SHORT PAPER

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Esterification of carboxylic acids with alcohols under microwave irradiation in the presence of zinc triflate[†]

Marzieh Shekarriz*, Sohrab Taghipoor, Ali Asghar Khalili and Mohammad Soleymani Jamarani

Additive department, Chemistry and Petrochemical Division, Research Institute of Petroleum Industry, Qom Road, PO Box: 18745-4163, Tehran, Iran

The esterification of aliphatic and aromatic carboxylic acids with various alcohols (1°, 2°, 3°, benzylic) was studied under microwave irradiation in the presence of zinc triflate as catalyst; the reaction times were short and the yield of reactions was good to excellent.

Keywords: esterification, zinc triflate, microwave irradiation

The esterification of carboxylic acids is a fundamental reaction in organic chemistry.[1,2] Although a number of esterification procedures have been reported up to now,[3-5] there are only a few methods for the effective preparation of esters from equimolar amounts of carboxylic acids and alcohols under mild conditions.[6-8]

During the past decade, our knowledge of microwave assisted organic synthesis has increased significantly.[9-12] The use of microwave irradiation under solvent free conditions provides clean chemical processes. The main advantage of this method is elimination of organic solvents, so making the process environmentally friendly.[13]

In this article we wish to report the catalytic esterification of acids with alcohols in the presence of zinc triflate as a Lewis acid under microwave irradiation. We studied the reaction of phenyl acetic acid (1 mmol) and nonan-1-ol (1 mmol) in the presence of 0.1 molar equivalents of $Zn(OTf)_2$ under microwave irradiation. The reaction was found to be highly effective and the related ester was obtained in 93% yield after 5 minutes. The same reaction in the absence of $Zn(OTf)_2$ produces only 10% of the product after 30 minutes. In order to study the effect of other Lewis acid for this transformation, the reaction was performed in the presence of 0.1 molar equivalents of various catalysts. The results are summarised in Table 1.

The results of Table 1, show the efficiency of $Zn(OTf)_2$ among the studied Lewis acids for this transformation.

The reaction was then studied for esterification of some acids and alcohols (Table 2). Esterification of primary, secondary, tertiary and benzylic alcohols was investigated with various acids under the same reaction conditions, reaction occurring in good to excellent yields. It was shown, that zinc triflate is a good reagent for the esterification of different types of alcohols.

Table 1 Reactions of phenyl acetic acid (1 mmol) with nonan-1-ol (1 mmol) in the presence of various Lewis acids (0.1 mmol) under microwave irradation

Lewis acid	Time/min	Yield/%[a]
$Cu(OAc)_2$	7	45
$CuSO_4$	10	50
$ZnSO_4$	7	60
$Zn(OTf)_2$	5	93
Zeolite HY	10	40
CF_3COOH/silica gel	10	30
Without catalyst	30	10

[a]Yields refer to isolated yield.

The esterification of benzoic acid is an important reaction in organic synthesis, but this transformation normally has the problems such as, low yield, vigorous reaction conditions, long reaction time and so on. We expanded our studies with $Zn(Otf)_2$ to the esterification of benzoic acid and its derivatives (Table 3). Under these conditions the desired esters were obtained in good yield (60–85%) and short reaction times (3–5 min).

Phenol was also reacted with some acids such as acetic acid, propionic acid, stearic acid, and benzoic acid, but the yields of these reactions were in the range 20–30% and the time of irradiation was high (>30 min).

In conclusion, this method could be useful for the esterification reactions which are often required in complex synthetic schemes. The possibility of performing the reactions under solvent-free conditions and with easy procedure and work-up make this method a useful addition to the present methodologies.

Note, aliphatic compounds are not environmentally hazardous and their esters are easily biodegradable. Aromatic compounds have been used in accordance with their Material Data Safety Sheets,[14] $Zn(Otf)_2$ has a hygroscopic nature. Therefore, the necessary precautions were taken (rapid weighing and immediate use) and it has been used in accordance with its MSDS.[14]

Experimental

All yields refer to isolated products after column chromatography. All of the products were characterized by a comparison of their spectral and physical data with samples with preferred by reported procedures. Melting or boiling points were not usually reported in the literature. IR spectra were run on a Perkin Elmer 781 spectrophotometer. NMR spectra were recorded on a Bruker Avance DPX-250. Mass spectra were recorded on a Shimadzu GCMS-QP 1000 EX. The purity of the substances and the progress of the reactions were accomplished by TLC on silica-gel polygram SILG/UV_{254} plates or by a Shimadzu Gas Chromatograph GC-10A instrument with a flame-ionisation detector using a column of 15% carbowax 20M chromosorb-w acid washed 60–80 mesh. The microwave oven used was a commercially available model (Butane M 245 kitchen oven) operating at a maximum power level of 1000 W. The silica gel used in reactions was Type 60 (Merck) which had been dried in a vacuum oven at 100°C and 2mmHg for 24h.

General procedure for catalytic esterification of acid with alcohol in the presence of $Zn(OTf)_2$ under microwave irradiation: In a glass open-ended tube, a mixture of acid (1 mmol), alcohol (1 mmol) and silica gel {see above} (2 g) was premixed with $Zn(Otf)_2$ (0.1 mmol). The mixture was irradiated with 1000 W power of domestic microwave for 2–10 min. A dish of silica gel was present in the microwave oven to absorb any moisture and a beaker of silicon oil to prevent overheating were used. The completion of the reaction was monitored with GLC or TLC. The reaction mixture solidified on cooling to room temperature. Then the reaction mixture was dissolved in $CHCl_3$ (40 ml) and filtered. The filtrate was washed with water (20 ml) to remove the catalyst. The organic layer was dried with anhydrous sodium sulfate. The solvent was evaporated and the crude

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* To receive any correspondence. E-mail: shekarriz@ripi.ir

[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 2 Esterification of acids with alcohols in the presence of $Zn(OTf)_2$ (0.1 mmol) under microwave irradiation

Entry	Acids	Alcohol	Time /min.	Yield[a] /%	M.p. (b.p.)/°C	Lit
1	Phenyl acetic acid	Octan-2-ol	6	75	49–50[15a]	d
2	Phenyl acetic acid	(-)-Menthol	10	65	46–47[15b]	d
3	Phenyl acetic acid	Benzyl alcohol	4	90	51–52[15c]	d
4	Phenyl acetic acid	Octan-1-ol	3	85	50–53[15d]	d
5	Phenyl acetic acid	Nonan-1-ol	5	93	52–54[15d]	d
6	Phenyl acetic acid	Propan-2-ol	3	75	25–27[15e]	d
7[c]	Phenyl acetic acid	Adamantan-1-ol	6	55	83–84	-
8	Phenyl acetic acid	Pentan-1-ol	2	87	31–32[15f]	d
9	Stearic	Octan-2-ol	7	70	43–45[6]	d
10	Stearic	(-)-Menthol	10	50	39–40[6]	d
11	Stearic	Benzyl alcohol	5	80	44–45[16]	45
12	Stearic	Octan-1-ol	5	78	43–44[6]	d
13	Stearic	Nonan-1-ol	6	83	46–47[17a]	d
14	Palmitic	Octan-2-ol	6	78	34–35[17a]	d
15	Palmitic	Benzyl alcohol	5	85	34–35[16]	36
16	Palmitic	Nonan-1-ol	4	87	38–39[17a]	d
17 [b]	Oleic	Octan-2-ol	4	75	(223)[17b]	d
18 [b]	Oleic	Benzyl alcohol	3	80	(235)[16]	(237)
19 [b]	Oleic	Nonan-1-ol	3	81	(241)[17b]	d

[a]Yield refers to isolated product. [b]Reactions were performed under 70% power of microwave irradiation. [c]Tentative structure attribution: ^{1}H-NMR ($CDCl_3$) δ: 7.24 (s, 5H), 3.6 (s, 2H), 1.6–1.8 (m, 15H), FT-IR (film) ν: 3056, 2983, 1715, 1455, 1375, 1266, 1107, 739 cm^{-1}, MS (M^+): 270.37. [d]Reference to the compound was reported.

Table 3 Esterification of benzoic acid and its derivatives with alcohols in the presence of $Zn(OTf)_2$ (0.1 mmol) under microwave irradiation

Entry	Acids	Alcohol	Time /min.	Yield[a] /%	M.p. (b.p.)/°C	Lit
1	Benzoic	Octan-2-ol	4	60	(287)[18a]	c
2	Benzoic	Octan-1-ol	3	70	(300)[18a]	c
3	Benzoic	Benzyl alcohol	4	72	(322)[16]	323
4	4-methylbenzoic	Octan-1-ol	3	85	45–46[18b]	c
5	4-methylbenzoic	Octan-2-ol	6	68	40–42[18b]	c
6	4-methylbenzoic	Benzyl alcohol	3	78	31–32[18c]	c
7	2-chlorobenzoic	Octan-1-ol	5	65	38–39[19a]	c
8	2-chlorobenzoic	Octan-2-ol	6	60	(300)[19a]	c
9	2-chlorobenzoic	Benzyl alcohol	3	65	(289)[19b]	c
10[b]	Terephetalic	Octan-1-ol	6	62	48–49[19a]	c
11[b]	Terephetalic	Octan-2-ol	8	58	40–41[19a]	c

[a]Yield refers to isolated product. [b]The ratio of alcohol/acid was 2/1; diester product. [c]Reference to the compound was reported.

product was chromatographed on a short column of silica gel using *n*-hexane-CH_2Cl_2 (3:2) as eluent. The pure ester product was obtanied in 50-93% yields (Tables 2, 3).

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