A Convenient Method of Esterification of Unsaturated Organic Acids Using a Boron Trifluoride Etherate-Alcohol Reagent

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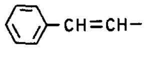
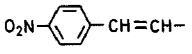
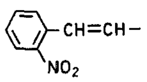
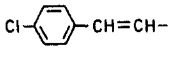
Although the boron trifluoride-methanol reagent is used routinely in the esterification of stable acids prior to G.L.C. analysis[1] and in the synthetic preparation of the methyl esters of a few simple hydroxy- and amino-substituted aromatic acids[2], it is not generally considered a useful reagent in ester synthesis. Recently, we found that a boron trifluoride etherate-alcohol mixture can function as an effective reagent in the direct esterification of 4-aminobenzoic acid leading to the synthesis in high yields of a number of alkyl 4-aminobenzoates[3]:

$$R^1\text{—COOH} + R^2\text{—OH} \xrightarrow[-\ H_2O]{BF_3\text{-etherate, reflux}} R^1\text{—COOR}^2$$

The boron trifluoride-alcohol procedure has also been found successful in the esterification of biphenyl-4,4′-dicarboxylic acid and 1,4-dihydrobenzoic acid, although in moderate yields[4].

We have now found that the boron trifluoride etherate-alcohol reagent is particularly useful in the direct esterifi-

Table 1. Results of Esterification of Aliphatic and Araliphatic Unsaturated Carboxylic Acids

R^1—COOR^2 or R^2OOC—A—COOR^2		Reflux time hr	Yield %	m.p. or b.p.
R^1 or A	R^2			
-CH=CH-	$-CH_3$	20	90	m.p. 101–102° (102°)[a]
$H_3C-CH=CH-CH=CH-$	$-CH_3$	24	70	b.p. 87–89°/19.5 mm (b.p. 180°/759 mm)
-C≡C-	$-CH_3$	24	54	b.p. 59.5–60°/0.7 mm (b.p. 98°/20 mm, b.p. 102°/20 mm)
	$-CH_3$	21	94	m.p. 35–36° (36.5°)
	$-C_2H_5$	24	80	b.p. 128–129.5°/4 mm (b.p. 128–133°/6 mm)
	$n-C_3H_7$	24	80	b.p. 115–120°/1 mm (b.p. 285°)
	$-CH_2-CH_2-OCH_3$	24	79	b.p. 135–138°/0.7 mm[b]
	$-CH_3$	24	92	m.p. 160–162° (161°)
	$-CH_3$	21	87	m.p. 72–73° (73°)
	$-CH_3$	21	85	m.p. 77–78°[b]

[a] The Lit. m.p. or b.p. is given in parenthesis.

[b] These esters do not appear to have been described in the literature.

$C_{11}H_{14}O$	calc.	C 81.48	H 8.64
	found	81.56	8.74
C_9H_9Cl	calc.	C 70.82	H 5.90
	found	71.00	6.10

I.R. analysis gave two strong absorption bands at 1700–1725 cm^{-1} (α,β-unsaturated ester C=O) and 1630–1635 cm^{-1} (conjugated C=C) characteristic of cinnamic esters.

cation of unsaturated carboxylic acids (Table 1). The reaction is convenient to perform and occurs with ease and esterification is selective at the carboxyl group leading to good yields of esters.

Esterification of Carboxylic Acids using Boron Trifluoride Etherate-Alcohol-Reagent; General Procedure:

The reaction mixture comprising the acid (0.1 mol), boron trifluoride etherate (0.1 or 0.2 mol, depending on the number of carboxyl groups in the acid) and the appropriate alcohol (ten times in excess of the boron trifluoride etherate) was refluxed for a period of time not exceeding 24 hr. The esters were precipitated by dilution with a 5% solution of sodium carbonate, followed by filtration, or extraction with ether, and purified by crysallization from appropriate solvents or by distillation under reduced pressure.

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