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Anupama Parmar [b] , Jatinder Kaur [b] , Rita Goyal [a] , Baldev Kumar [b] & Harish Kumar [a]

[a] Department of Chemistry , Sant Longowal Institute of Engg. & Technology , Longowal, 148 106, India

[b] Department of Chemistry , Punjabi University , Patiala, 147 002

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ESTERIFICATION IN DRY MEDIA USING FERRIC PERCHLORATE ADSORBED ON SILICA GEL

Anupama Parmar[a], Jatinder Kaur[a], Rita Goyal, Baldev Kumar[a] and Harish Kumar*

Department of Chemistry, Sant Longowal Institute of Engg.& Technology, Longowal - 148 106 (India)
[a]Department of Chemistry, Punjabi University, Patiala-147 002.

Abstract : Adsorption of $Fe(ClO_4)_3(H_2O)_6$ onto chromatographic grade silica gel in the presence of alcohol (to be used for esterification) produces a supported reagent, $Fe(ClO_4)_3(ROH)_6/SiO_2$.This reagent, has been found effective for the rapid and high yield of esters, on grinding in the presence of carboxylic acids using pestle and mortar in the solid state.

Recently, considerable attention has been focused on solid state organic chemistry[1]. Many organic reactions, such as Baeyer-Villiger oxidation[2], pinacol rearrangement[3], grignard, reformatsky, luche, wittig reaction[4,5], $NaBH_4$ reduction of ketones, aldol condensation and Michael addition[1] reaction have been carried out efficiently in the solid state. We were interested in studying the applications of ferric perchlorate[6,7] in the dry medium and hence these "Supported reagents" were prepared.These supported reagents has the advantage[8,9] of being easily removed from the organic product by filtration.

* To whom correspondence should be addressed

Further advantage of these supported reagents is improved storage stability in moisture in comparison to $Fe(ClO_4)_3(H_2O)_6$ which is very sensitive to moisture.

The "supported reagents" of interest were prepared by simple dissolution of $Fe(ClO_4)_3(H_2O)_6$ in the appropriate alcohol (which is to be used for esterification) followed by addition of an appropriate amount of dried chromatographic grade silica gel. Evaporation of the solvent gave $Fe(ClO_4)_3(ROH)_6/SiO_2$ complex as a homogeneous, free flowing, light yellow to creamish powder. The formation of such complexes [$Fe(ClO_4)_3(S)_6$; S=solvent] from $Fe(ClO_4)_3(H_2O)_6$ has already been reported[10].The amount of iron present in each batch of reagent was accurately determined by titration.

A large number of reagents have been reported in literature for effective esterification of the carboxylic group. However, these reagents suffer from many limitations such as vigorous reaction conditions, longer reaction periods[11],instability of the reagent[12] and formation of side products[13]. We herein report a very simple and efficient method for the esterification of carboxylic acids (I) using $Fe(ClO_4)_3(ROH)_6/SiO_2$ reagents. When supported reagent [$Fe(ClO_4)_3(ROH)_6/SiO_2$] was mixed and grinded with an equimolar amounts of carboxylic acids (I) in pastle and mortar, the corresponding esters (II) were obtained in almost quantitative yields (Table-1). The structure of the esters obtained was confirmed through NMR, IR and Mass spectra of some representative samples and also by comparison with authentic samples.

$$\underset{(I)}{R^1COOH} + Fe(ClO_4)_3(ROH)_6/SiO_2 \longrightarrow \underset{(II)}{R^1COOR}$$

This method has been found successful for the quantitative esterification with primary and secondary alcohols but tertiary alcohols did not give the satisfactory results.

Table-1
Esterification of Carboxylic acids (I) with $Fe(ClO_4)_3(ROH)_6/SiO_2$ reagent

Entry	R^1COOH	ROH	Yield of Ester[a](II) [%]	b.pt/m.pt [°C]
1.	Hippuric acid	Methanol	55	85
		Ethanol	60	67
		2-Propanol	83	65
		Isoamyl alcohol	90	oil
2.	Succinic acid	Methanol	62	195
		2-Propanol	59	82/3
		Isoamyl alcohol	68	132/4
3.	Oxalic acid	Methanol	67	53
		Ethanol	67	186
		2-Propanol	70	192
		Isoamyl alcohol	81	127/7
4.	Adipic acid	Methanol	72	121/17
		2-Propanol	69	120/6
		Isoamyl alcohol	84	184/13
5.	Phenyl acetic acid	Methanol	88	214
		Ethanol	78	227
		2-Propanol	68	234
		Isoamyl alcohol	79	oil
6.	Malic acid	Methanol	75	205
		Ethanol	70	224
		2-Propanol	73	252
		Isoamyl alcohol	71	oil
7.	Cinnamic acid	Methanol	59	36
		2-Propanol	73	260
		Isoamyl alcohol	60	oil
8.	Crotonic acid	Methanol	66	119
		Ethanol	69	137
		Isoamyl alcohol	80	60/7

a) The structure of all these esters have been confirmed from their NMR, IR and in some cases Mass spectra and also with comparison to authentic samples.

In conclusion, the "supported reagents" described here for the esterification are simple, unaffected by moisture, have greater storage stability, easy to use, efficient and easily separable from the reaction mixture and avoid many disadvantages of the previous methods.

EXPERIMENTAL

All melting points recorded are uncorrected, open capillary measurements, using sulphuric acid bath. Infrared spectra were recorded using KBr pellets on a Perkin-Elmer spectrophotometer. Nuclear Magnetic Resonance spectra were recorded on EM-390, 90 MHz instrument using tetramethylsilane (TMS) as internal standard. All product spectra were compared with spectra of authentic samples taken on the same instrument.

All solvents were reagent grade and used as received. Silica gel for column chromatography was used as received from E Merck.

Preparation of $Fe(ClO_4)_3(ROH)_6/SiO_2$ reagent.

An appropriate amount of $Fe(ClO_4)_3(H_2O)_6$ is dissolved in alcohol (to be used for esterification). Enough alcohol is added to assure the complete dissolution of $Fe(ClO_4)_3(H_2O)_6$. To this is added the appropriate amount of dried chromatographic grade silica gel. The mixture is mixed properly and allowed to stand for one hour. The excess alcohol is filtered off under vacuum. The supported reagent at this point is reproducibly a homogeneous, free flowing, creamish powder. The supported reagent is stored in a bottle after drying in air for 1-2 days. The reagent is unaffected by light or moisture.

Determination of iron (iii) present in $Fe(ClO_4)_3(ROH)_6/SiO_2$ reagent

A weighed sample of $Fe(ClO_4)_3(ROH)_6/SiO_2$ reagent was analysed for determining the amount of iron present by a series of redox reactions[14].

General Procedure for Esterification

Equimolar amounts of "supported reagent" and the carboxylic acid were mixed together and grinded in a pastle and morter for 15 minutes. Usually an immediate colour change was observed. The reaction mixture was allowed to stand for 2 hrs. To this crude reaction mixture was added methylene chloride (50 mL) and distilled water (5 mL) to quench the reaction mixture as well as destroy any inorganic complexes that may have formed during the reaction. The mixture was stirred for 1 minute and then suction filtered. The spent reagent was washed twice with methylene chloride (10 mL each). The combined organics were washed with saturated $NaHCO_3$ solution followed by 1% hydrochloric acid, water, dried over sodium sulphate and solvent was removed under reduced pressure. This crude reaction mixture was analyzed and purified in a conventional manner. Esters (Table-I) formed were identified by comparison of NMR, IR and in some cases Mass spectra with authentic samples

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