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Oxidative Dehydrogenation of Substituted Dihydropyridine Dicarboxylates Using Ceric Sulfate Tetra Hydrate in Aqueous Acetonitrile as a Favorable Medium in Air

DD Kumbhar, BY Waghamare and SK Pardeshi*

Department of Chemistry, University of Pune, Ganeshkhind, Pune-411007 (INDIA)

ABSTRACT

Ceric sulfate tetra hydrate in aqueous acetonitrile acts as an efficient oxidant for the aromatization of substituted dihydropyridine dicarboxylates. Out of seven different solvent systems employed acetonitrile water combination and substituted dihydropyridine dicarboxylates: Ce $(SO_4)_2.4H_2O$ ratio as 1:2 was found to be the most favorable condition for synthesis of fourteen substituted pyridine dicarboxylates. The products of high purity were isolated in high – excellent yield with fine crystals. The reversible conversion of Ce^{3+} to Ce^{4+} due to oxygen present in air plays an important role in synthesis was also traced. Formation of radical cation and radical in the process of oxidative dehydrogenation of substituted dihydropyridine dicarboxylates were also ascertained by using tertiary butyl alcohol as radical scavenger.

Keywords: Aqueous acetonitrile, Oxidative dehydrogenation, Heterocyclic, Electron transfer, ceric sulfate tetrahydrate

Corresponding author

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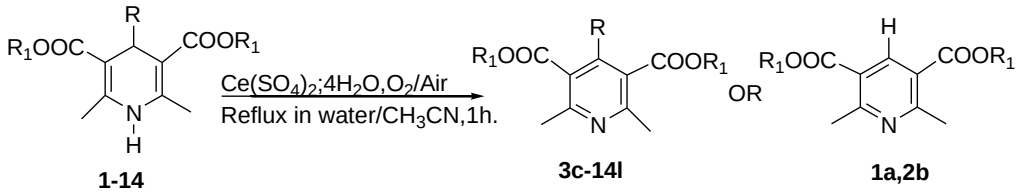
INTRODUCTION

Synthesis of dialkyl - 2, 6 - dimethyl - 4 - alkyl / aryl - 3, 5 - pyridine dicarboxylates are well known due to the fact that these compounds based antihypertensive drugs (calcium antagonists) are oxidatively converted to pyridine derivatives by cytochrome P- 450 in liver [1]. These substituted dihydropyridine dicarboxylates (DHPs) have also been extensively utilized as the analogs of NAD (P) H co-enzymes to study the mechanism and synthetic potential of various redox processes [2, 3]. These compounds bind to specific receptors and are Ca^{2+} channel blockers for the treatment of cardiovascular disease [4-6]. Consequently this oxidation reaction continues to attract the attention of researchers for the discovery of milder and general procedure applicable to a wide range of 1, 4-DHP. Several inorganic reagents have been used for the synthesis of dialkyl - 2, 6 - dimethyl - 4 - alkyl / aryl -3, 5- pyridine dicarboxylates which includes, $KMnO_4$ [7], CrO_3 [8], Bi $(NO_3)_3.\ 5H_2O$ [9], solid supported pyridium chlorochromate (PCC) [10], silica gel supported ferric nitrate [11], $BaMnO_4$ [12], $K_2S_2O_8$ [13], elemental sulfur [14], Cu $(NO_3)_2$ [15], Mn $(OAc)_3$ [16], H_2O_2 / $Co(OAc)_2$ [17], $NaNO_2$ in the presence of oxalic acid, sodium hydrogen sulfate, magnesium hydrogen sulfate, wet SiO_2 [18], $FeCl_3$.$6H_2O$ [19], etc. Although a variety of methods using inorganic reagents as mentioned above are available for the oxidation of dihydropyridines, these methods suffer from several drawbacks for example poor yield, prolong time, costly reagents and dealkylation of benzyl and alkyl substituents at 4^{th} position. Some reagents produce byproducts which are difficult to remove, while some of them are highly toxic or possess serious disposal problems. Many methods utilize strong oxidizing agents in excess. Moreover, there are very few reports in which effect of medium has been studied, especially aqueous medium, leaving considerable scope for the development of an environmental friendly aqueous medium for this transformation. In the present work we report, synthesis of fourteen dialkyl - 2, 6 - dimethyl - 4 - alkyl / aryl -3, 5- pyridine dicarboxylates using molecular Ce $(SO_4)_2$. $4H_2O$ in air by refluxing in 20 mL water and addition of 5mL of acetonitrile as the most favorable medium out of seven different organic solvent system (**Scheme 1**).



1-14 **3c-14l** **1a,2b**

Scheme 1- Synthesis of dialkyl-2, 6-dimethyl-4-alkyl/aryl-3, 5-pyridine dicarboxylates

MATERIALS AND METHODS

AR grade chemicals purchased from local companies were used without further purification. IR spectra were recorded on FT-IR 8400 Shimadzu Model.^{1}H NMR spectra were recorded on Varian Mercury, YH- 300 MHz spectrometer in $CDCl_3$ and chemical shifts are recorded as delta in ppm units. The reaction products were analyzed with a gas chromatograph (Shimadzu QP5050 instrument) equipped with a DB-5 capillary column and Quadra pole detector. Helium was used as carrier gas. The GC injection volume of 2µL and the split ratio of

25:30 were used. Some of the reaction products are known and few are synthesized for the first time. These reaction products are identified by mp, IR and NMR spectroscopy. The product obtained after work up was purified by recrystallzation from ethanol. Dialkyl - 2, 6 - dimethyl -1, 4 - dihydropyridine - 3, 5 - dicarboxylates were synthesized by standard procedure [20].

A typical Procedure for the synthesis of Diethyl - 2, 6 - dimethylpyridine - 3, 5 -dicarboxylate (1a)

A mixture of the diethyl – 2 , 6 - dimethyl -1,4- dihydropyridine - 3,5 - dicarboxylate (0.253 g,1mmol) and Ceric sulfate tetra hydrate (0.8086 g, 2mmol) in 20mL distilled water and 5 mL of acetonitrile heated under reflux for 1h. The solution was cooled to room temperature and neutralized with aqueous $NaHCO_3$. It was then extracted with Et_2O (3x10mL) and dried with anhydrous Na_2SO_4. The solvent was removed by distillation under reduced pressure and the resulting crude product obtained was recrystallized from EtOH to give colorless crystals of the product **1a** yield (98%) (0.247g) m.p.69 ^oC (Lit.68-69 ^oC) [6].

Spectral data

Synthesis of dialkyl - 2, 6 - dimethyl - 4 – alkyl / aryl - 3, 5 -pyridine dicarboxylates

Product (1a): Diethyl -2, 6 -dimethyl - 3, 5 - pyridine dicarboxylate.
Mol. formula: ($C_{13}H_{17}NO_4$), m.p. 69 ^oC (68-69 ^oC), FTIR (KBr)cm^{-1} 2927, 2981, 1720, 1550, 1591, 1440, 1220, ^{1}HNMR ($CDCl_3$, TMS, 300MHz) δ 1.413(t, 6H, J=4.3 Hz), 2.83 (s, 6H), 4.37 (q, 4H, J=4.4Hz), 8.64 (s, 1H).

Product (2b): Dimethyl - 2, 6 –dimethyl - 3, 5 - pyridine dicarboxylate.
Mol.formula: ($C_{11}H_{13}NO_4$), m.p. 98 ^oC (100 ^oC), FTIR (KBr) cm^{-1} 2981, 1720, 1591,1440, 1220, ^{1}HNMR ($CDCl_3$, TMS, 300MHz) δ 2.88(s,6H),3.9(s,6H), 8.70(s,1H).

Product (3c): Diethyl – 2 -dimethyl - 4 – phenyl -3, 5 -pyridine dicarboxylate.
Mol.formula: ($C_{19}H_{21}NO_4$), m.p. 67 ^oC (68-69 ^oC), FTIR (KBr) cm^{-1} 2981, 1728, 1554, 1228, ^{1}H NMR ($CDCl_3$, TMS, 300MHz) δ 0.89(t,6H,J=7,1Hz), 2.60(s,6H), 4.01(q,4H,J=7.1Hz), 7.22-7.35(m, 5H).

Product (4d): Dimethyl -2-dimethyl - 4 - phenyl -3, 5 - pyridine dicarboxylate.
Mol. formula: ($C_{17}H_{17}NO_4$), m.p. 135 ^oC (135-136 ^oC), FTIR (KBr) cm^{-1} 2981, 1728, 1554, 1228, ^{1}H NMR ($CDCl_3$ TMS, 300MHz) δ 2.59 (s,6H), 3.32, (s, 6H), 7.199-7.37 (m,5H).

Product (5e): Diethyl -2, 6 - dimethyl - 4 - (3 -nitrophenyl) - 3, 5-pyridine dicarboxylate.
Mol. formula: ($C_{19}H_{20}N_2O_6$), m.p. 61^oC (62-63^oC),FTIR (KBr) cm^{-1} 2981, 1720, 1591, 1523, 1220, ^{1}H NMR $CDCl_3$, TMS, 300MHz) δ 0.99(t, 6H, J=7.1Hz), 2.63(s,6H), 4.07(q,4H,J=7.1Hz), 7.5(d,2H,J=6.60Hz),8.16(s,1H),8.24(d,1H,J=1.92 Hz).

Product (6f): Dimethyl - 2, 6 -dimethyl - 4 -(3-nitrophenyl) - 3, 5 – pyridine dicarboxylate.
Mol. formula: ($C_{17}H_{16}N_2O_6$), m.p. 120 ^oC (122-125 ^oC),

FTIR (KBr) cm^{-1} 3080, 2955, 1722, 1531, 1442, 1103,
^{1}HNMR ($CDCl_3$, TMS, 300MHz) δ 2.63(s,6H), 3.59
(s,6H), 7.57(m,2H), 8.4(m,2H).

Product (7g): Diethyl -2,6 - dimethyl - 4 -(2-furyl) - 3, 5 - pyridine dicarboxylate
Mol .formula: ($C_{17}H_{19}NO_5$), mp. 40 ^oC , FTIR (KBr) cm^{-1} 2984, 1730, 1561, 1107, ^{1}HNMR ($CDCl_3$, TMS, 300MHz) δ 1.22(t, 6H, J=7.1Hz), 2.57(s, 6H), 4.28(q, 4H, J=7.1Hz), 6.47(d,1H,J=1.6Hz), 6.60 (d,1H,J=3.30Hz),7.48(s,1H).

Product (8h): Dimethyl - 2, 6 - dimethyl - 4 - (2-furyl) -3, 5 – pyridine dicarboxylate.
Mol. formula: ($C_{15}H_{15}NO_5$), m.p. 60 ^oC , FTIR (KBr), cm^{-1} 2997, 1728, 1550,1587, 1238, 1107,^{1}HNMR ($CDCl_3$,TMS,300MHz)δ2.57(s,6H),3.81(s,6H),6.47(dd,1H, J=1.65Hz), 6.60(d, 1H,J=3.30),7.49(d,1H,J=1.1Hz).

Product (9i): Diethyl - 2, 4, 6 - trimethyl, 3, 5 - pyridine dicarboxylate.
Mol .formula: ($C_{14}H_{19}NO_4$), m.p. 79^oC , FTIR (KBr) cm^{-1} 2981, 1720, 1591, 1440, 1220, ^{1}H NMR ($CDCl_3$, TMS, 300MHz) δ 1.39(t, 6H, J=7.3Hz), 2.27(s, 3H), 2.52(s, 6H), 4.41(q, 4H, J=7.3Hz).

Product (10j): Dimethyl - 2, 4, 6 - trimethyl - 3, 5 – pyridine dicarboxylate.
Mol. formula: ($C_{12}H_{15}$ NO_4), m.p. 76 ^oC, FTIR (KBr) cm^{-1} 2955, 2931, 1728, 1570,1431, 1246,1190, ^{1}H NMR ($CDCl_3$, TMS, 300MHz) δ 2,24(s,3H), 2.50(s, 6H), 3.92(s,6H).

Product (**13k**): **Diethyl -2, 6 - dimethyl - 4 - (4-methoxyphenyl) - 3, 5 - pyridine dicarboxylate.**
Mol .formula: ($C_{20}H_{23}NO_5$), m.p. 49 ^oC (49-50 ^oC), FTIR (KBr) cm^{-1} 3040,1720,1591,1240,^{1}H NMR ($CDCl_3$, TMS, 300MHz) δ 0.98(t,6H, J=5.5Hz), 2.58(s,6H), 3.80(s,3H), 4.0(q,4H,J=5.5Hz), 6.87(d,2H,J=1.3Hz), 7.15(d,2H,J=1.3Hz).

Product (14l): Dimethyl - 2, 6 - dimethyl - 4 - (4 – methoxyphenyl) -3, 5 - pyridine dicarboxylate.
Mol. formula: ($C_{18}H_{19}NO_5$), m.p. 114 ^oC (115 ^oC), FTIR (KBr) cm^{-1} 3040, 1720, 1591, 1240, ^{1}H NMR ($CDCl_3$ TMS, 300MHz) δ, 2.55(s,6H), 3.55(s,6H), 3.8(s,3H), 6.90(d,2H), J=1.3Hz),7.17(d,2H,J=1.3Hz).

RESULTS AND DISCUSSION

Optimization of reaction conditions

Effect of solvent

A series of dialkyl - 2, 6 – dimethyl-1, 4 - dihydro pyridine-3, 5- dicarboxylate (1, 4- DHPs) were synthesized by known procedure [20]. When oxidative dehydrogenation of fourteen substituted dihydropyridine dicarboxylates were carried out in presence of ceric sulfate tetra hydrate and water only, the reaction mixture contained the aromatized pyridine derivative and unaromatized starting material; this may be due to less solubility of ceric sulfate in water at

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room temperature. Generally the ceric sulfate is soluble in acidic and warm condition. To overcome this difficulty and in order to determine the best reaction condition, the applicability of variety of solvents (5mL) in the oxidation of dialkyl - 2, 6 - dimethyl - 4 - alkyl / aryl -3, 5-pyridine dicarboxylates in the presence of ceric sulfate tetra hydrate (1:2 molar ratio) and 20 mL of water under reflux condition were used (**Table 1**).

Table 1- Effect of the solvent on the synthesis of Dimethyl 1,4- dihydro - 4 - methyl phenyl - 2, 6 –dimethyl pyridine 3, 5 - dicarboxylate in the presence of ceric sulphate tetra hydrate and water under reflux condition

Solvent	Temperature (^{o}C)	Time (h)	Conversion (%) [a]
DCM	40	1.5	52
Water	100	1.5	59
Chloroform	61	1	65
DMF	120	1	68
Acetone	60	1.5	75
Ethanol	80	1	91
Acetonitrile	100	1	100

[a]Conversions were determined by GC and counted with area normalization

Among the various solvents studied, acetonitrile gave excellent conversion (100%) at 100 ^{o}C in 1h (**Figure 1**). Acetonitrile is acidic in nature, its unique role [21] in promoting oxidation may be attributed to (i) Increase the solubility of ceric sulfate tetra hydrate in water appreciably and (ii) generation of the active oxidant species. Since acetonitrile gave best results, further all reactions were carried out using acetonitrile as acidic medium.

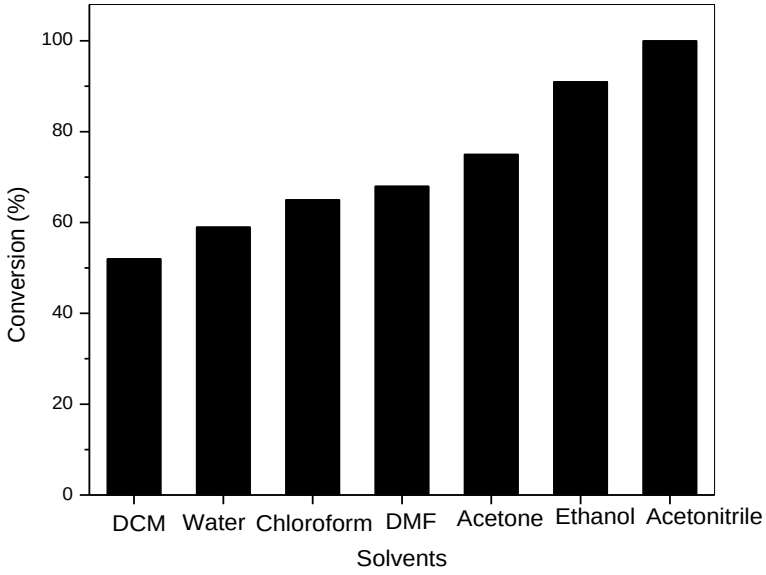

Figure 1 - Effect of reaction medium (solvent) on the conversion DHP to pyridine

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Effect of amount of ceric sulfate tetra hydrate

The synthesis of dialkyl - 2, 6 - dimethyl - 4 - alkyl / aryl - 3, 5 - pyridine dicarboxylates were also tried by using various molar ratio of 1, 4 - DHP: ceric sulfate tetra hydrate (1:1, 1:1.5, 1:2 and 1: 2.5) in presence of water (20 mL) and acetonitrile (5mL) under reflux condition. It was found that when 1:1and 1:1.5 molar ratios were taken a mixture of aromatized and unaromatized pyridine derivatives were obtained. When 2 equivalent of ceric sulfate and 5 mL of acetonitrile were taken and the product obtained was studied by TLC, IR, ^{1}HNMR, and GCMS to check for any unoxidized 1, 4 - DHP, there was no trace amount of starting material in the product (**Figure 2**). Negligible change was observed by taking 2.5 equivalent of ceric sulfate and 5 mL of acetonitrile. Finally under the condition of 2 equivalent ceric sulfate and 5 mL of acetonitrile were taken and fourteen dialkyl - 2, 6 - dimethyl - 4 - alkyl / aryl - 3, 5 - pyridine dicarboxylates were successfully synthesized (**Table 2**).

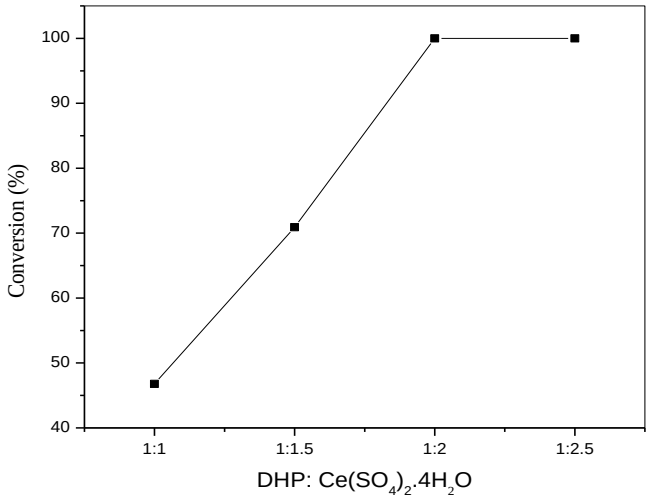

Figure 2 - Effect of amount of Ce $(SO_4)_2$,$4H_2O$ on the conversion DHP to pyridine

Role of water and effect of substituent's on the product selectivity

It is important to note here that until now in the literature, the reaction for synthesis of dialkyl - 2, 6 - dimethyl - 4 - alkyl / aryl - 3, 5 - pyridine dicarboxylates were carried out in a variety of reagent or catalyst in different medium. However, to the best of our knowledge nobody has reported the synthesis of dialkyl - 2, 6 - dimethyl - 4 -alkyl / aryl - 3, 5 - pyridine dicarboxylates using water as solvent which probably may be due to low solubility of both 1, 4-DHP and ceric sulfate which can be overcome by using 5 mL acetonitrile. This process also reports the efficiency of this reagent towards the synthesis of dialkyl - 2, 6 - dimethyl - 4 - alkyl / aryl - 3, 5 - pyridine dicarboxylates, in which the compounds **7g, 8h,** and **9i** were reported in literature as isolated oil products, but by using ceric sulfate tetra hydrate in water along with 5mL acetonitrile, fine solids with sharp melting points for these compounds were obtained (**Table 2**).

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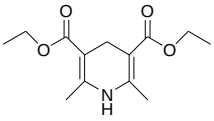
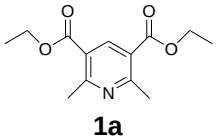
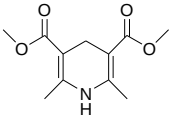
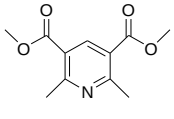
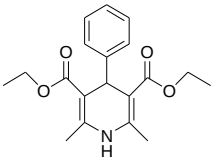
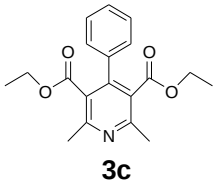
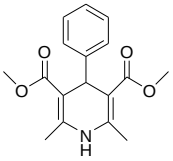
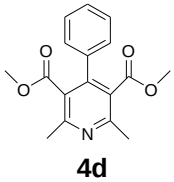
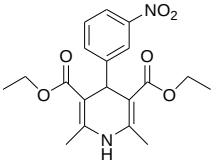
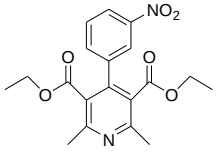
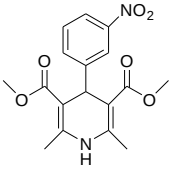
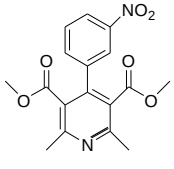
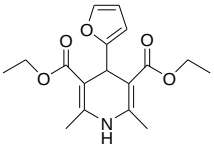
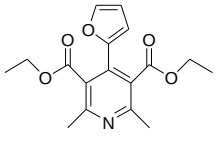
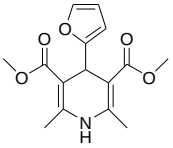
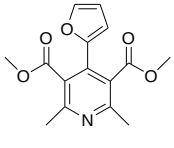
Table 2 - Synthesis of dialkyl - 2, 6 - dimethyl - 4 – alkyl / aryl - 3, 5 - pyridine dicarboxylates[a]

Entry	Substrate	Product	Yield (%)	Mp ^{0}C
1		 **1a**	98	69 (Lit.[6] 68-69)
2		 **2b**	93	98 (Lit.[5]100)
3		 **3c**	95	67 (Lit.[22]68- 69)
4		 **4d**	97	135 (Lit.[23] 135-136)
5		 **5e**	98	61 (Lit.[6]62- 63)
6		 **6f**	97	120 (Lit. [24]122-125)
7		 **7g**	90	40 (Lit.[6]oil)
8		 **8h**	96	60 (Lit.[16]oil)

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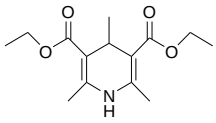
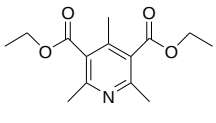
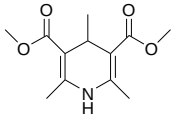
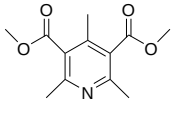
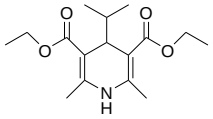
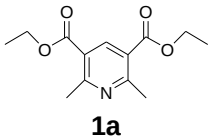
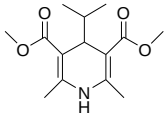
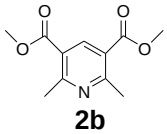
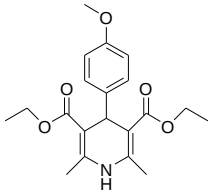
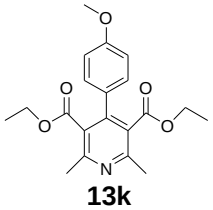
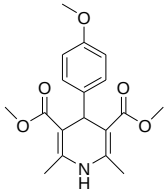
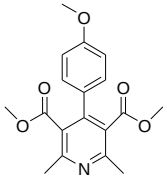
9		 **9i**	94	79 (Lit.[17] oil)
10		 **10j**	92	76 (Lit.----)
11		 **1a**	95	69 (Lit.[6] 68-69)
12		 **2b**	94	98 (Lit. [5]100)
13		 **13k**	95	49 (Lit.[6] 49- 50)
14		 **14l**	94	114 (Lit.[23] 115)

[a] All reactions are carried out under reflux in aqueous acidic medium for 1h by using 2 equivalent of ceric sulfate tetra hydrate in air. Reference numbers 5, 6, 16, 17 are cited both in the text and in a table, while 22, 23, 24 are cited only in a table

The better efficiency of ceric sulfate tetra hydrate reagent over other reported reagents is thus justified. Moreover, the compound (entry 10) is easily synthesized and conveniently oxidized to **10j** by using above reagent. This compound therefore can be added newly to the list of pyridine derivatives. The physical constant (m.p.), ^{1}H NMR and IR data is reported for the first time of the compound **10j.**

Apart from this, in general it is observed that a proton or alkyl / aryl groups are lost as a cation in the oxidation process. In case of entry **1 to 10** and **13** to **14** selective oxidation products are obtained by loss of proton. However, in case of entries **11** and **12** it gave oxidized products by loss of isopropyl cation. Isopropyl cation is well stabilized [25], in polar solvent such as water. On the other hand the primary alkyl or aryl cations which would be formed after fragmentation in other DHPs may not be stabilized after the dealkylation or dearylation to give the oxidized product.

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The group with sufficient electron releasing ability at 4th position of the DHP is released easily as compared to the groups which lack this electron releasing ability. This may be due to the stability of the fragmented cation formed after dealkylation / dearylation of the group at 4th position.

Mechanism for oxidative dehydrogenation of substituted dihydropyridine dicarboxylates

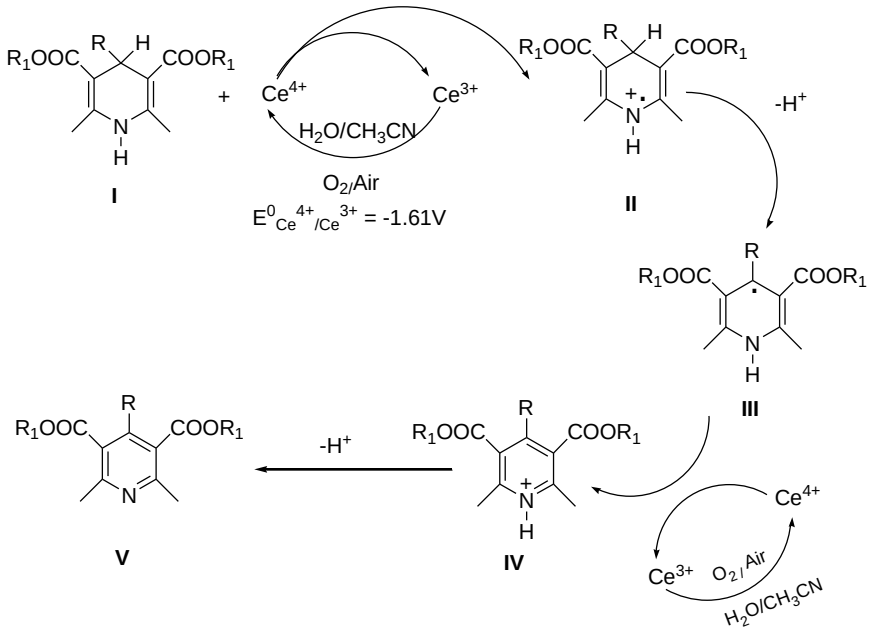

Figure 3 - Possible mechanism for the synthesis of dialkyl -2, 6 - dimethyl - 4- alkyl / aryl - 3, 5 - pyridine dicarboxylates in air

The reactions for synthesis of dialkyl - 2, 6 - dimethyl - 4 - alkyl / aryl - 3, 5 - pyridine dicarboxylates are initiated by an electron transfer followed by radical formation (**Figure 3**). Ce (IV) from ceric sulphate abstracts an electron from substituted dihydropyridine dicarboxylates and gets converted to Ce (III) [26]. The DHP simultaneously gets converted into radical cation **II** which subsequently loses a proton to generate radical **III.** The second mole of Ce (IV) then oxidizes radical **III** to the protonated pyridine **IV**, which subsequently loses a second proton, to give the desired pyridine derivative **V** (**Figure 3**). Since the reaction is carried out in open air and in presence of acetonitrile, the species Ce (III) immediately converts back to Ce (IV) due to which no external oxidant is required. The presence of Ce (III) and Ce (IV) was qualitatively checked and confirmed by withdrawing small amount of reaction mixture [27].

To ascertain the role of ceric sulphate tetra hydrate, oxygen and radical formation the same reaction was carried out under controlled condition. When the reaction is carried out by keeping all the reaction conditions same but in the absence of ceric sulfate tetra hydrate. The zero % pyridine conversion was observed. It suggests that no reaction takes place in the absence of ceric sulfate tetra hydrate.

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Similarly this reaction was also carried out in absence of oxygen by purging nitrogen gas by keeping same reaction condition constant, 6 % pyridine conversion was observed which clearly indicates that oxygen plays an important role in the conversion of species Ce (III) back to Ce (IV) and hence assist in the synthesis of dialkyl -2, 6 - dimethyl - 4 -alkyl / aryl -3, 5 - pyridine dicarboxylates.

The formation of radical cation **(II)** and radical **(III) (Figure 3)** were confirmed by carrying out the same reaction in presence of 1 mole of tertiary butyl alcohol which acts as radical scavenger. It was interesting to find that the no % conversion of substituted dihydropyridine to substituted pyridine dicarboxylates occurred. This observation confirms the formation of radical cation and radical during the synthesis of substituted pyridine dicarboxylates.

CONCLUSIONS

The solubility of both 1, 4-DHP and ceric sulfate tetra hydrate was enhanced by using 5mL acetonitrile. Out of various organic solvents used acetonitrile water combination and substituted dihydropyridine dicarboxylates: Ce $(SO_4)_2.4H_2O$ ratio as 1:2 was found to be the best with 100 % conversion into products. The reaction for synthesis of substituted pyridine dicarboxylates are initiated by an electron transfer followed by radical formation. The reversible conversion of Ce^{3+} to Ce^{4+} is an electron transfer process achieved by the oxygen present in the air, due to which no external oxidant is required in synthesis. Role of ceric sulphate, atmospheric oxygen was traced out by carrying out the reaction under controlled conditions. Formation of radical cation **II** and radical **III** were ascertained by using tertiary butyl alcohol as radical scavenger.

The product **7g, 8h, 9i,** and **10j** are successfully obtained as solid fine crystals, also the compound **10j** can be a new addition to the group of oxidized pyridine derivatives. The substituents at 3^{rd} and 5^{th} position of 1, 4-DHPs are stable in this reaction medium.

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