Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

$Fe_2(SO_4)_3 \cdot xH_2O$ Catalytic Esterification of Aliphatic Carboxylic Acids with Alcohols

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Published online: 15 Aug 2006.

To cite this article: Gui-Sheng Zhang (1998): $Fe_2(SO_4)_3 \cdot xH_2O$ Catalytic Esterification of Aliphatic Carboxylic Acids with Alcohols, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 28:7, 1159-1162

To link to this article: http://dx.doi.org/10.1080/00397919808005956

SYNTHETIC COMMUNICATIONS, 28(7), 1159-1162 (1998)

$Fe_2(SO_4)_3 \cdot xH_2O$ CATALYTIC ESTERIFICATION OF ALIPHATIC CARBOXYLIC ACIDS WITH ALCOHOLS

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Abstract: Treatment of various alcohols with aliphatic carboxylic acids in the presence of a catalytic amount of $Fe_2(SO_4)_3 \cdot xH_2O$ to give the corresponding esters in good yields.

It has long been known that the process of esterification may be enormously hastened by the addition of a strong acid, such as sulfuric acid[1~4]. The classical methods for the synthesis of esters are not suitable for acid sensitive compounds and have the disadvantages of the corrosiveness of strong acid and usually accompanying side reactions such as carbonization, oxidation, etc.. Several esterification catalysts have been used which have been found some advantages over the classical acid catalyst[5~8]. This paper report the catalytic esterification of aliphatic carboxylic acid with alcohols using $Fe_2(SO_4)_3 \cdot xH_2O$ as a convenient and efficient catalyst.

The reaction is simply performed by refluxing a mixture of alcohols, acids and entrainer (if necessary) with a catalytic amount of $Fe_2(SO_4)_3 \cdot xH_2O$ for several hours .The product is then isolated by filtration of the catalyst and removal the free acid or alcohols by distillation and washing. The results obtained from the

preparation of 17 aliphatic esters of mono- and dibasic carboxylic acids are reported in the Table 1and Table 2.

In conclusion, with the easily available catalyst, high yields, mild conditions and short reaction time, as well as easy operation, we think that the present work described herein may not only provide a useful method for a preparation of aliphatic carboxylic esters, but also open a new way for using ferric sulfate instead of strong acids in organic synthesis.

Scheme 1

$$RCO_2H + R'OH \underset{}{\overset{Fe_2(SO_4)_3 \cdot xH_2O}{\rightleftharpoons}} RCO_2R' + H_2O$$

1 2 3

a: R= CH_3, R'= C_2H_5 b: R= CH_3, R'= $CH_3(CH_2)_3$

c: R= CH_3, R'= $CH_3(CH_2)_4$ d: R= $CH_3(CH_2)_8$, R' =CH_3

e: R= $CH_3(CH_2)_{10}$, R'= CH_3 f: R= $CH_3(CH_2)_{12}$, R'= CH_3

g: R= $CH_3(CH_2)_{14}$, R'= CH_3 h: R= $CH_3(CH_2)_{16}$, R'= CH_3

Table 1. The Preparation of Aliphatic Esters of Monobasic carboxylic acids[a]

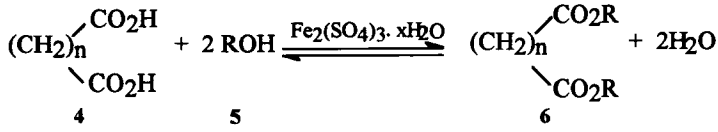
Product	Ratio of 1/2	Entrainer	Reflux time(h)	b.p.(℃/mmHg)	Yields(%)[b]
3a	2	toluene	1.5		93[c]
3b	2		2		90[c]
3c	2		1.5	145~148/760	94
3d	0.4	benzene	1.6	115~120/10	93
3e	0.4	benzene	2	152~158/18	85
3f	0.3	benzene	1.5	155~160/6	89
3g	0.3	benzene	1.5	174~180/5	91
3h	0.3	benzene	1.5	197~204/7	94

a. The weight ratio of catal./acid was 2%.

b. Isolated yield, unless otherwise noted. All compounds isolated had identical spectral characteristics with the corresponding authentic samples.

c. determined by GLC.

Scheme 2



4 5 6

a: n= 0, R= C_2H_5 b: n= 1, R= C_2H_5

c: n= 2, R= C_2H_5 d: n= 4, R= C_2H_5

e: n= 4, R= C_2H_5 f: n= 4, R= $CH_3(CH_2)_2$

g: n= 4, R= $CH_3(CH_2)_4$ h: n= 4, R= $CH_3(CH_2)_5$

i: n= 4, R= $CH_3(CH_2)_6$

Table 2. The Preparation of Aromatic Esters of Monobasic carboxylic acids[a]

Product	Ratio of 5/4	Entrainer	Reflux time(h)	b.p.(℃/mmHg)	Yields(%)[b]
6a	4	toluene	1.2	74~76/6	90
6b	4	toluene	1.6	79~81/9	93
6c	4	toluene	3	108~110/17	95
6d	4	toluene	3	116~117/9	96
6e	4	toluene	3	108~112/10	86
6f	4	toluene	2	143~145/8	98
6g	4		1	169~172/11	96
6h	4		1	187~190/8	95
6i	4		0.5	208~210/8	92

a. The weight ratio of catal./acid was 3%.

b. Isolated yield. All compounds isolated had identical spectral characteristics with the corresponding authentic samples.

Experimental

The Eserification of Adipic Acid with Ethanol; Typical Procedure

Place a mixture of 14.5g (0.1mol) of adipic acid, 18.5g (0.4mol) of absolute ethyl alcohol, 35 ml of dry benzene and 0.3g of commercial ferric sulfate in a flask, equipped with an

automatic water separator carrying an efficient reflux condenser at its upper end. Reflux the mixture on a steam bath for 3h or until water no longer collects in appreciable amount in the water separator, run off the water from time to time. Filter off the catalyst and wash it with two 20 ml portions of ether. The combined filtrate is washed with saturated sodium carbonate solution, then with cool water, and dry with anhydrous magnesium sulfate . Remove most of the ether and benzene by distillation under normal pressure, then distil under reduced pressure and collect the diethyl adipate at 116~117/9mm. The yield is 19.4g (96%).

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(Received in The Netherlands 03 November 1997)