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AN IMPROVED ESTERIFICATION OF CARBOXYLIC ACIDS USING PHASE TRANSFER CONDITIONS WITHOUT SOLVENTS

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ABSTRACT:

Esterification of sodium salt of carboxilic acids were performed with alkyl bromide in phase-transfer conditions without solvent.

The esterification of carboxylic acid is a common procedure of organic synthesis which starts from carboxylic acids directly[1-12] or from their salts[13-19].

Applying phase-transfer conditions the esterification can made without solvent if one of the reactants is liquid[14,22,23]. This process was developed

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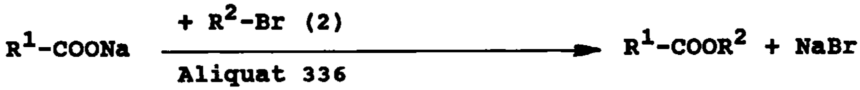
for the synthesis of acetates[20,23] and aromatic carboxylic esters[22].

We elaborated this process for the synthesis of aliphatic carboxylic esters, too. Sodium salt of carboxylic acids and Aliquat 336 (FLUKA) as PTC catalyst were dissolved in alkyl bromide, and after heating at 120°C for several hours and filtered off the bromide formed the esters were obtained by distillation from the reaction mixture.



$$R^1\text{-COONa} \xrightarrow[\text{Aliquat 336}]{+\ R^2\text{-Br}\ (2)} R^1\text{-COOR}^2 + \text{NaBr}$$

(1) 5-24 hrs at reflux (3)

This process can be applied when the alkyl bromides are liquid and the esters formed can be purified by distillation. The best yield can be achieved by applying alkyl bromides with low volatility (propyl or higher homologues)

The viscosity of the reaction mixture determine the amount of alkyl bromide (2), which is 2 ml/g R^1COONa generally. In case of preparation of methyl and ethyl ester the amount of methyl iodide or ethyl bromide is 5 ml/g R^1COONa.

EXPERIMENTAL

General Procedure for Preparation of Sodium Salt of Carboxylic Acids:

Sodium (1.0 equiv.) was dissolved in dry methanol (50 ml/g Na) and carboxylic acid (1.0 equiv) was added to the solution under stirring. The resulting mixture was evaporated in vacuo to yield the solid sodium salt of carboxylic acid quantitatively.

General Procedure for the Esterification:

Aliquat 336 (FLUKA; 0.07 ml/g R^1COONa) was dissolved in alkyl halogenide (2-5 ml/g R^1COONa) and sodium salt of carboxylic acid (1) was added to the solution under vigorous stirring. The resulting mixture was heated at 120°C (bath temperature) for 5-24 hrs under stirring. The time of reaction depends on the amount of carboxylic acid and is controlled by TLC. After cooling the mixture was diluted with ether (10 ml/g R^1COONa) and the precipitate was filtered off. The filtrate was concentrated in vacuo without heating. The residue was fractionated in vacuo to afford the ester of carboxylic acid (3; 60-90%).

Butyl acetate (3a; $R^1= CH_3-$; $R^2= C_4H_9-$):

Starting from sodium acetate (1a) and butyl bromide (2a) to yield butyl acetate (3a; 90%)
B.p.: 123-125°C

Butyl propionate *(3b; $R^1 = C_2H_5-$; $R^2 = C_4H_9-$):*

Starting from sodium propionate (1b) and butyl bromide (2a) to yield butyl propionate (3b; 95%).

B.p.: 144-146°C

Amyl acetate *(3c; $R^1 = CH_3-$; $R^2 = C_5H_{11}-$):*

Starting from sodium acetate (1a) and pentyl bromide (2b) to yield amyl acetate (3c; 95%).

B.p.: 141-143°C

Butyl 11-hydroxy-undecanoate *(3d; $R^1 = HO(CH_2)_{10}-$; $R^2 = C_4H_9-$):*

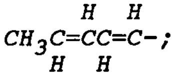
Starting from sodium 11-hydroxy-undecanoate (1c) and butyl bromide (2a) to yield butyl 11-hydroxy-undecanoate (3d; 85%).

B.p.: 166°C/0.3 torr

^{1}H-NMR (100 MHz;$CDCl_3$) δ 0.93(t,J=7Hz,3H,$-CH_3$), 1.25-1.70(m,20H,10xCH_2), 2.29(t,J=7.5Hz,2H,$CH_2C=O$), 3.64(t,J=6Hz,2H,$C\underline{H}_2OH$), 4.09(t,J=6Hz,2H,$CH_2OC=O$);

^{13}C-NMR (25.2 MHz;$CDCl_3$):δ174.07(C^1), 34.42(C^2), 25.04(C^3), 25.83(C^9), 32.08(C^{10}), 62.80(C^{11}), 64.15($C^{1'}$), 30.77($C^{2'}$), 19.19($C^{3'}$), 13.71($C^{4'}$).

Butyl 2(E),4(E)-hexadienoate *(3e; $R^1 =$*



$CH_3\underset{H}{C}=\overset{H}{C}\underset{H}{C}=\overset{H}{C}-$

; $R^2 = C_4H_9-$):

Starting from sodium 2(E),4(E)-hexadienoate (1d) and butyl bromide (2a) to yield butyl 2(E),4(E)-hexadienoate (3e; 90%).

B.p.: 108-110°C/14 torr.

^{1}H-NMR (400 MHz,CDCl$_3$):δ 0.92(t,J=7Hz,3H,CH$_3$-), 1.2-1.8(m,4H,2xCH$_2$-), 1.83(dd,J$_1$=5Hz,J$_2$=0.5Hz,3H,CH$_3$C=),
4.14(t,J=6Hz,2H,OCH$_2$),
5.80(dd,J$_1$=15Hz,J$_2$=1Hz,1H,=C^{2}HC=O), 6.11(m,1H,-C^{5}H=),
6.24(m,1H,=C^{4}H-), 7.28(dd+l.r.,J$_1$=15Hz,J$_2$=10Hz,1H,-C^{3}H=).
^{13}C-NMR (101 MHz;CDCl$_3$):δ167.28(C^1), 119.25(C^2),
144.83(C^3), 129.97(C^4), 139.00(C^5), 18.59(C^6),
64.06(C$^{1'}$), 30.91(C$^{2'}$), 19.27(C$^{3'}$), 13.76(C$^{4'}$).

__Amyl propionate__ (3f; R^1= C_3H_7-; R^2= C_5H_{11}-):

Starting from sodium propionate (1b) and pentyl bromide (2b) to yield amyl propionate (3f; 85%).
B.p.: 66°C/14 torr.

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