
Benzoyl	Methyl	B	(-)-Bornyl	24	50
Benzoyl	Methyl	B	(-)-Menthyl	23	48
Benzoyl	Methyl	B	Benzyl	42	36
Benzoyl	(-)-2-Methylbutyl	B	Methyl	40	37
Benzoyl	(-)-Bornyl	B	Methyl	40	42
Benzoyl	(-)-Menthyl	B	Methyl	38	42
Benzoyl	Benzyl	B	Methyl	43	35

a) 0.5 F $\mathrm{mol^{-1}}$ current was passed through acetonitrile solution (10 ml) of substrate (1 mmol) and alcohol (20 mmol) containing $\mathrm{Et_4NClO_4}$ (A) or $\mathrm{LiClO_4}$ (B) as supporting electrolyte, at the constant potential of -1.7 V (A) or -1.0 V (B) vs. SCE. b) Isolated yield.

References and Notes

1. M.M.Falkovich and K.M.Goldberg, Lakokrasoch. Mater. Ikh Primen., 6 (1967).
2. S.Torii, T.Inokuchi, K.Kondo and H.Ito, Bull. Chem. Soc. Jpn., 58, 1347 (1985).
3. Guranteed grade reagent (Kanto Chemical Co.,Ltd.), after dried by refluxing with $\mathrm{CaH_2}$ for 3 hrs and distilled, was used.

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