Transesterification of Bio Based Fatty Acid Esters by Solid Base Catalysts

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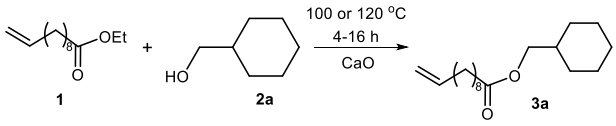
1. Introduction

Long chain aliphatic esters derived from plant oil are promising starting chemicals for their possibility of applications as biobased polymers[1] as well as oleochemicals. Development of efficient catalytic transesterification process under mild conditions without excess alkaline reagent has been an important subject. Recently, efficient conversion of plant oils by the transesterification with methanol by CaO catalyst has been demonstrated.[2] We thus report our results in the reaction of ethyl 10-undecenoate (**1**) with cyclohexanemethanol (**2a**) in the presence of CaO (**Scheme 1**) under various conditions and present the substrate scope with various alcohols.



Scheme 1

2. Experimental

Reagent grade CaO was activated upon heating in vacuo and stored under N_2. Ethyl 10-undecenoate (**1**, 6.0 mmol), cyclohexanemethanol (**2a**, 12.0 mmol) and CaO (25 mg) were charged in the glass reaction tube, and the mixture was heated at 100 or 120 °C with stirring. The conversion, yield, selectivity, and TON were calculated based on gas chromatography using an internal standard.

3. Results and discussion

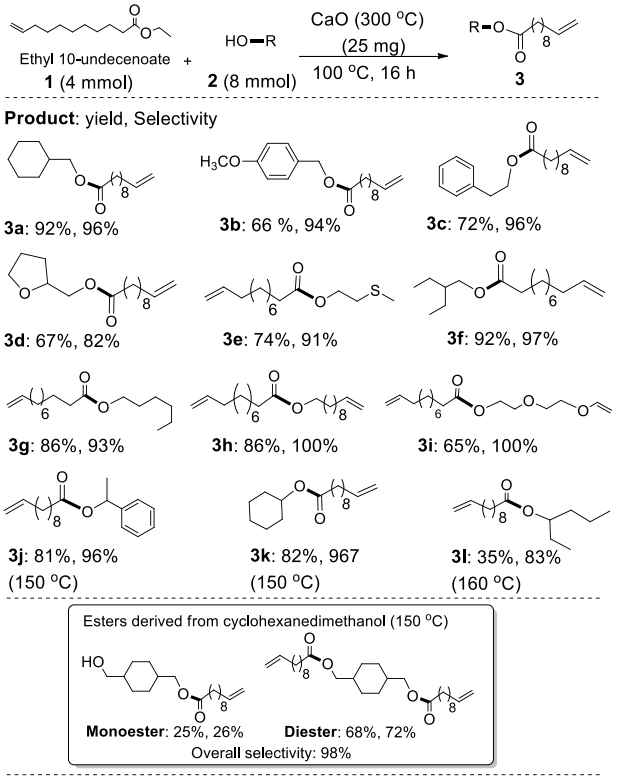
It was revealed that the activity was affected by the activation (pre-baking) temperature employed (120, 200, 300 ºC, 6 h). As summarized in **Table 1**, the activities (and the yield after 16 h) conducted at 120 ºC were higher than those at 100 ºC; the reaction at 120 ºC almost completed after 6 h. The activity was affected by **1**:**2a** molar ratios, and rather excess **2a** favored to proceed the reaction. In most cases, the reaction proceeded with high selectivity (>95 %) to afford the ester (**3a**) in high yield.

The reactions with various mono alcohols (primary, secondary alcohols) and diols also afforded esters in moderate to good yield with high selectivity (**Scheme 2**). More details will be introduced in the symposium.

Table 1. Transesterification of **1** with **2a**.

temp / ºC	time / h	**1**:**2a** / mmol	conv.[b] / %	yield[b] / %	select[b] / %	TON[c]
100	6	6:12	87	83	96	11
100	16	6:12	88	86	98	12
120	2	6:12	61	58	95	7.8
120	4	6:12	88	86	97	12
120	6	6:12	95	93	98	12
120	16	6:12	96	94	97	13
120	16	6:9	92	89	96	12
120	16	6:7.5	88	86	98	12
120	16	6:6	67	65	97	8.7

[a]Conditions: CaO (25 mg) activated at 300 ºC. [b]Based on **1**. [c]Based on Ca.



Scheme 2. Alcohol scope in the transesterification.

References

1. K. Nomura, N. W. B. Awang, *ACS Sustainable Chem. Eng.*, **9**, 5486 (2021).
2. U. Palawat, B. Kitiyanan, to be submitted.

