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Short Communication

Phase-Transfer Catalyzed Synthesis of 2-Propenyl Esters of Carboxylic Acids

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Summary. The tetrabutylammonium bromide catalyzed esterification of salts of carboxylic acids **1 a – e** with 2-propenyl halides **2 a**, **b** is described.

Keywords. Esterification; Phase-transfer catalysis; 2-Propenyl esters.

Phasentransferkatalysierte Synthese von 2-Propenylestern von Carbonsäuren (Kurze Mitt.)

Zusammenfassung. Es wird die tetrabutylammoniumkatalysierte Veresterung von Carbonsäuresalzen **1 a – e** mit 2-propenylhalogeniden **2 a**, **b** beschrieben.

A convenient phase-transfer procedure of esterification [1 – 4] was applied to the preparation of 2-propenyl esters of several carboxylic acids where a new approach was formulated based on the results of the synthesis of (*E*,*E*)-hexa-2,4-dienoic acid 2-propenyl ester and its application to other derivatives. 2-Propenyl esters of carboxylic acids **3 a – e** have been reported [5 – 9].

$$\underset{\mathbf{1\,a{-}e}}{R\text{-COO}M} \quad + \quad \underset{\mathbf{2\,a,\,b}}{CH_2=CHCH_2\text{-}Hal} \quad \xrightarrow[6-79\%]{\substack{TBA\text{Br}/H_2O/CH_2Cl_2 \\ 20-40^\circ C,\, 40-80\,h}} \quad \underset{\mathbf{3\,a{-}e}}{R\text{-COOCH}_2CH=CH_2}$$

M = Na, K; TBABr = tetrabutylammonium bromide

1	*R*-COO*M* (corresponding acids)	2	*Hal*
a	(*E*,*E*)-hexa-2,4-dienoic	**a**	Br
b	2-propenoic	**b**	Cl
c	octadecanoic		
d	*cis*-9-octadecenoic		
e	tricyclo[3.3.1.1^{3,7}]decane-1-carboxylic		

Table 1. 2-Propenyl esters **3**

M in **1**	Substrates		Product	Reaction time (h)	Reaction temperature (°C)	Purification [b.p. (°C/hPa) or solvent]	Yield (%)
K	**1a** [10]	**2a**	**3a**	80	20–22	69–71/1	72
Na	**1a**	**2a**	**3a**	80	20–22		64
K	**1a**	**2b**	**3a**	80	30		6
K	**1b** [11]	**2a**	**3b**	50	30	$120-125/10^3$	75
K	**1c** [12]	**2a**	**3c**	50	20–22	acetone	66
K	**1d** [13]	**2a**	**3d**	40	20–22	195–198/4	79
K	**1e**[a]	**2a**	**3e**	40	40	112–115/4	65

[a] Prepared by a similar method as **1d**; preparation of the acid was reported in Ref. [14]

Table 2. ^{1}H-NMR spectral data of compounds **3a–e**

Compound	Molecular formula[a]	^{1}H-NMR ($CDCl_3$/*TMS*): δ =
3a	$C_9H_{12}O_2$	1.87 (d, 3 H), 4.4–4.9 (m, 2 H), 5.0–5.5 (m, 2 H), 5.6–6.5 (m, 4 H), 7.0–7.5 (m, 1 H)
3b	$C_7H_{10}O_2$	4.5–4.8 (m, 2 H), 5.0–5.6 (m, 2 H), 5.7–6.7 (m, 4 H)
3c	$C_{21}H_{40}O_2$	0.6–1.1 (br, 3 H), 1.25 (br, 30 H), 2.35 (t, 2 H), 4.5–4.7 (m, 2 H), 5.1–5.5 (m, 2 H), 5.6–6.2 (m, 1 H)
3d	$C_{21}H_{38}O_2$	0.7–1.1 (br, 3 H), 1.25 (br, 2 H), 1.60 (br, 2 H), 2.00 (br, 2 H), 2.32 (t, 2 H), 4.4–4.7 (m, 2 H), 5.1–5.5 (m, 4 H), 5.6–6.2 (m, 1 H)
3e	$C_{13}H_{20}O_2$	1.3–2.3 (m, 15 H), 4.3–4.8 (m, 2 H), 5.0–5.5 (m, 2 H), 5.6–6.3 (m, 1 H)

[a] Elemental analyses (C, H) were in good agreement with the calculated values

During the course of our reaction studies we found a dependence of the yield on the halogen atom in **2** (Table 1); the reactions with 2-propenyl chloride (**2b**) had unsatisfying yields. When the salt **1** was formed in situ in a reaction mixture by neutralization of appropriate acids the yields of esters **3** were on the average 10 – 20% lower than in the described method. Replacement of potassium by sodium in **1** did not significantly decrease the yield. We also carried out the reactions with other phase-transfer catalysts [triethylbenzylammonium chloride, tetrabutylammonium iodide or hydrogensulfate and tris(dioxa-3,6-heptyl)amine] with similar results.

The reactions were also performed in different media and it was found that in non-aqueous solvents with an undissolved salt the phase-transfer between solid and liquid phases was negligible and even the use of ultrasound had no influence on the course of the reaction. No mixing effect of ultrasound on the yield could be noticed in a water – organic phase system as well.

The method is useful owing to the absence of acid catalysts and undesirable acid waste products that appear in a common esterification and could cause polymerization.

Experimental Part

NMR spectra were obtained on a Bruker WP 80 SY spectrometer and EA on a Perkin Elmer CHN Analyzator 2400. The ultrasonic generator (bath) Tesla UC 003 CS1 (36 – 42 kHz, 250 ± 50 W) was used.

General Procedure for the Preparation of Compounds **3a – e**

To a mixture of salt **1** (10 mmol), water (30 ml), freshly distilled 2-propenyl halide **2** (10 mmol) and dichloromethane (30 ml), placed in a 100 ml round-bottom flask with a mechanical stirrer, was added tetrabutylammonium bromide (0.16 g, 0.5 mmol). The mixture was stirred vigorously for the time interval and at a temperature described in Table 1. After finishing, the reaction mixture was cooled, the organic dichloromethane layer was dried ($MgSO_4$) and the solvent was evaporated in vacuo. The products were purified by distillation or recrystallization (Table 1). The ^{1}H-NMR data are collected in Table 2.

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