

Yttria-zirconia based Lewis acid catalysed acylation of activated aromatic compounds

Abstract

The heterogeneous Yttria- zirconia based Lewis acid serves an efficient catalyst for regioselective acylation of diverse range of activated aromatics including heteroaromatic such as thiophene. Phenols were acylated at the aryl position, and no O-acylated product was obtained. In acylation of acetanilide, no transacylated product was obtained. The main advantage of this catalyst is its recovery and repeated reuse for several times.

Keywords: Yttria-zirconia; Lewis acid; Acylation; Friedel Craft acylation; Aromatic compounds.

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Introduction

Friedal-Crafts acylation reaction (Heaney H., 1991; Sarvari MH and Sharghi H., 2004; Guena F. et al., 2008), is an important reaction in synthesis tool box for preparation of various aromatic ketones by C – C bond creation and is generally performed employing acyl chlorides, carboxylic anhydride or carboxylic acids and an stoichiometric amount of acidic promoter. The use of stoichiometric amount of acidic promoter is known to produce gaseous effluents and mineral wastes. Catalysis by FeCl₃(Pearson DE and Buchler CA.,1972; Cornelis A., et al., 1990), ZnCl₂ (Naeimi H., et al., 2014; Paul S., et al., 2003)& zeolites(Sartori G and Maggi R, 2006; Bejblova M., et al., 2009) have been reported for the acylation of activated aromatics. Super acid(El-Sharkawy EA and Al-Shihry SS, 2010; SuryaPrakash GK, et al., 2015),&sulfonic acid (triflic acid)(Melero JA., et al., 2004; Tachrim ZP., et al., 2017) also catalyse the reaction, however the latter is associated with disadvantage such as extremely hygroscopic in nature and soluble in reaction media (Gramstad T and Haszeldine RN. 1957). Triflates of boron, aluminium and gallium(SuryaPrakash GK, et al., 2003) also catalyse the reaction, however, these catalyst are sensitive to hydrolysis. Triflic acid (Kawada A, et al., 1993 and 1994)bis(trifluoromethylsulfonyl)amide(Mikami K, et al., 1996) hafnium triflate(Mitsuhiro IH and Kobayashi

MS. 1995) bromopentacarbonylrhuthenium (I) (Hiroyuki K. and Koichi N. 1995), bismuth(III) trifluoromethanesulfonate (Balaguer AM., et al., 2014) were employed in the last decades. Unlike bismuth (III) triflate (Desmurs JR., et al., 1997), $\text{SbCl}_5\text{-LiClO}_4$ (Teruaki M., et al., 1992) & HZSM-5 (Sreekumar R. and Padmakumar R. 2006; Boström Z and Holmberg K. 2013) was found to be water stable with high catalytic activity. A combination of $\text{TiCl}(\text{OTf})_3$ & TfOH , hydrated Zirconia (Nikoofar K. and Khademi Z. 2016; Patil ML., et al., 1997) were reported for the acylation of activated aromatics.

Recently gallium nono fluorobutanesulfonate (Matsuo J. et al., 2000) & yttriumtris(per)fluoroalkanesulfonyl)methide (Barrett AGM. et al., 2000) are found to catalyse Friedel-Crafts acylation in good to moderate yield. As part of our continued interest in application of solid catalyst for different synthetic organic transformations, we have earlier reported yttria-zirconia Lewis acid as promising catalyst for the Diels-Alder reaction, transesterification of β -keto esters, acylation of alcohols, amines & thiols (Keshavaraja A., et al., 1995; Kumar P and Pandey RK. 2000; Kumar P. et al., 2001 and 2002; Pandey RK., et al. 2002) This promoted us to explore this catalyst for Friedel-Crafts acylation reactions, and herein we describe our findings on the yttria-zirconia Lewis acid catalysed Friedel-Crafts acylation of activated arenes.

Experimental Section

Yttria-zirconia based catalyst was procured from the catalysis division of CSIR-NCL, Pune. It was synthesized and characterized as per the method published by us, (Keshavaraja A. et al. 1995).

General experimental procedure for yttria-zirconia Lewis acid catalysed acylation of activated aromatic compounds

A slurry of activated aromatics (1eq), acid chloride or acid anhydride (5eq) & yttria-zirconia (10 mol%) were stirred at reflux temperature in acetonitrile (Table 1). The reaction was monitored by Thin Layer Chromatography. The removal of catalyst was done by filtration and filtrate quenched with 10% NaHCO_3 solution & extracted with $\text{CH}_3\text{COOC}_2\text{H}_5$ (2x50mL) and dried over Sodium sulfate. The solvent was concentrated to give the corresponding acylated product as crude. The required product was obtained in pure form. using silica gel column chromatography employing petroleum ether: EtOAc (95:5) as eluent.

1-(4-Methoxy-phenyl)-ethanone (2a)

Yield: 93%

Yellow Oil

IR (Neat, cm^{-1}): ν_{max} 3487, 3334, 3100, 2950, 2840, 2550, 2410, 2070, 1950, 1673, 1600, 1508

$^1\text{H NMR}$ (200 MHz, CDCl_3): δ 2.51 (s, 3H), 3.82 (s, 3H), 6.88 (d, 2H, $J = 10\text{Hz}$), 7.88 (d, 2H, $J = 8\text{Hz}$)

Mass: 150 (M+), 136, 135, 120, 107, 92, 77, 64

Analysis calcd for $\text{C}_9\text{H}_{10}\text{O}_2$ (150.17): Found C, 71.81; H, 6.56 {Required C, 71.98; H, 6.71}

(4-Methoxy-phenyl)-phenyl-methanone (2b)

Yield: 91% **Yellow oil.**

IR (Neat, cm^{-1}): ν_{max} 3420, 3067, 3035, 2671, 2552, 1918, 1693, 1650, 1599.

$^1\text{H NMR}$ (200 MHz, CDCl_3): δ 3.89 (s, 3H), 6.96 (d, 2H, $J = 10\text{Hz}$), 7.40–7.64 (m, 5H), 8.15 (d, 2H, $J = 8\text{Hz}$)

Mass: 212 (M+), 181, 169, 135, 122, 105, 92, 77

Analysis calcd for $\text{C}_{14}\text{H}_{12}\text{O}_2$ (212.24): Found C, 79.10; H, 5.76 {Required C, 79.23; H, 5.70}

(3-Benzoyl-4,6-dimethoxy-2-methylphenyl)-phenyl-methanone (2c)

Yield: 87%

Pale Yellow Oil

IR (Neat, cm^{-1}): ν_{max} 3454, 3019, 2910, 2900, 2850, 1665, 1588, 1464, 1449, 1323, 1280, 1245, 1215, 1174, 1122, 1085, 915

^1H NMR (200 MHz, CDCl_3): δ 1.92 (s, 3H), 3.76 (s, 6H), 6.48 (s, 1H), 7.46 (t, 4H, $J = 4$ Hz), 7.60 (t, 2H, $J = 4$ Hz), 7.87 (d, 4H, $J = 8$ Hz)

Mass: 361(M++1), 360, 359, 343, 315, 289, 283, 267, 254, 240, 225, 211, 198, 181, 165, 152, 122, 105, 77

Analysis calcd for $\text{C}_{23}\text{H}_{20}\text{O}_4$ (360.38): Found C, 76.56; H, 5.51 {Required C, 76.65; H, 5.59}

1-(2, 4-Dimethoxy-6-methyl-phenyl)-ethanone (2d)

Yield: 89%

Colorless oil

IR (Neat, cm^{-1}): ν_{max} 3449, 2933, 2843, 2395, 1752, 1690, 1602

^1H NMR (200 MHz, CDCl_3): δ 2.25(s, 3H), 2.46 (s, 3H), 3.81 (s, 6H), 6.30 (s, 2H)

Mass: 194 (M+), 180, 179, 171, 164, 150, 136, 135, 128, 122, 121, 105, 99, 93, 91, 83, 77, 69, 65

Analysis calcd for $\text{C}_{11}\text{H}_{14}\text{O}_3$ (194.22): Found C, 67.89; H, 7.17 {Required C, 68.02; H, 7.26}

1-(2,4,6-Trimethoxy-phenyl)-ethanone (2e)

Yield: 89%

Colorless solid

M.P.: 72-75°C

IR (CHCl_3 , cm^{-1}): ν_{max} 3430, 2400, 1746, 1667, 1600, 1581, 1450, 1394

^1H NMR (200 MHz, CDCl_3): δ 2.44(s, 3H), 3.79(s, 6H), 3.81(s, 3H), 6.08(s, 2H)

Mass: 211(M++1), 196, 181, 168, 166, 122, 107, 92, 77

Analysis calcd for $\text{C}_{11}\text{H}_{14}\text{O}_4$ (210.227): Found C, 58.29; H, 6.12 {Required C, 58.40; H, 6.24}

Phenyl-(2,4,6-trimethoxy-phenyl)-methanone (2f)

Yield: 95%

Colorless Solid

M.P.: 110-112°C

IR (CHCl_3 , cm^{-1}): ν_{max} 3449, 3080, 2942, 2840, 1738, 1666, 1595, 1459, 1405

^1H NMR (200 MHz, CDCl_3): δ 3.68 (s, 6H), 3.86 (s, 3H), 6.16 (s, 2H), 7.35-7.60 (m, 3H), 7.83 (d, 2H, $J = 8$ Hz)

Mass: 272, 255, 241, 227, 196, 195, 181, 180, 171, 152, 137, 122, 105, 91, 77, 69, 57.

Analysis calcd for $\text{C}_{16}\text{H}_{16}\text{O}_4$ (272.30): Found C, 70.68; H, 5.79 {Required C, 70.58; H, 5.92}

(2,5-Dimethoxy-phenyl)-phenyl-methanone (2g)

Yield: 94%

Brown oil

IR (CHCl_3 , cm^{-1}): ν_{max} 3414, 3154, 3101, 3055, 2948, 2836, 2668.51, 2150, 1690, 1663, 1605, 1495

¹H NMR (200 MHz, CDCl₃): δ 3.68 (s, 3H), 3.80 (s, 3H), 6.93 (d, 1H, *J* = 4 Hz), 7.01 (d, 1H, *J* = 4 Hz), 7.40-7.65 (m, 3H), 7.82 (d, 2H), 8.14 (d, 1H, *J* = 2 Hz)

Mass: 242 (M⁺), 225, 211, 197, 181, 165, 151, 122, 105, 92, 77.

Analysis caclcd for C₁₅H₁₄O₃ (242.273): Found C, 74.41; H, 5.69 {Required C, 74.36; H, 82}

(2,5-Dimethyl-3-hydroxy-phenyl)-phenyl-methanone(2h)

Yield: 87%

Colorless solid.

M.P.: 98-99°C

IR (CHCl₃, cm⁻¹): v_{max} 3296, 1691, 1627, 1573, 1377, 1319, 1276, 1264

¹H NMR (200 MHz, CDCl₃): δ 2.20 (s, 6H), 2.32 (s, 1H), 6.69 (s, 1H), 7.18 (s, 1H), 7.45-7.70 (m, 3H), 7.78 (d, 2H, *J* = 8 Hz)

Mass: 226, 210, 121, 105, 77

Analysis caclcd for C₁₅H₁₄O₂ (226.271): Found C, 79.51; H, 6.09; {Required C, 79.62; H, 6.23}

N-(4-Acetyl-phenyl)-acetamide(2i)

Yield: 80%

Brown Oil

IR(Neat, cm⁻¹): v_{max} 3410, 3950, 3294, 3197, 3136, 3020, 2400, 2100, 1950, 1711, 1664, 1601, 1545

¹H NMR (200 MHz, CDCl₃): δ 2.34 (s, 6H), 7.22 (s, 1H), 7.34 (brs, 1H), 7.50 (m, 3H).

Mass: 177 (M⁺), 136, 135, 120, 118, 105, 94, 93, 91, 77, 65

Analysis caclcd for C₁₀H₁₁O₂ (171.192): Found C, 67.85; H, 6.07; N, 7.91 {Required C, 67.79; H, 6.25; N, 8.12}

1-Thiophen-3yl-ethanone (2j)

Yield: 79%

Brown Oil.

IR (CHCl₃, cm⁻¹): v_{max} 3474, 3095, 2920, 1725, 1661, 1550

¹H NMR (200 MHz, CDCl₃): δ 2.71 (s, 3H), 7.27 (s, 1H), 7.79 (d, 2H, *J* = 8 Hz)

Mass: 126, 110, 83

Analysis caclcd for C₆H₆OS (126.112): Found C, 57.05; H, 4.63 {Required C, 57.14; H, 4.79}

N-(2-Acetyl-4-methoxy-6-nitro-phenyl)-acetamide(2k)

Yield: 83%

Dark yellow solid

M.P.: 115-116⁰C

IR (CHCl₃, cm⁻¹): v_{max} 3421, 2955, 1725, 1690, 1545, 1243

¹H NMR (200 MHz, CDCl₃): δ 2.31 (s, 6H), 3.93 (s, 3H), 7.21 (s, 1H), 7.63 (s, 1H)

Mass: 252 (M⁺), 210, 194, 168, 164, 153, 134, 122, 95, 77, 63

Analysis caclcd for C₁₁H₁₂N₂O₅ (252.225): Found C, 52.19; H, 4.65 {Required C, 52.38; H, 4.80}

1-Cyclo-oct-1-enyl-ethanone (2l)

Yield: 49%

Pale Yellow Oil.

IR (CHCl₃, cm⁻¹): v_{max} 3365, 2965, 1715, 1670, 1601, 1559

¹H NMR (200 MHz, CDCl₃): δ 1.25-2.65 (m, 15H), 5.52-5.77 (m, 1H)

Mass: 152, 136, 109

Analysis caclcd for C₁₀H₁₆O (152.2): Found C, 78.79; H, 10.39{Required C, 78.95; H, 10.52}

Cyclooct-1enyl-phenyl-methanone (2m)

Yield: 52%

Yellow Oil.

IR (Neat,cm⁻¹): v_{max} 3412, 2933, 1723, 1667, 1606, 1515, 1201.

¹H NMR (200 MHz, CDCl₃): δ 1.27-2.70 (m, 12H), 5.65-5.85 (m, 1H), 7.40-7.95 (m, 5H)

Mass: 214, 198, 137, 109, 105, 77

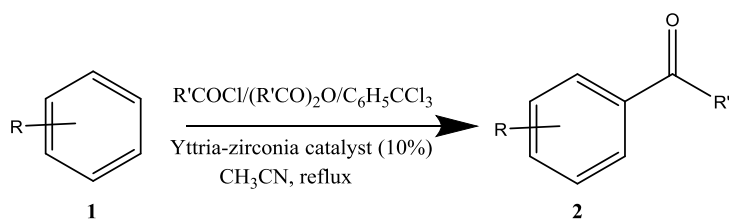
Analysis caclcd for C₁₅H₁₈O (214.23): Found C, 84.25; H, 8.79{Required C, 84.11; H, 8.88}

Results and discussion:

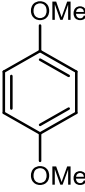
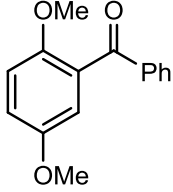
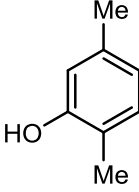
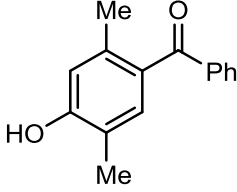
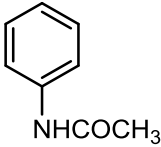
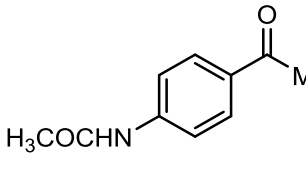

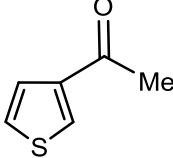
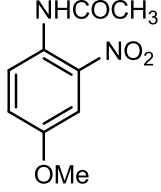
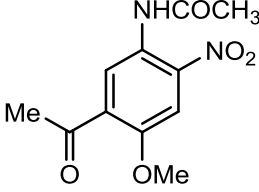
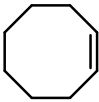
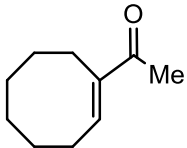
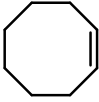
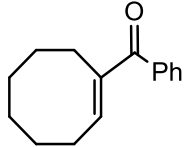
A variety of activated aromatic compounds on reaction with acid chloride or anhydride (or) benzotrichloride using 10 mol% amount of Yttria-zirconia based catalyst gave aromatic ketones in moderate to good yield. It is pertinent to note that the acylation of acetanilide with benzoyl chloride gave the aryl ketones without trans-acylation. The acylation or benzoylation of acetanilide went on regiospecifically in para position. Acylation of thiophene was successfully achieved with good yield. Mention must be made regarding regiospecific acylation of activated aromatic compound (**Table 1**) with electron donating groups such methoxy, hydroxyl & methyl groups. In all the above cases, the acylation was carried out regiospecifically at position para to methoxy, hydroxy, methyl groups. It is also worth mentioning that when benzoylation of 1,4-dimethylphenol was carried out with benzoyl chloride using 10 mol % of catalyst, benzoylation was observed on aryl position instead of O-benzoylation. When we treated anisole with neat acetyl chloride in presence of 10 mol% of Yttria-zirconia Lewis acid catalyst, it gave exclusively 4-methoxyacetophenone **2a** in 93% yield. In IR spectrum of **2a**, peak at 1673 cm⁻¹ indicated the presence of aromatic carbonyl group. The ¹H NMR spectrum of **2a** showed a singlet at δ 2.51 for acyl protons, and singlet at δ 3.82 for methoxy protons. The aromatic protons appeared as two doublets at δ 6.85-6.90 and at δ 7.86-7.90 indicating the regiospecific acylation at *para*-position. The molecular ion peak at 150 in the mass spectrum of **2a** also confirmed the formation of acylated product. The exclusive acylation at aryl position of acetanilide was confirmed by its spectral data. The IR spectrum of compound **2i** showed peaks at 1711cm⁻¹ & 1664cm⁻¹ corresponding to the carbonyl of amide and ketones. The ¹H NMR spectrum of **2i** showed a peak at δ 2.34 for 6 protons of the acyl group. The aromatic protons appeared as doublet at δ 7.18-7.22 & at δ 7.50-7.54. The presence of fragmentation peaks at 120 & at 105 (for PhCOCH₃&PhCO) in the mass spectrum confirmed the acylation at the aryl positions.

Scheme:

Yttria-zirconia Lewis acid catalysed acylation of activated aromatic compounds

**Table: 1**

Entry	Aromatic Used	Acylation Agent Used	Product	Reaction Time (h)	Yield*	Product code
1		MeCOCl		4	93	2a
2		PhCOCl		3	91	2b
3		PhCOCl		8	85	2c
4		PhCOCl		6	87	2d
5		MeCOCl		3.5	89	2e
6		PhCOCl		7	95	2f

7		PhCOCl		9	94	2g
8		PhCOCl		11	87	2h
9		MeCOCl		1	80	2i
10		MeCOCl		2	79	2j
11		MeCOCl		8	83	2k
12		MeCOCl		1	49	2l
13		PhCOCl		1	52	2m

*Isolated Yield after column purification.

Conclusion

The Yttria-zirconia Lewis acid serves a very good heterogeneous catalyst for acylation of activated aromatic compound in regioselective manner. Heteroaromatics like thiophene was acylated with moderate yields. Phenols were acylated at the aryl position, & no O-acylated product was obtained. In acylation of acetanilide, no transacylated product was obtained. The main advantage of this catalyst is its recovery and repeated reuse for several reactions.

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