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Research Paper

Modification of Hunsdiecker Reaction using TBATB as the brominating agent

Chemistry

KEYWORDS : Halo decarboxylation, Cinnamic acid, Tetra Butyl Ammonium Tri Bromide (TBATB), Et_3N

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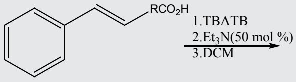
ABSTRACT

α,β-unsaturated aromatic carboxylic acids react with TBATB as brominating agent, Et_3N as catalyst and DCM as solvent giving β-bromostyrene in good yield and in relatively less time.(Scheme 1)

Scheme 1



Introduction

The halodecarboxylation of metal carboxylates with molecular bromine is popularly known as the Hunsdiecker reaction[1]. It is an extremely useful methodology for the synthesis of halogenated organic substrates in the field of organic synthesis.

Review of literatures

Several methods have been developed in this regard. Carboxylic acid is refluxed with excess of red P, mercuric oxide and bromine in CCl_4 solvent[2] In many cases NBS has been used as the brominating agent, using LiOAc as catalyst and MeCN-H_2O as solvent[3] Again NBS was used with $Mn(OAc)_2$ as catalyst and MeCN-H_2O as solvent[4] Metal free catalytic reaction was carried using N-bromosuccinamide as brominating agent and tetrabutyl ammoniumtrifluoroacetate (TBATFA) as catalyst in dichloroethane as solvent[5] N-halosuccinimides and tetrabutylammoniumtrifluoroacetate as catalyst in dichloroethane was reacted in catalytic Hunsdiecker reaction[6] In some cases KBr was used as the brominating agent. In green Hunsdiecker reaction α,β-unsaturated aromatic carboxylic acids was reacted with KBr and H_2O_2 catalysed by $Na_2MoO_4 \cdot 2H_2O$ in aqueous medium[7,8.] UV-vis spectrophotometry was used to measure the relative efficiency of lithium acetate, tetrabutylammoniumtrifluoroacetate, and triethylamine as catalysts for the conversion of 4-methoxycinnamic acid to 4-methoxy-α-bromo- styrene, acetonitrile-water, dichloro methane and acetonitrile as solvent[9] Halodecarboxylation of β-arylacrylic acids was carried out with the ceric ammonium nitrate using KBr as brominating agent[10]

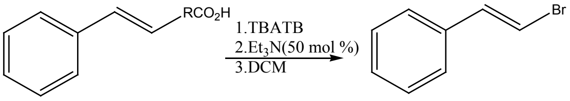
There are cases where tetra butyl agent[11,12,13,14,15.] ammonium tri bromide (TBATB) is used as brominating agent[11,12,13,14,15.] TBATB was synthesised from CAN and tetra alkyl ammonium bromide in water solvent in a greener way[16]

Instead of several modifications there are still several limitations like necessity of high temperature, very poor yields in cases of substrates such as α,β-unsaturated carboxylic acids, the toxicity inherent with molecular bromine and salts of Hg,Tl,Pb,Ag.

Results and discussions

We are discussing herewith the rapid and efficient procedure for the synthesis of β-bromostyrene from cinnamic acid using tetra butyl ammonium tribromide,as brominating agent. At first the reaction was carried out with cinnamic acid (1mM) with TBATB (1.2mM) as brominating agent, Et_3N as catalyst in (3ml) and dichloro methane (DCM) as solvent at room temperature. (scheme 2)

Scheme 2



Our study begins with using TBATB as the brominating agent and Et^3N as the catalyst. Cinnamic acid (1mmol) was reacted with TBATB (1.2mmol). Reactions were carried out in two different solvent mediums. In DMF as the solvent with 30 mol% catalyst the reaction time was 9 hour 30 min. But with increasing catalyst amount the time decreased to 15 min for 50 mol% catalyst. In DCM as the solvent, reaction time using 30 mol% catalyst reaction time was 30 min, that decreased to 5 min using 50 mol% catalyst. The products were characterised by NMR spectral analysis.

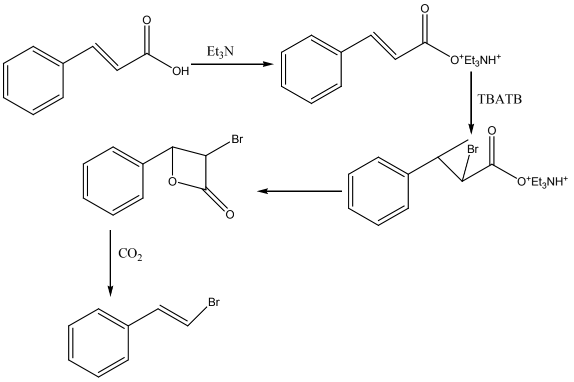
Table:1 Halo decarboxylation of cinnamic acid to β- bromostyrene using TBATB as brominating agent

Entry	Solvent	Et_3N (mol%)	Time	Yield (%)
1	DMF	30	9 h 30 min	50
2	DMF	40	30 min	25
3	DMF	50	15	20
4	DCM	30	30	55
5	DCM	40	15	60
6	DCM	50	5	65

Reaction condition: Substrate 1mmol, room temperature

Probable mechanism

Probable mechanism is as follows.



Experimental:

General procedure for synthesis of Tetra Butyl Ammonium Tri Bromide Ceric ammonium nitrate, CAN (1mM) and Tetrabutyl ammonium bromide (1.5mM) were dissolved in 10 ml H_2O. They were stirred together at room temperature. Yellow precipitation of Tetrabutyl ammonium bromide formed was filtered, dried and collected. It was kept in the desiccator.

General procedure for synthesis of β- bromostyrene

Chemicals required: Cinnamic acid, TBATB, Et_3N, Solvent.Procedure: Cinnamic acid (1mM) and Et3N(0.5mM) were stirred in DMF (3ml) at room temperature for 5 minutes. Then TBATB (1.2mM) was added in that medium. Course of the reaction was checked using TLC plate. It was worked up after the completion of the reaction and the product was purified with column chromatography using petroleum ether as eluent.

Conclusion

In conclusion it can be said that tetrabutyl bromide can be used as a good source of bromine for hunsdiecker reaction with 50 mol % of Et_3N as catalyst at room temperature using dichloromethane as solvent system in a very short time period.

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