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Ceric Ammonium Nitrate Oxidation of Cinnamic Ester Derivatives for the Synthesis of Benzaldehydes

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The preparation of aldehydes by oxidative cleavage of carbon-carbon double bonds is a useful reaction. But the problem is of getting good yields and requires drastic reaction conditions. Cinnamic ester derivatives yield correspondingly substituted benzaldehydes when oxidized by ceric ammonium nitrate under mild conditions with acetonitrile in moderate to good yields is described. In the present paper a simple and effective method for synthesis of benzaldehydes using ceric ammonium nitrate is described in the light of existing literature.

Key Words: Oxidative cleavage, Cinnamic acids, Cinnamic esters, Benzaldehydes, Ceric ammonium nitrate, Acetonitrile.

INTRODUCTION

Among the methods currently available for the syntheisis of benzaldehydes include and use heterogeneous permagenate[1], oxidation[2], alcohols[3], arenes[4], sulfides[5], thiols[6], enamines[7] and unsaturated compounds[8]. Ceric ammonium nitrate (CAN) has been employed as a mild oxidizing agent[9-11] and also a versatile reagent in modern organic synthesis[12]. It is useful for industry as well as academic purpose. In academia, ceric ammonium nitrate, is explored extensively in organic reactions such as oxidation, oxidation, oxidative addition, photoxidation, nitration, deprotection, graft polymerization and cleavages of C-H and C-C bonds.

In a typical experimental procedure, a mixture of ceric ammonium nitrate and compound **III** (entry 3, Table-1) in acetonitrile was stirred for 2-4 h at room temperature and the product was obtained in more than 80 % of yields. In a similar fashion various aldehydes were synthesized and their isolated yields are tabulated in Table-1. Substitution on the phenyl ring, especially with electron-donating groups, improved the yields while electron withdrawing group substitution could not give more yields due to a less probability of reaction with those groups.

EXPERIMENTAL

Preparation of cinnamic esters to cinnamic acids: Cinnamic acid derivative 0.5 g (0.4 mol), 1.2 g (4 mol) of absolute ethanol and 3 mL of conc. H_2SO_4 were refluxed for 5 h. After cooling the reaction mixture, ethanol was removed through rotary evaporator and then the residue was poured into 50 mL of water. Ether (50 mL) was added and the process was repeated thrice. The ether layer was dried using Na_2SO_4 and the solvent was removed by rotary evaporator. The crude compound was recrystallised using ethanol.

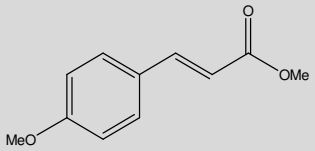
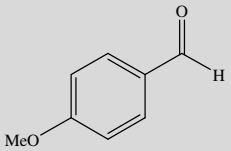
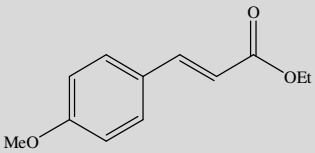
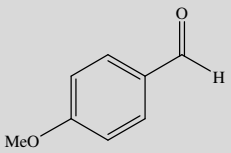
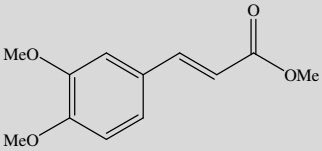
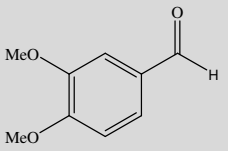
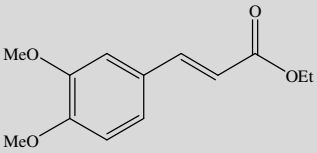
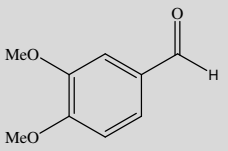
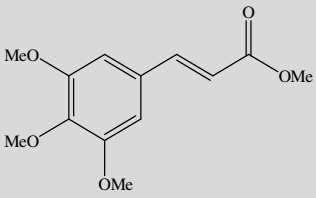
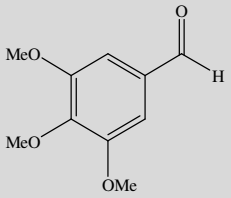
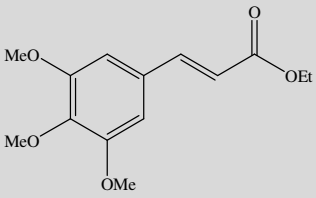
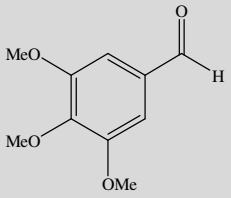
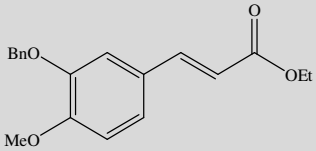
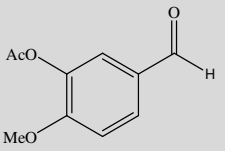
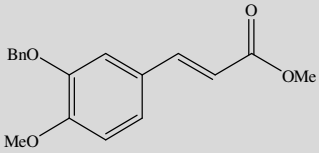
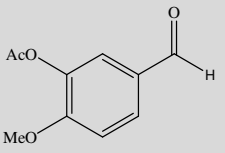
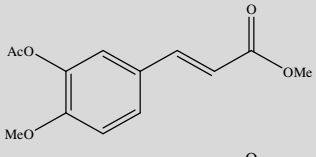
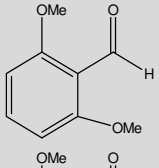
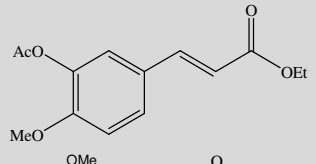
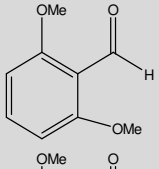
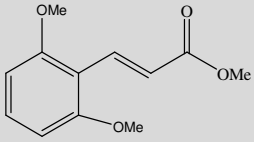
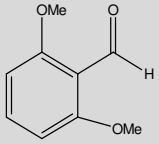
Preparation of aldehydes to cinnamic esters: Ester (0.515 mmol) and ceric ammonium nitrate (1 mmol, 2 eq) are stirred in acetonitrile (20 mL) at room temperature for 1 and 0.5 h. The reaction was monitored by TLC. After completion of the reaction, the acetonitrile was removed under vacuum and the residue dissolved in EtOAc, the solution washed with water then dried over anhydrous Na_2SO_4. The crude product was subjected to column chromatography over silica gel and eluted with 5 % EtOAc in hexane to obtain the pure compound. All the products were characterized by IR, ^{1}H NMR and mass spectroscopic methods.

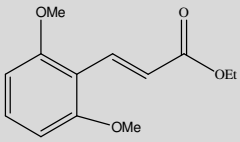
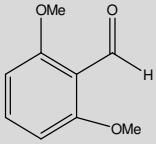
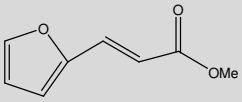
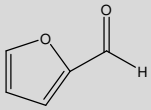
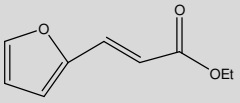
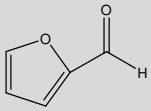
Methoxy-4-acetoxy benzaldehyde: ^{1}H NMR ($CDCl_3$, 200 MHz): 2.18 (s, 3H, $COCH_3$), 3.88 (s, 3H, OMe), 7.51-7.68 (m, 3H) and 7.22 (d, 1H, J = 12 Hz) and 9.97 (s, 1H, aldehyde). Mass *m/z*: 194 (100 %).

Methoxy-4-benzyloxy benzaldehyde: ^{1}H NMR ($CDCl_3$, 200 MHz): 3.75 (s, 3H, OMe), 5.23 (s, 2H, -OCH_2), 7.40-7.60 (m, 6H), 7.70 (d, 1H, J = 12.0 Hz) and 9.87 (s, 1H, aldehyde). Mass *m/z*: 242 (100 %).

2,6-Dimethoxy benzaldehyde: ^{1}H NMR ($CDCl_3$, 200 MHz): 3.65 (s, 6H, OMe), 6.52-7.32 (m, 3H) and 10.15 (s, 1H, aldehyde). Mass *m/z*: 166 (100 %).

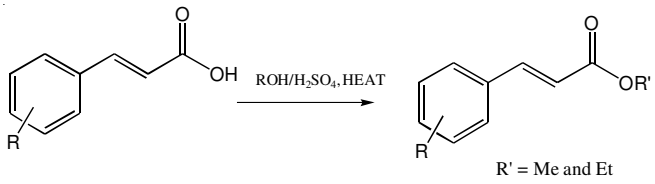
TABLE-1
OXIDATIVE CLEAVAGE OF CINNAMIC ESTERS TO ALDEHYDES

S. No.	Substrate	Product	Time (h)	Yeild (%)
1			2.5	71.1
2			2.5	71.1
3			1.5	75.8
4			1.5	75.8
5			1.5	80.7
6			1.5	80.7
7			3.5	69.3
8			3.5	69.3
9			4.0	55.6
10			4.0	55.6
11			2.5	72.3

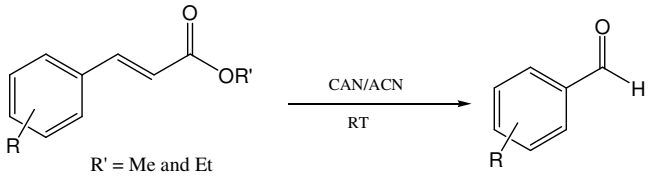
12			2.5	72.3
13			3.5	68.1
14			3.5	68.1

RESULTS AND DISCUSSION

The work deals with the formation of the aldehydes in good to moderate yields at ambient temperatures by using ceric ammonium nitrate in acetonitrile. It is suggested that the carbonyl group is stabilized by phenyl ring by resonance responsible for the generation of good yields of resulting products. Fisher *et al*.[13] reported the formation of aldehydes by oxidative cleavage reaction of some lignin model compounds used by ceric ammonium nitrate. To further explore the usage, herein we report a new method for the synthesis of aldehydes from cinnamic esters using ceric ammonium nitrate in acetonitrile at room temperature (**Scheme-I** and **II**).



Scheme-I



Scheme-II

Conclusion

We have developed a simple, efficient and mild methodology for the conversion of aryl α,β-unsaturated esters into substituted benzaldehydes by using ceric ammonium nitrate at room temperatures. Benzaldehydes are good precursors for various organic reactions sofar wide chemistry developed with benzaldehydes and also good useful precursor for modern organic chemistry.

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