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Amberlyst-15 catalysed oxidative esterification of aldehydes using H_2O_2 trapped Oxidant as terminal oxidant

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Abstract

A simple efficient method has been developed for the selective oxidative esterification of aldehyde using commercially available Amberlyst-15 as a catalyst. The H₂O₂ released from clathrate structured 4Na₂SO₄.2H₂O₂.NaCl oxidant serves as an efficient source of terminal oxidant. Various aromatic, heteroaromatic, and aliphatic aldehydes undergo selective esterification to give good to excellent yield. The heterogeneous catalyst, Amberlyst-15 exhibit high reactivity and can be recycled over several runs. The 4Na₂SO₄.2H₂O₂.NaCl oxidant was found to be superior to commonly used oxidizing agents providing anhydrous, eassily handled and stable form of H₂O₂.

Introduction

Esters are important compounds because of their fragrances¹, biological activities², and readily conversion to other useful classes of compounds³ Due to such versatile characteristics, esters are considered as a compound of prime importance in perfumery⁴, chemical, polymer⁵, medicinal^{6,7} and many more fields. The conventional esterification process involves nucleophilic acyl substitution reaction of alcohol with acid in the presence of dehydrating agents⁸,⁹ or with activated form of acid such as acid chloride^{10–12} and acid anhydride¹³. The prefunctionalization of the acids leads to addition of extra steps and use of additional reagents that in turn affects the yield and economy of the process¹⁴.

The oxidative esterification of aldehyde offers a potentially useful alternative for the synthesis of ester functionality. This transformation was performed by various oxidizing agents such as PhI(OAc), $-I_2^{15}$, $[Bmim]N_3^{16}$, $TsNBr_2$ - $K_2CO_3^{17}$. The use of oxidant with transition metal catalyst was also employed for oxidative esterification for instance, use of H₂O₂ with various as Mn-phthalocyanine¹⁸, such anchored catalysts phosphotungstates (PW₁₂)₃/MCM-41¹⁹, manganese oxide²⁰, pyridine dichromate, methyltrioxorhenium^{21,22}, supported iron oxide^{23,24}, nickel²⁵, rhodium²⁶, and Ag catalysts. The other protocols used are Amberlyst-15 with m-CPBA and DBU²⁷, potassium iodide²⁸, $(CIO_4)_2$ and $InBr_3^{29}$, Cu-quinolate with tetra-butyl ammonium bromide³⁰, and copper bromide with *tert*-Butyl hydroperoxide³¹, peroxovanadium with $H_2O_2^{32}$

TEMPO-TBAB, $ln(TfO)_3$ with $Oxone^{33}$, sodium perborate, and sodium percarbonate³⁴, and $[IrCl(Cod)]_2$ and $[CpIrCl_2]_2/MAE$ with acetone as hydrogen acceptor under basic conditions³⁵. Although, most of the above protocols offer good yield with good TON, reaction suffer certain shortcomings such as use of toxic and costly transition metal catalysts, required longer reaction time (12 to 24 h)^{28,29,36–38} and higher temperature (100-120 °C), use of magnesium sulphate as a dehydrating agent for selective esterification³⁹ and excess use of oxidants.

Aerobic oxidation serves as an environmentally benign as well as efficient alternative utilizing molecular O_2 or air along with metal catalysts such as gold on oxide support⁴⁰, CoNP, Pd/C under microwave irradiation⁴¹. But the reaction requires to be performed under O₂ pressure with high temperature and longer reaction time. Thus, as continuation of our work to develop mild and selective oxidation protocols^{42–45} herein we report an efficient, transition metal free approach for selective oxidative esterification of aldehydes by using Amberlyst-15 as catalyst. The oxidizing agent reported is clathrate structure adduct⁴⁶ of H₂O₂ prepared from non-toxic, easily available, inexpensive Na2SO4 and NaCl47. The 4Na2SO4.2H2O2.NaCl is neutral in nature, easy to prepare as well as handle, stable at room temperature and provides anhydrous condition to the reaction medium. On other hand, Amberlyst-15 is a sulfonated. crosslinked polystyrene resin, available commercially and exhibits good catalytic activity and recyclability48.

Result and discussion

Benzaldehyde **1a** was selected as key substrate to investigate the reaction conditions for the oxidative transformation of aldehyde to ester. The effect of various reaction parameters

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were examined for oxidative esterification of 1a (Table 1). Initially, optimization of 4Na₂SO₄.2H₂O₂.NaCl oxidant was done by taking 1a (0.94 mmol), Amberlyst-15 (20% w/w) in methanolic medium (2 mL) under reflux conditions at 70 °C (Table 1, entries 1-4). The oxidant equivalent study demonstrated that the maximum yield of 90% was obtained for **3a** when 1.5 equivalents of oxidant were used in 4 h (Table 1, entry 3). The reaction temperature optimization study shows that rate of reaction increases as we increase the reaction temperature from room temperature to 70 °C (Table 1, entries 5-7). Further increase in the temperature had no significant effect on the yield of 3a as well as reaction time (Table 1, entry 8). The influence of catalyst loading on reaction rate and yield of 3a was investigated by varying catalyst loading from 15% (w/w) to 22.5% (w/w) (Table 1, entries 9-11). When 15% of Amberlyst-15 was used, only 59% yield of 3a was obtained in 10 h (Table 1, entry 9), whereas increasing the Amberlyst-15 loading to 22.5% (w/w) gives 88% yield of 3a in 4 h (Table 1, entry 11). When the reaction was performed in the absence of Amberlyst-15, only 28% yield of 3a was obtained in 10 h (Table 1, entry 12).

Investigation of effect of other sulphonic acid containing catalysts such as Amberlite IR-120, sulphated zirconia, Indion-130, sulphated tungstate, and p-toluene sulphonic acid (PTSA) on oxidative esterification of **1a** under optimized conditions showed poor to moderate yield of **3a** in 10 h (Table 2, entries 1-6). The lowest yield of 47% was obtained for Amberlite IR-120 whereas for PTSA 73% yield of **3a** was obtained in 10 h. This confirmed that the Amberlyst-15 plays vital role in enhancing the reaction rate as well as yield of **3a**. Thus, the reaction parameters were finalized as oxidant (1.5 equiv), Amberlyst-15 (20%, w/w) at 70 °C temperature.

We have also calculated acidic sites for all the catalysts studied here (except P-Toluene sulphonic acid) that corresponds to acidic sites available with 20% w/w of Amberlyst-15 (Table 2, entries 1-6). The reactions were performed by taking those quantities of the catalysts. The results obtained are summarized in Table 2. After performing reaction with new quantities of catalyst loading the yield of **3a** was found to be increased in all the cases. In the case of Amberlite-IR and Indion-130 moderate yield was obtained for **3a**. It is noticeable that in the case of Sulphated zirconia⁴⁹ and Sulphated tungstate⁵⁰ comparative yields were obtained but due to the lower active sites, excess catalyst is required. Additionally, reaction requires more time to get respective yields. Thus, from these results it is confirmed that the catalyst Amberlyst-15 is superior over other catalysts for the present work.

In order to investigate the efficacy of oxidant, oxidative esterification of **1a** was performed by using other oxidizing – agents (Table 3, entries 1-7). It was noticeable that, with 50% H_2O_2 , sodium perborate, and sodium percarbonate traces of **3a** formation was observed in 10 h (Table 3, entries 1-3). Whereas, Oxone gives moderate yield of **3a** in 10 h (Table 3, ______entry 4). In case of, urea hydrogen peroxide (UHP), m-CPBA, and 70%

tert-utyl hydrogen peroxide (TBHP) poor yield of **3a** was obtained in 10 h (Table 3, entries 5-7).

The oxidative esterification reaction proceeds through hemiacetal formation^{51–53} which further undergo oxidation in presence of oxidizing agent to yield ester. The presence of water in this reaction is detrimental towards ester formation^{39,54}. If Water is present in the system reverts back the unstable intermediate hemiacetal to starting aldehyde. Hence it is essentially important to remove the already present or water that is formed during the course of reaction to accelerate the reaction in forward direction. The adduct used here provides anhydrous form of oxidant, additionally it comprises of a dehydrating agent i.e. sodium sulphate which takes care of the water formed during the reaction. Further, the adduct has a clathrate structure in which H_2O_2 is trapped⁴⁶ that prevents its decomposition at higher temperature. Thus the overall combined effect results in higher esters selectivity with good yields.

Table-1 Optimization of reaction parameters^a



Entry	Catalyst	Catalyst conc. (%, w/w)	Oxidant equiv.	Time (h)	Temp (°C)	Isolated yield (%)	
Oxidant equivalent study							
1	Amberlyst- 15	20	0.5	10	70	64	
2		20	1	10	70	81	
3		20	1.5	4	70	90	
4		20	2	4	70	91	
Tempera	ture study						
5	Amberlyst- 15	20	1.5	10	30-32	33	
6		20	1.5	10	50	57	
7		20	1.5	10	60	76	
8		20	1.5	4	80	89	
Catalyst equivalent study							
9	Amberlyst- 15	15	1.5	10	70	59	
10		17.5	1.5	10	70	77	
11		22.5	1.5	4	70	88	
12	No Catalyst	-	1.5	10	70	28	

^aReaction conditions: **1a** (0.94 mmol, 1 equiv), methanol: 2 mL; RT: room temperature.

Table-2 Study with other catalysts

Entry	Catalyst	Active sites (mmol/g)	Oxidant eq.	Temp (°C)	Time (h)	Isolated Yield (Base on)	
		(20 %w/w	Active sites
1	Amberlite IR- 120	4.4	1.5	70	10	47	58
2 ^b	Sulphated Zirconia	2.07	1.5	70	10	56	82
3	Indion- 130	4.8	1.5	70	10	70	72
4 ^b	Sulphated tungstate	0.65	1.5	70	10	69	87
5	PTSA	-	1.5	70	10	73	69

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6	Amberlyst-15	4.7	1.5	70	4	90	90

^aReaction conditions: 1a: (0.94 mmol, 1 equiv); Oxidant: (1.5 equiv), Methanol: 2 mL,Temperature: 70 °C,PTSA : p-toluene sulphonic acid; ^bAcids sites are determined by potentiometric titration.

Table-3 Comparison with other oxidizing agents^a

Entry	Oxidizing agent	Catalyst conc. (%,w/w)	Oxidant equiv	Time (h)	Temp (°C)	Isolated yield (%)
1	50% H ₂ O ₂	20	1.5	10	70	Traces
2	Sodium perborate	20	1.5	10	70	Traces
3	Sodium percarbonate	20	1.5	10	70	Traces
4	Oxone Urea	20	1.5	10	70	70
5	hydrogen peroxide	20	1.5	10	70	40
6	m-CPBA 70% tert.	20	1.5	10	70	40
7	Butyl hydrogen peroxide	20	1.5	10	70	20

^aReaction conditions: 1a (0.94 mmol, 1 equiv), methanol: 2 mL.

Various aromatic, hetero-aromatic and aliphatic aldehydes were verified under the optimized reaction conditions (Table 4). The esterification of unsubstituted benzaldehyde 1a was a sluggish reaction compared to substituted benzaldehyde derivatives and takes 4 h to give 90% yield of the corresponding methyl benzoate 3a (Table 4, entry 1). Whereas electron donating (-CH₃) and withdrawing (-NO₂, -Cl) substituents readily undergo esterification to give desired esterification that in turn reduces the yield. (Table 4, entries 9-11). The 4-methoxy 1i and 4-hydroxy benzaldehyde 1j gives only 69% and 50% yield of respective esters (Table 4, entries 9, 10). The 2-hydroxy benzaldehyde 1k selectively gives 90% yield of catechol 3k (Table 4, entry 11). Hetero-aromatic aldehydes such as thiophene-2-carbaldehyde 1l and furan-2carbaldehyde **1m** also promptly undergo oxidative esterification to give 88% yield of 3I and 90% yield of 3m (Table 4, entries 12, 13). On the other hand, aliphatic aldehydes (table 4, entries 14, 15) gives moderate yield of desired ester under optimized conditions. Butyraldehyde 1n gives 70% yield of 3n (Table 4, entry 14) and heptanal 1m gives 60% yield of **3m** in 4 h (Table 4, entry 15).

After investigating various aldehydes under optimized conditions, the effect of alcohol chain (straight chain, branched, and aromatic) on oxidative esterification of **1a** was investigated (Table 5, entries 1-7). It was observed that the yield and the rate of formation of **3** was dependent on the type of alcohol used. As the alcohol chain increased from ethanol **2b** to *n*-butanol **2d**,

Entry	Substrate	Product	Time (h)	Isolated Yield (%)
1	O H 1a	G J J J J J J J J J J J J J J J J J J J	4 h	90
2	H H		2h	85
3	H Ic		2h	82
4	O H 1d	3d	2 h	89
5	NO ₂ O H 1e	NO ₂ O 3e	50 min	84
6	O ₂ N If	O ₂ N 3f	50 min	87
7	O_{2N}	O ₂ N 3g	50 min	86
8			1.75 h	92
9		J J J J J J J J J J J J J J J J J J J	1 h	69
10	HO		50 min	50
11 ^c		OH 3k	50 min	90
12	S H	S S S S S S S S S S S S S S S S S S S	2.5 h	88
13	1m ^O	3m 0	2.15 h	90
14	O H In	0 	4	70
15		→→→→→ 30	4	60

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^aReaction conditions: 1 (1 equiv); Oxidant: (1.5 equiv), Amberlyst-15: (20% w/w),

Methanol: 2 mL, Temperature: 70 °C.



 a Reaction conditions: 1a (0.94 mmol, 1 equiv); 4Na_2SO_4.2H_2O_2.NaCl: (1.8 mole, 1.5 equiv), Amberlyst-15: (20% w/w), Alcohol: 2 mL, Temperature: 70 $^\circ$ C.

Table-6 Selective mono esterification with diols⁶





^aReaction conditions: Aldehyde, (1 equiv); $4Na_2SO_4.2H_2O_2.NaCl:$ (1.8 mole, 1.5 equiv), Amberlyst-15: (20% w/w), Alcohol: 2 ml, Temperature : $70^{\circ}C$.

Recyclability study of Amberlyst-15

After successful oxidative esterification of various aldehydes, we investigated the recyclability of Amberlyst-15 by taking **1a** (1.8 mmol, 1 equiv), $4Na_2SO_4.2H_2O_2.NaCl$ (2.8 mmole, 1.5 equiv), Amberlyst-15 (20% w/w), methanol: 2 ml, and temperature was kept at 70 °C. After completion of the reaction, the solid residue containing oxidant remains and Amberlyst-15 was filtered and water was added to it (3 mL). The insoluble Amberlyst-15 was filtered off from the aqueous phase and treated with 0.1 N HCl. It was dried at 60-65 °C for 30 min and used for the successive cycles. As depicted in Figure 1, there was no significant loss in the catalytic activity of Amberlyst-15 even after fifth cycle.

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reaction time for the esterification was also increases from 5 h to 8 h (Table 5, entries 1-3). Ethanol **2b** on reaction with **1a** gives 89% yield of **3p** in 5 h (Table 5, entry 1) whereas *n*-butanol gives 86% yield of **3q** in 8 h (Table 5, entry 3).

In the case of branched chain alcohols such as isopropyl **2e** and isobutyl alcohol **2f** rate as well as yield of ester reduced significantly (Table 5, entries 4, 5). The present protocol failed for sterically hindered alcohols such as *tert*. butyl alcohol **2g** and benzyl alcohol **2h** as only starting material was observed even after keeping reaction for 24 h (Table 5, entry 6, 7). This confirms that the present protocol was selective for primary and secondary alcohols whereas sterically hindered alcohols and benzylic alcohols remain unaffected under optimized conditions.

The present protocol was found to give selective monoesterification with diols. The ethylene glycol **2h** on treatment with an aldehyde under optimized conditions selectively gives mono-ester product (Table 6, entries 1-3). The unsubstituted benzaldehyde **1a** on reaction with **2h** gives 88% yield of **3u** (Table 6, entry 1), whereas benzaldehyde with electron donating substituent **1d** (4-CH₃) gives 80% yield of **3v** in 5 h (Table 6, entry 2). Unlike **1d**, the benzaldehyde with electron withdrawing substituent **1i** (4-NO₂) gives a moderate yield of **3w** in 5 h (Table 6, entry 3). When ethanolamine **2i** was treated with **1a** under optimized conditions, instead of ester, formation of 2-(benzylidineamino) ethanol **3x** (an imine product of **2i**) was obtained with 20% yield (Table 6, entry 4).

Table-5 Effect of carbon chain of alcohol on rate of esterification^a







Fig.1 Recyclability study of Amberlyst-15

Plausible reaction mechanism

The present reaction proceeds through hemiacetal^{51–53} formation (Fig.2). The catalyst plays an important role in hemiacetal formation step. It protonates the carbonyl oxygen of the aldehyde rendering the carbonyl carbon more electron deficient and thus susceptible towards nucleophilic attack. In order to confirm the hemiacetal formation, we performed a separate reaction that generates hemiacetal and monitored it by gas chromatography. Then we conducted an esterification reaction and monitored it on gas chromatography. The retention time of the intermediate formed during esterification reaction is exactly the same as that of hemiacetal formed in initial reaction. Thus it is confirmed that both the catalyst and the oxidant plays an important role to shift the reaction in forward direction.



Fig.2 Plausible reaction pathway

Conclusions

In summary, we have developed an efficient, metal-free catalytic system for selective esterification of various aromatic, hetero-aromatic and aliphatic aldehydes. The addition of Amberlyst-15 resulted into increase in the rate esterification and demonstrated excellent recyclability. The Na₂SO₄.2H₂O₂.NaCl oxidant exhibits superior oxidizing property than H₂O₂ and other commonly used oxidants under present conditions. Aldehyde possessing methoxy and hydroxy substituents showed the formation of Dakin product along with ester. In the case of ethylene glycol selective mono-ester formation was observed.

Experimental

Material and equipments

Common reagent grade chemicals were purchased from Alfa Aesar, Spectrochem, Sigma Aldrich and Sd fine chemicals. FT-IR spectra were recorded on a Bomen Hartmann and Braun MB-Series FT-IR spectrometer. GC–MS was carried out with a GC–MS-QP 2010 instrument. The ¹H NMR spectroscopic data was recorded with Agilent 500 MHz spectrometer with CDCl₃ as the solvent. GC analysis was carried out with Thermo scientific, column-TR-1, 30mX0.25mm, IDX0.25um film, FID detector and sample size 0.1 l µl.

Experimental procedure for the synthesis of methyl benzoate (3a)

In a 25 ml round bottom flask was charged, benzaldehyde (0.94 mmol, 1 equiv), methanol (2 ml), Amberlyst-15 (20%, w/w) and oxidant (1.4 mmol, 1.5 equiv) and stirred at 65-70 °C. The progress of the reaction was monitored by TLC. After reaction completion, the reaction mixture was filtered off to separate insoluble oxidant residue and catalyst. The oxidant residue was dissolved in water (5 mL) and the insoluble catalyst was filtered off. Both the filtrates were combined and extracted with ethyl acetate (3 X 5 mL). The ethyl acetate extract was dried over anhydrous sodium sulphate and the solvent was evaporated under vacuum to give the crude product that was further purified by column chromatography using hexane: ethyl acetate as an eluting system.

Spectral data

- Methyl benzoate (3a):⁵⁵ Colorless oil; Yield: 230 mg, 90%; ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, J = 7.0 Hz, 2H), 7.58 (t, J = 7.0 Hz, 1H), 7.46 (t, J = 7.1 Hz, 2H), 3.94 (d, J = 1.8 Hz, 3H). GC-MS (EI, 70 eV): m/z, [M]⁺ = 136.
- Methyl 4-methyl benzoate (3d):⁵³ white crystals; Yield: 222 mg, 89%; mp 34-36⁰C ¹H NMR (400 MHz, CDCl₃) δ 7.92 (d, *J* = 7.1 Hz, 2H), 7.20 (d, *J* = 7.6 Hz, 2H), 3.87 (s, *J* = 1.0 Hz, 3H), 2.37 (s, 3H). GC-MS (EI, 70 eV): m/z, [M]⁺ = 150.

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- Methyl 4-nitrobenzoate (3g):⁵³ Light yellow solid; 4 Yield: 206 mg, 86%; mp 94⁰C ¹H NMR (400 MHz, 5 CDCl₃) δ 8.30 (d, *J* = 7.6 Hz, 2H), 8.23 (d, *J* = 7.5 Hz, 2H), 4.00 (s, 3H). GC-MS (EI, 70 eV): m/z, [M]⁺ = 181.
 Methyl 4-chlorobenzoate (3h):⁵⁶ white crystal: Yield: 6
- Methyl 4-chlorobenzoate (3h):⁵⁶ white crystal; Yield: 223 mg, 92%; mp 40-42⁰C ¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, J = 8.0 Hz, 2H), 6.78 (d, J = 19.2 Hz, 2H), 3.82 (s, 3H). GC-MS (EI, 70 eV): m/z, [M]⁺ = 170.
- Methyl 4-methoxybenzoate (3i):⁵⁷ white solid; Yield: 168 mg, 69%; mp 46-48⁰C ¹H NMR (400 MHz, CDCl₃) δ 8.01 (d, *J* = 7.6 Hz, 2H), 6.93 (d, *J* = 7.6 Hz, 2H), 3.90 (s, 3H), 3.87 (s, 3H). GC-MS (EI, 70 eV): m/z, [M]⁺ = 166.
- Catechol (3k):⁵⁸ white crystal; Yield: 163 mg, 91 %, mp 104-106⁰C; ¹H NMR (400 MHz, DMSO) δ 8.80 (s, 2H), 6.76 (dd, *J* = 18.2, 13.1 Hz, 2H), 6.66 – 6.54 (m, 2H); GC-MS (EI, 70 eV): m/z, [M]⁺ = 110.
- Ethyl benzoate (3p):⁵⁷ oil; Yield: 251 mg, 89%; ¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, J = 7.1 Hz, 2H), 7.46 (t, J = 13 6.9 Hz, 1H), 7.35 (t, J = 6.9 Hz, 2H), 4.35 4.24 (q, 2H), 1.38 1.23 (t, 3H). GC-MS (EI, 70 eV): m/z, [M]⁺ = 150. 14
- Butyl benzoate(3r):⁵⁹ Colourless oil; Yield: 288 mg, 86%; ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, J = 7.7 Hz, 15 2H), 7.56 (t, J = 7.3 Hz, 1H), 7.45 (t, J = 7.3 Hz, 2H), 16 4.35 (t, J = 6.4 Hz, 2H), 1.83 - 1.72 (m, 2H), 1.56 -1.42 (m, 2H), 1.01 (t, J = 7.2 Hz, 3H). GC-MS (EI, 70 17 eV): m/z, [M]⁺ = 178.
- 9. Isopropyl benzoate (3s):³⁶ oil; Yield: 179 mg, 58% ¹H 18 NMR (400 MHz, CDCl₃) δ 8.06 (dt, J = 36.8, 21.0 Hz, 2H), 7.63 7.52 (m, 1H), 7.51 7.29 (m, 2H), 5.36 19 5.11 (m, 1H), 1.41 (dd, J = 10.4, 6.3 Hz, 6H). GC-MS 20 (EI, 70 eV): m/z, [M]⁺ = 164.
- 10. 2-hydroxyethyl benzoate (3u):60 Yellowish oil; Yield: 21275 mg, 88%; ¹H NMR (400 MHz, CDCl₃) δ 8.09 (d, J =7.5 Hz, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.4 Hz, 222H), 4.54 4.43 (m, 2H), 3.97 (d, J = 15.6 Hz, 2H), 2.27(s, 1H). GC-MS (EI, 70 eV): m/z, [M+1] = 167. 23
- 2-hydroxy ethyl 4-methyl benzoate (3v):⁶¹ Colourless oil; Yield: 241 mg, 80 %; ¹H NMR (400 MHz CDCl₃) δ
 7.93 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 8.8 Hz, 2H), 4.48 –
 4.39 (t, 2H), 3.94 (t, 2H), 2.39 (t, 3H), 2.05 (s, 1H). GC-MS (EI, 70 eV): m/z, [M-1] = 180.
- 2-hydroxy ethyl 4-nitro benzoate (3w):⁶² Yellowish solid; Yield: 140 mg, 50 % , mp 77-78⁰ C; ¹H NMR (400 MHz, CDCl₃) δ 8.28 (d, J = 8.7 Hz, 2H), 8.22 (d, J = 8.6 Hz, 2H), 4.55 4.44 (t, 2H), 3.98 (t, J = 3.4 Hz, 2H), 1.92 (s, 1H). GC-MS (EI, 70 eV): m/z, [M-1] = 211.

References

- 1 N. R. Khan and V. K. Rathod, *Process Biochem.*, 2015, **50**, 1793–1806.
- 2 E. A. Terpetschnig, H. Szmacinski and J. R. Lakowicz, 1994, vol. 2137, pp. 608–617.
- E. S. H. El-Ashry, N. Rashed, L. F. Awad, E. S. Ramadan, S.
 M. Abdel-Maggeed and N. Rezki, *J. Carbohydr. Chem.*, 2008, 27, 70–85.

- A. A. Schleppnik, 1986.
- K. J. Edgar, C. M. Buchanan, J. S. Debenham, P. A. Rundquist, B. D. Seiler, M. C. Shelton and D. Tindall, *Prog. Polym. Sci.*, 2001, **26**, 1605–1688.
- O. Hromatka, 1938.
- Z. Hadidian, 1952.
- C. S. de Oliveira, B. F. Lira, V. dos Santos Falcão-Silva, J. P. Siqueira-Junior, J. M. Barbosa-Filho and P. F. de Athayde-Filho, *Molecules*, 2012, **17**, 5095.
- B. Neises and W. Steglich, Angew. Chemie Int. Ed. English, 1978, **17**, 522–524.
- 10 F. E. A. Van Waes, J. Drabowicz, A. Cukalovic and C. V Stevens, *Green Chem.*, 2012, **14**, 2776–2779.
- 11 A. R. Hajipour and G. Mazloumi, *Synth. Commun.*, 2002, **32**, 23–30.
 - F. Tamaddon, M. A. Amrollahi and L. Sharafat, *Tetrahedron* Lett., 2005, **46**, 7841–7844.
 - A. Sakakura, K. Kawajiri, T. Ohkubo, Y. Kosugi and K. Ishihara, *J. Am. Chem. Soc.*, 2007, **129**, 14775–14779.
 - Z. Huang, J. E. Reilly and R. N. Buckle, *Synlett*, 2007, **2007**, 1026–1030.
 - N. N. Karade, Arkivoc, 2006, **2006**, 162–167.
 - H. Valizadeh and M. Ahmadi, *Comptes Rendus Chim.*, 2012, **15**, 1077–1080.
 - K. K. Rajbongshi, M. J. Sarma and P. Phukan, *Tetrahedron Lett.*, 2014, **55**, 5358–5360.
 - R. K. Sharma and S. Gulati, *J. Mol. Catal. A Chem.*, 2012, **363–364**, 291–303.
 - S. Singh and A. Patel, Catal. Letters, 2014, 144, 1557–1567.
 - B. E. Maki and K. A. Scheidt, *Org. Lett.*, 2008, **10**, 4331– 4334.
 - R. Xie, X. Wang, J. Wang, J. Ye, M. Zhou and S. Zang, J. Saudi Chem. Soc.
 - J. H. Espenson, Z. Zhu and T. H. Zauche, *J. Org. Chem.*, 1999, **64**, 1191–1196.
- 23 R. Kashyap, D. J. Talukdar and S. Pratihar, New J. Chem., 2015, **39**, 1430–1437.
 - X.-F. Wu and C. Darcel, *European J. Org. Chem.*, 2009, **2009**, 1144–1147.
 - A. Patel, S. Pathan and P. Prakashan, *RSC Adv.*, 2016, **6**, 51394–51402.
- 26 R. Grigg, T. R. B. Mitchell and S. Sutthivaiyakit, Tetrahedron, 1981, **37**, 4313–4319.
- H. Rhee and J. Y. Kim, *Tetrahedron Lett.*, 1998, **39**, 1365–1368.
- 28 K. R. Reddy, M. Venkateshwar, C. U. Maheswari and S. Prashanthi, *Synth. Commun.*, 2009, **40**, 186–195.
- W.-J. Yoo and C.-J. Li, *Tetrahedron Lett.*, 2007, 48, 1033– 1035.
- 30 Y. Zhu, H. Yan, L. Lu, D. Liu, G. Rong and J. Mao, J. Org. Chem., 2013, 78, 9898–9905.
- 31 W.-J. Yoo and C.-J. Li, J. Org. Chem., 2006, **71**, 6266–6268.
- 32 R. Gopinath and B. K. Patel, *Org. Lett.*, 2000, **2**, 577–579.
- T. Mineno, S. Yoshino and A. Ubukata, *Green Sustain. Chem.*, 2014, 4, 20–23, 4 pp.
- 34 R. Gopinath, B. Barkakaty, B. Talukdar and B. K. Patel, J. Org. Chem., 2003, 68, 2944–2947.

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Journal Name

- N. Yamamoto, Y. Obora and Y. Ishii, J. Org. Chem., 2011,
 76, 2937–2941.
- 36 B. R. Travis, M. Sivakumar, G. O. Hollist and B. Borhan, *Org. Lett.*, 2003, **5**, 1031–1034.
- 37 S. D. Guggilapu, S. K. Prajapti and B. N. Babu, *Tetrahedron Lett.*, 2015, **56**, 889–892.
- 38 X.-F. Wu, Tetrahedron Lett., 2012, **53**, 3397–3399.
- S. L. Jain and B. Sain, Appl. Catal. A Gen., 2006, 301, 259–264.
- K. Suzuki, T. Yamaguchi, K. Matsushita, C. litsuka, J. Miura,
 T. Akaogi and H. Ishida, ACS Catal., 2013, 3, 1845–1849.
- M. Caporaso, G. Cravotto, S. Georgakopoulos, G.
 Heropoulos, K. Martina and S. Tagliapietra, *Beilstein J. Org. Chem.*, 2014, **10**, 1454–1461.
- 42 V. V. Patil and G. S. Shankarling, *J. Org. Chem.*, 2015, **80**, 7876–7883.
- 43 V. V Patil, E. M. Gayakwad and G. S. Shankarling, *New J. Chem.*, 2015, **39**, 6677–6682.
- 44 E. M. Gayakwad, V. V Patil and G. S. Shankarling, *New J. Chem.*, 2016, **40**, 223–230.
- 45 V. V Patil, E. M. Gayakwad and G. S. Shankarling, *J. Org. Chem.*, 2016, **81**, 781–786.
- 46 J. M. Adams, R. G. Pritchard and J. M. Thomas, *J. Chem. Soc. Chem. Commun.*, 1978, 288–289.
- 47 US4005182 A, 1977.
- 48 V. V. Patil and G. S. Shankarling, *Catal. Commun.*, 2014, **57**, 138–142.
- 49 S. S. Kahandal, S. R. Kale, S. T. Disale and R. V Jayaram, *Catal. Sci. Technol.*, 2012, **2**, 1493–1499.
- 50 P. S. Chaudhari, S. D. Salim, R. V Sawant and K. G. Akamanchi, *Green Chem.*, 2010, **12**, 1707–1710.
- 51 J. C. Craig and E. C. Horning, *J. Org. Chem.*, 1960, **25**, 2098–2102.
- 52 J. Gao and G.-W. Wang, Arch. Org. Chem., 2006, 162–167.
- 53 R. Tank, U. Pathak, M. Vimal, S. Bhattacharyya and L. K. Pandey, *Green Chem.*, 2011, **13**, 3350–3354.
- 54 A. Shokrolahi, A. Zali, H. R. Pouretedal and M. Mahdavi, *Catal. Commun.*, 2008, **9**, 859–863.
- Q. Xia, X. Liu, Y. Zhang, C. Chen and W. Chen, *Org. Lett.*, 2013, 15, 3326–3329.
- 56 L. Ma, L. Yuan, C. Xu, G. Li, M. Tao and W. Zhang, *Synthesis* (*Stuttg*)., 2013, **45**, 45–52.
- 57 S. Ushijima, K. Moriyama and H. Togo, *Tetrahedron*, 2012,
 68, 4701–4709.
- S. Maurer, W. Liu, X. Zhang, Y. Jiang and D. Ma, *Synlett*, 2010, **2010**, 976–978.
- 59 M. Blümel, J.-M. Noy, D. Enders, M. H. Stenzel and T. V Nguyen, Org. Lett., 2016, 18, 2208–2211.
- 60 R. Ray, R. D. Jana, M. Bhadra, D. Maiti and G. K. Lahiri, *Chem. – A Eur. J.*, 2014, **20**, 15618–15624.
- 61 H. Sharghi and M. H. Sarvari, J. Org. Chem., 2003, **68**, 4096–4099.
- 62 T. Yasukawa, H. Miyamura and S. Kobayashi, *Chem. An Asian J.*, 2011, **6**, 621–627.

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