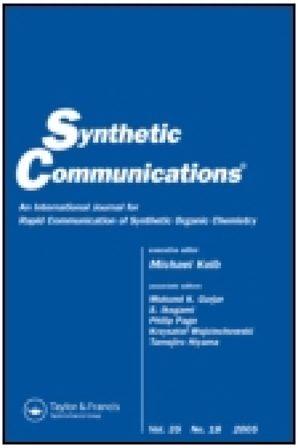

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# Transetherification of Allylic and Benzylic Ethers in the Presence of Ferric Ion

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SYNTHETIC COMMUNICATIONS, 30(10), 1743–1747 (2000)

# TRANSETHERIFICATION OF ALLYLIC AND BENZYLIC ETHERS IN THE PRESENCE OF FERRIC ION

Peyman Salehi[a*], Mohsen Irandoost[a], Behnam Seddighi[a], Farahnaz Kargar Behbahani[a], Daryush Poor Tahmasebi[b]

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***ABSTRACT :*** Alcoholysis of allylic, secondary and tertiary benzylic ethers is proceeded efficiently in the presence of catalytic amounts of ferric ion as anhydrous $FeCl_3$ and $Fe(ClO_4)_3$.

The exchange of one alkoxy group for another is very rare for ethers.[1] Some special kinds of alkoxy groups can be exchanged in the presence of p-toluenesulfonic acid as catalyst.[2] Treatment of alkylaryl ethers with alkoxide ions is also another method for the exchange of the alkoxy groups.[3] Enol ethers can be prepared by alcoholysis of an enol ether with catalytic amount of mercuric acetate.[4]

In continuation of our study on the application of ferric ion in cleavage of carbon-oxygen bond in alcohols and ethers,[5,6] we wish to report a selective

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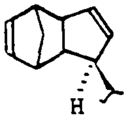
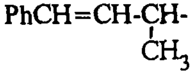
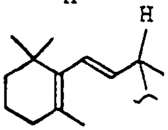
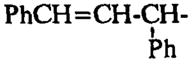
and efficient method for transetherification of some kinds of ethers in the presence of $Fe^{3+}$ ion as anhydrous ferric chloride and ferric perchlorate.

Reaction of allylic, secondary and tertiary benzylic ethers was carried out in different alcoholic solvents in the presence of catalytic amounts of ferric ion (Scheme, Table).

$$\underset{1(a\text{-}g)}{ROR'} \xrightarrow[Fe^{3+},cat.]{R''OH} \underset{2(a\text{-}g)}{ROR''}$$

R',R'' = Me,n-Pr,i-Pr,t-Bu

| | R | | R |
|---|---|---|---|
| 1a |  | 1d |  $PhCH{=}CH\text{-}\underset{CH_3}{CH}\text{-}$ |
| 1b |  | 1e |  $PhCH{=}CH\text{-}\underset{Ph}{CH}\text{-}$ |
| 1c | PhCH=CH-$CH_2$- | 1f | $Ph_2CH$- |
| | | 1g | $Ph_3C$- |

Scheme

All of the reactions were performed under reflux condition. Comparison of the results show that in similar cases $Fe(ClO_4)_3$ is more reactive than $FeCl_3$ as expected. Although ferric perchlorate promoted the etherification of secondary benzylic alcohols the same reaction did not proceed in the presence of ferric chloride (Table, entries 13-15).

Table. Alcoholysis of allylic and benzylic ethers in the presence of ferric ion.

| Entry | R | R′ | $Fe(ClO_4)_3$ | | | $FeCl_3$ | | | R″ | Product |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Mole ratio | Time (min) | Yield (%) | Mole ratio | Time (hr) | Yield (%) | | |
| 1 | 1a | Me | 0.05 | 10 | 85 | 0.3 | 4.5 | 80 | i-Pr | 2a |
| 2 | 1a | i-Pr | 0.05 | 10 | 91 | 0.3 | 2.5 | 75 | n-Pr | 2a |
| 3 | 1b | n-Pr | 0.05 | 20 | 87 | 0.3 | 2 | 78 | Me | 2b |
| 4 | 1b | t-Bu | 0.05 | 15 | 89 | 0.3 | 2.5 | 70 | n-Pr | 2b |
| 5 | 1c | n-Pr | 0.05 | 90 | 95 | 0.4 | 7 | 65 | i-Pr | 2c |
| 6 | 1c | i-Pr | 0.1 | 240 | 92 | 0.4 | 7 | 60 | Me | 2c |
| 7 | 1d | Me | 0.05 | 25 | 83 | 0.3 | 1.5 | 83 | n-Pr | 2d |
| 8 | 1d | n-Pr | 0.05 | 35 | 96 | 0.3 | 3 | 78 | i-Pr | 2d |
| 9 | 1d | i-Pr | 0.05 | 35 | 80 | 0.3 | 2.5 | 87 | Me | 2d |
| 10 | 1e | Me | 0.02 | 40 | 87 | 0.3 | 3.5 | 85 | i-Pr | 2e |
| 11 | 1e | n-Pr | 0.02 | 35 | 84 | 0.3 | 3 | 83 | i-Pr | 2e |
| 12 | 1e | i-Pr | 0.02 | 40 | 92 | 0.3 | 3 | 75 | Me | 2e |
| 13 | 1f | Me | 0.1 | 150 | 97 | no reaction | | | n-Pr | 2f |
| 14 | 1f | n-Pr | 0.2 | 180 | 96 | no reaction | | | i-Pr | 2f |
| 15 | 1f | i-Pr | 0.2 | 180 | 92 | no reaction | | | Me | 2f |
| 16 | 1g | Me | 0.05 | 40 | 97 | 0.2 | 0.25 | 90 | n-Pr | 2g |
| 17 | 1g | n-Pr | 0.05 | 40 | 96 | 0.2 | 0.25 | 93 | Me | 2g |

According to the catalytic nature of the reactions, ease of workup procedure, excellent yields, availability and non-toxic nature of the reagents, this method could be used widely for selective transetherification of ethers.

## *EXPERIMENTAL*

All of the products are known compounds and were characterized by comparison of their spectral data and physical properties with those of authentic samples. The purity determination of substrates and reaction monitoring were accomplished by TLC using silica gel polygrams SIL G/UV 254 plates. $^1$H NMR spectra were run on a Jeol JNM-PMX 60 MHz spectrometer. Infrared spectra were obtained using a Shimadzu 470 spectrophotometer. All yields refer to isolated products.

### General Procedure for the Alcoholysis of Ethers in the Presence of Ferric ion.

To a solution of the ether(1 mmol) in an alcoholic solvent(4 ml) ferric ion(0.02-0.1 mmol) was added. The mixture was stirred magnetically under reflux condition until the complete consumption of the substrate. Solvent was evaporated under vaccum and the residue was purified by column chromatography on silica gel. The desired products were obtained in 25-98% yields.

## *ACKNOWLEDGMENT*

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