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RESEARCH LETTER

Formylation and acetylation of alcohols using Amberlyst-15[®] as a recyclable heterogeneous catalyst

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Formylation of alcohols with ethyl formate in the presence of solid acidic resin Amberlyst-15 as a catalyst was carried out. Good to excellent yields of products were obtained. The catalyst also works for the acetylation of alcohols with ethyl acetate at reflux temperature. Simple work-up, reusability, nontoxicity, and stability of the catalyst are the advantages of this work as compared to conventional protocols.

Keywords: Amberlyst-15; formylation; alcohols; ethyl formate; acetylation; ethyl acetate

Introduction

In recent years, heterogeneous catalysts have been widely used in industry because of their merits such as easy separation, less hazardous nature, easy regeneration, recyclability, better reaction selectivity, and extensive standing stability. Heterogeneous catalysis remains one of the most vital key aspects of green chemistry as it minimizes harmful and toxic waste, thereby preventing pollution. The major benefit of a heterogeneous catalyst is its ability to catalyze a reaction in solvent-free conditions. Heterogeneous catalysis plays a key role in the development of the most organic transformations (1, 2). Environmentally benign reusable heterogeneous catalysts such as ion-exchange resins (cation or anion), zeolites, sulfated zirconia, and clays are significant catalysts for organic transformation reactions (3–5).

Functional group protection plays a crucial role in the synthetic methodologies of various complex organic molecules. Among the diverse functional groups, hydroxyl group is very common, because of its protection as formyl ester in the most pharmaceutical process. O-formylation is the most common process for alcohol group protection. Some of the explored methods showed the potential utility but suffer from drawbacks such as harsh reaction environment, poor yields of the desired product, the formation of side products, and longer reaction time (6). Easily accessible formylating agents such as formic acid are hazardous for reaction and may lead to formation of undesirable products whereas

the anhydride and the acid chloride of formic acid are highly unstable at room temperature. Formylation using ethyl formate offers numerous advantages such as simple work-up and easy accessibility of the reagent at relatively low rate. Common metal triflates generally used for this reaction are In(OTf)₃ (7), Ce(OTf)₄ (8), and Bi(III)salts (9). Heteropoly acids such as (K₅CoW₁₂O₄₀·3H₂O) (10), silphos[PCl₃-*n*(SiO₂)_{*n*}] (11), silica sulfuric acid and Al(HSO₄)₃ (12), TiCl₃(OTf) (13), cerium polyoxometalate (14), silica-bonded *N*-propyl sulfamic acid (15), and sulfuric acid ([3-(3-silicapropyl)sulfanyl] propyl)ester (16) are the various solid acid catalysts used for formylation with ethyl formate.

Acid anhydride or acyl chlorides are commonly used acylating reagents for acetylation of various functional groups by using the protic acids (17), Lewis acid catalysts, or alkali reagents such as 4-(dimethylamino)pyridine (18, 19), tributylphosphine (20), and lanthanum nitrate (La(NO₃)₃·6H₂O) (21). Metal triflates used for acetylation of alcohols and phenols are gadolinium triflate (22), aluminum triflate (23), and scandium triflate (24, 25). TaCl₅ (26), InCl₃ (27), and ZrOCl₂·8H₂O (28) are frequently used metal halides for acetylation. Solid acid catalyst such as aluminum-supported MoO₃ (29), Mg(NTf₂)₂ (30), and cation-exchanged montmorillonite K-10 clay (31) have also been explored. Acid anhydride and acyl chlorides are toxic and hazardous in nature, and most of the above-mentioned catalysts are either costly or not easily available. Metal triflates are also moisture-sensitive. In view of these drawbacks, acetylation of

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alcohols using ethyl acetate is a better alternative because of its nontoxic nature, low cost, and easy availability.

Amberlyst-15 is highly acidic and is made up of macroreticular polymeric resin based on cross-linked styrene divinyl benzene copolymers. Amberlyst-15 acts as an acid catalyst in many reactions such as Friedlander synthesis of quinolines (32), hydroamination (33), benzylation, and hydroalkylation of β -dicarbonyl compounds (34). Amberlyst-15 fascinated our attention because of its nonhazardous nature and easy separation from the reaction mixture, and because it is an environmentally benign catalyst. Here in we report a highly simple, low-cost, and environmentally benign reusable solid acid catalyst, Amberlyst-15, as a new protocol for O-formylation and acetylation of alcohol under solvent-free conditions.

Results and discussion

In this article, formylation and acetylation of alcohols with ethyl formate and ethyl acetate, respectively, in the presence of Amberlyst-15 as catalyst was investigated. The reaction parameters were optimized using formylation reaction of benzyl alcohol with ethyl formate. Table 1 indicates various characteristics of the catalysts used for screening of reaction. The probable reason for the higher activity of Amberlyst-15 can be explained on the basis of physical properties such as high H^+ exchange capacity (4.2 meq/g) and surface area (42 m^2/g) (Table 1) (34). Amberlyst-15 and Amberlite-IR have more or less

Table 1. Characteristics of catalyst: H^+ capacity, surface area (m^2/g), and particle size (mesh).

Entry	Catalyst	H^+ capacity	Surface area (m^2/g)	Particle size (mesh)
1	Sulfated zirconia	–	180 ^a	–
2	Phosphated zirconia	–	85 ^a	–
3	Montmorillonite K-10	3–4 meq/g	220	<200
4	Aluminum oxide	4.5 meq/g	200	150–300
5	Amberlite IR-120	4.4 meq/g	45	16–50
6	Indion-225H	1.8 meq/mL	–	14–52
7	Catalyst	4.2 meq/g	42	20–50

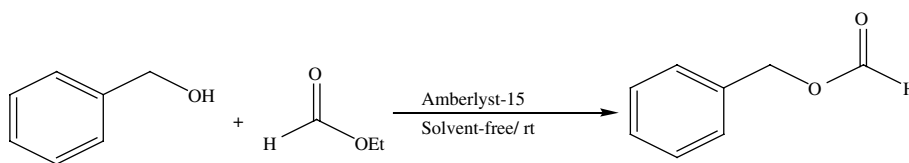
^aThe surface area of phosphated and sulfated zirconia is determined using BET method.

similar H^+ exchange capacity and surface area, but the moisture content of Amberlyst-15 is 1.5–1.6% and that of Amberlite-IR is 53–58%. Since the reaction is in an organic medium, the excess moisture content of Amberlite IR-120 may affect the yield of the desired product. This proves the superior activity of Amberlyst-15. Aluminum oxide is amphoteric in nature, and hence, has acidic as well as basic sites. However, only acidic sites catalyze the reaction whereas basic sites hamper the reaction. The moisture content of Al_2O_3 is approximately 12%, which may be the reason for reduced activity and hence low yield of the product. Ziyauddin et al. also observed the higher activity of Amberlyst-15 than Al_2O_3 for benzylation and hydroalkylation of β -dicarbonyl compounds.

Optimized reaction conditions for various catalysts for the above-mentioned reaction are shown in Table 2. Benzyl alcohol on reaction with ethyl formate remains unconsumed in the absence of a catalyst, even after reaction time of 24 h (Table 2, entry 1). Sulfated zirconia, phosphated zirconia, montmorillonite, and aluminum oxide (Table 2, entries 2–5) were also found to be less promising, giving very low yield of the desired product. However, different types of commercially available ion-exchange resins such as gel-type Amberlite IR-120, Indion-225H, and Amberlyst-15 (Table 2, entries 6–8) gave good to excellent yield of the desired product. It was found that Amberlyst-15 was the most active catalyst for model reaction of benzyl alcohol with ethyl formate. The data of H^+ exchange capacity and surface area were provided by the supplier (Rohm and Haas). The surface area of phosphated zirconia and sulfated zirconia was determined by using the Brunauer–Emmet–Teller method.

Formylation

Table 3 indicates the effect of catalyst loading on formylation of benzyl alcohol with ethyl formate. It was found that 50 mg of catalyst was sufficient to catalyze formylation of benzyl alcohol with ethyl formate (Table 3, entries 1 and 2). The yield was found to decrease with decrease in the catalyst loading (Table 3, entries 3 and 4). It is mainly due to the proportional decrease in the number of acidic sites and surface area of the catalyst. The optimal amount of catalyst was 50 mg per 1 mmol of alcohol and 3 mL of ethyl formate at room temperature. The present method signifies a simple formylating procedure under environmentally safe, solvent-free, and heterogeneous reaction conditions for a wide range of benzylic, aliphatic, primary, secondary, and allylic alcohols, as illustrated in Scheme 1.

Table 2. Effect of the various catalysts on the formylation of benzyl alcohol with ethyl formate at room temperature.^a

Entry	Catalyst	Amount (mg)	Time (h)	Yield (%) ^b
1	None	None	24	0
2	Sulfated zirconia	50	2.5	15
3	Phosphated zirconia	50	2.5	13
4	Montmorillonite K-10	50	2.5	32
5	Aluminum oxide	100	2.5	30
6	Amberlite IR-120	50	2.5	45
7	Indion-225H	50	2.5	60
8	Amberlyst-15	50	2.5	98

^aThe reaction conditions: alcohol (1 mmol), ethyl formate (3 mL) at room temperature and under neat conditions.

^bYield based on GC analysis.

As shown in Table 4 (Scheme 1), primary alcohols reacted faster with ethyl formate than did secondary alcohols whereas tertiary alcohols remain unreacted in the presence of catalyst at room temperature. Formylation of electron-withdrawing substituent such as 2-nitrobenzyl alcohol was poor and the corresponding ester was isolated with only 40% yield (Table 4, entry 2). The formylation of other electron-donating substituents such as 2-methoxy and 2-methyl benzyl alcohol gave 76 and 73% yield of respective products (Table 4, entries 3 and 4). The formylation of 2-chlorobenzylalcohol resulted in 71% yield (Table 4, entry 5). The nature of electron-withdrawing group predominates the steric effect for less yield of the product. The formylation of 3-nitrobenzyl alcohol resulted in 70% yield (Table 4, entry 6), which may be due to less steric effect and the 3-position of nitro group. Electron-donating substituents on the aromatic ring such as 4-methoxy benzyl alcohol reacted faster than did benzyl alcohol (Table 4, entry 7). In addition, the formylation of primary, secondary, and allylic alcohols was done selectively in the presence of tertiary alcohol and excellent result was obtained for corresponding ester (Scheme 1). Primary and secondary alcohols were easily converted to their corresponding formate ester at reaction time 2–5 h (Table 4, entries 11–13) whereas excellent yields of cyclic aliphatic alcohols were obtained on formylation with ethyl formate at room temperature in the presence of catalyst (Table 4, entries 14–16). However, thiols, phenols, and tertiary alcohols remain unreacted when their formylation was done under similar conditions, demonstrating

chemoselectivity of the reaction (13) (Table 4, entries 17–19).

The recyclability of the catalyst was tested for benzyl alcohol formylation. Upon completion of the reaction, the catalyst was separated by filtration and washed with volatile solvent such as diethyl ether. Catalyst was activated by drying in an oven for 30 min at 100°C and then it was conserved for the next cycle of reaction. The activated catalyst was reused for three consecutive cycles without any considerable loss in the yield of benzyl formate (Table 4, entry 1).

Acetylation

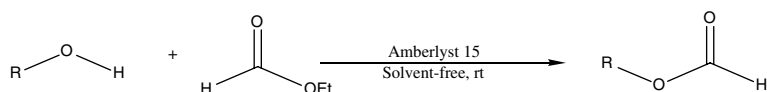
Acetylation of alcohols using ethyl acetate as a solvent and reagent is a useful and practical protocol. Hydroxy groups can be smoothly protected by using acetyl group because of its easy exclusion under basic condition. Amberlyst-15 has proved to be an efficient catalyst for the same purpose at reflux temperature.

Table 3. Influence of the amounts of Amberlyst-15 on the formylation of the benzyl alcohol with ethyl formate at room temperature.^a

Entry	Amounts of Amberlyst-15 (mg)	Time (h)	Yield ^b (%)
1	100	2.5	98
2	50	2.5	98
3	40	3.0	84
4	30	4.0	71

^aThe reaction conditions: alcohol (1 mmol), ethyl formate (3 mL) at room temperature and under neat conditions.

^bYield based on GC analysis.



Scheme 1. Conversion of alcohols into corresponding formate esters and with ethyl formates in the presence of Amberlyst-15. The optimized reaction conditions (i.e. 50 mg of Amberlyst-15 and 3 mL of ethyl formate) were then used in the formylation of various other alcohols under mild, nearly neutral, and heterogeneous conditions (Table 4). R = primary, secondary and, allylic.

As illustrated in Table 5, the diverse alcohols were acetylated with ethyl acetate in the presence of Amberlyst-15 at reflux temperature (Scheme 2).

Initially, the reaction of benzyl alcohol (1 mmol) with ethyl acetate (5 mL) in the presence of catalyst (50 mg) was carried out at room temperature. It was found that benzyl alcohol remained unconsumed even after 24 h. However, under reflux condition, the reaction was completed in 7.5 h with 92% yield (Table 5, entry 1). Structurally diverse alcohols were esterified easily by using this method, and their corresponding acetates were isolated in good to excellent yields (Table 5). Benzylic alcohol bearing electron-withdrawing group at 2-position gave low yield (Table 5, entry 2) whereas electron-donating group at 2-position on phenyl ring gave well to moderate yield (Table 5, entries 3 and 4). The acetylation of 2-chlorobenzyl alcohol under similar conditions gave 69% yield (Table 5, entry 5). The electron-withdrawing substituent at 3-position on phenyl ring suffers less steric hindrance, giving 75% yield (Table 5, entry 6). The electron-donating adduct gave excellent yield with the reaction time of 3–7 h (Table 5, entry 7). Allylic alcohol was converted to its corresponding acetate without forming a by-product (Table 5, entry 10). Aliphatic alcohols except tertiary alcohols were easily converted to corresponding acetate ester, giving excellent yield of the product with reaction time of 5 h (Table 5, entries 11–13). Cyclic aliphatic alcohols also gave excellent yields when reacted with ethyl acetate at reflux temperature in the presence of Amberlyst-15 (Table 5, entries 14–16). Phenols, thiols, and tertiary alcohols were quite inactive toward esterification by ethyl acetate in the presence of Amberlyst-15, indicating chemoselectivity of the catalyst for acetylation (Table 5, entries 17–19). Similar results were observed by Firouzabadi et al. when they carried out the reaction in the presence of another solid acid catalyst (13).

The recyclability of the catalyst was determined by considering the reaction of benzyl alcohol with ethyl acetate as model substrate. Upon completion, the reaction mixture was filtered, the solid acid catalyst was washed with diethyl ether (2×10 mL), and then it was activated by drying in an oven at 100°C for 30 min. The used catalyst was tested thrice

with no significant loss in the catalytic activity of Amberlyst-15 (Table 5, entry 1).

Experimental

General

Chemicals were purchased from Fluka, Merck, and s.d.fine-chem chemical companies and used without any purification. Amberlyst-15 was purchased from Rohm and Hass; its pH range is 0–14, and the concentration of acidic sites, i.e. the mmol of H^+ , is 0.235/50 mg. The yields of all volatile formylated and acylated products have been determined by gas chromatography (GC) (PerkinElmer Clarus 400). The formylated and acylated products were

Table 4. Formylation of alcohols with ethyl formate in the presence of Amberlyst-15 at room temperature.^a

Entry	Substrate	Time (h)	Yield (%) ^b
1	Benzyl alcohol	2.5	91, 89 ^c , 89 ^c , 88 ^c
2	2-Nitrobenzyl alcohol	3.0	40
3	2-Methoxybenzyl alcohol	3.5	76
4	2-Methylbenzyl alcohol	3.5	73
5	2-Chlorobenzyl alcohol	3.5	71
6	3-Nitrobenzyl alcohol	4.0	70
7	4-Methoxybenzyl alcohol	1.5	80
8	2-Phenoxyethanol	4.5	74
9	1-Phenylethanol	3.5	72
10	Cinnamyl alcohol	2.5	90
11	Isoamyl alcohol	2.0	90
12	2-Ethylhexanol	2.0	95
13	1-Octanol	3.0	92
14	Cyclopentanol	2.5	93
15	Cyclohexanol	3.0	91
16	Menthol	5.0	85
17	Phenol	6.0	NR
18	Thiol	6.0	NR
19	2-Methyl-1-phenyl-2-propanol	6.0	NR

NR, Not reported.

^aThe reaction conditions: substrate (1 mmol), ethyl formate (3 mL), and catalyst Amberlyst-15 (50 mg) at room temperature and under neat conditions.

^bIsolated yield.

^cThe recyclability of the catalyst.

Table 5. Acetylation of alcohols with ethyl acetate in the presence of Amberlyst-15 at reflux temperature.^a

Entry	Substrate	Time (h)	Yield (%) ^b
1	Benzyl alcohol	7.5	92, 91 ^c , 91 ^c , 89 ^c
2	2-Nitrobenzyl alcohol	8.0	45
3	2-Methoxybenzyl alcohol	6.5	78
4	2-Methylbenzyl alcohol	6.5	73
5	2-Chlorobenzyl alcohol	6.5	69
6	3-Nitrobenzyl alcohol	9.0	75
7	4-Methoxybenzyl alcohol	3.0	80
8	2-Phenoxyethanol	6.5	88
9	1-Phenylethanol	12.0	72
10	Cinnamyl alcohol	7.0	90
11	Isoamyl alcohol	5.0	91
12	2-Ethylhexanol	5.0	91
13	1-Octanol	5.0	92
14	Cyclopentanol	6.0	90
15	Cyclohexanol	7.0	91
16	Menthol	5.0	85
17	Phenol	6.0	NR
18	Thiol	6.0	NR
19	2-Methyl-1-phenyl-2-propanol	6.0	NR

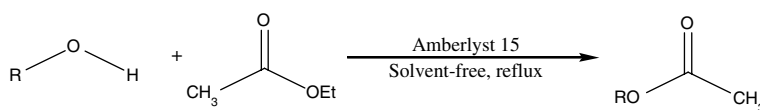
NR, Not reported.

^aThe reaction conditions: substrate (1 mmol), ethyl acetate (5 mL), and catalyst Amberlyst-15 (50 mg) at reflux temperature.^bIsolated yield.^cThe recyclability of the catalyst.

characterized by comparison of their spectral and physical data with previously reported data or with authentic samples. Purity of all the compounds was determined with the help of GC–mass spectrometry (MS) analysis (Shimadzu QP-2010).

General procedure for formylation of alcohols with ethyl formate

Amberlyst-15 (50 mg) and the substrate (1 mmol) were added to ethyl formate (3 mL), and the suspension was stirred at room temperature for the specified time given in Table 4. The progress of the reaction was monitored by thin layer chromatography or GC.



Scheme 2. Conversion of hydroxyl group into corresponding acetate esters with ethyl acetate in the presence of Amberlyst-15. R = Primary, secondary and allylic.

When the reaction was complete, the suspension was filtered off and the catalyst Amberlyst-15 was washed with diethyl ether (2 × 10 mL). The organic phases were combined and passed through a short pad of column chromatography to obtain the pure product.

General procedure for acetylation of alcohols with ethyl acetate

Solid acid Amberlyst-15 (50 mg) and the alcohol (1 mmol) were added to ethyl acetate (5 mL) and suspension was stirred at reflux temperature for the specified time given in Table 5. The progress of the reaction was monitored by TLC or GC. When the reaction was complete, the suspension was filtered off and the solid was washed with diethyl ether (2 × 10 mL). The organic phases were combined and passed through a short pad of column chromatography to obtain the pure product.

Product characterization: spectroscopic data of the reaction products

Benzyl formate: GC–MS (EI, 70 eV): m/z (%) = 136 (72) $[M]^+$, 91 (100), 90 (85), 79 (40), 65 (26). IR (neat): 3066, 2933, 1616, 1587, 1260, 901, 698 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ = 5.22 (s, 2H, CH_2), 7.37–7.40 (m, 5H, ArH), 8.14 (s, 1H, CHO).

Benzyl acetate: GC–MS (EI, 70 eV): m/z (%) = 150 (32) $[M]^+$, 108 (100), 107 (17), 91 (59). IR (KBr): 3066, 3044, 1742, 1608, 1497, 1380, 1027, 749, 698 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ = 7.38 (s, 5H, ArH), 5.13 (s, 2H, CH_2), 2.12 (s, 3H, OCH_3).

4-Methoxybenzyl formate: GC–MS (EI, 70 eV): m/z (%) = 166 (27) $[M]^+$, 121 (100), 109 (11), 77 (19). IR (neat): 3053, 2935, 2837, 1736, 1612, 1512, 1464, 1373, 1265, 1174, 1035, 823 cm^{-1} . δ = 3.80 (s, 3H, CH_3), 5.09 (s, 2H, CH_2), 6.89 (d, J = 8.6 Hz, 2H ArH), 7.30 (d, J = 8.6 Hz, 2H ArH), 8.14 (s, 1H, CHO).

4-Methoxybenzyl acetate: GC–MS (EI, 70 eV): m/z (%) = 180 49 $[M]^+$, 121 (100), 120 (39), 91 (29). IR (KBr): 3010, 2941, 1752, 1516, 1232, 1176, 1128, 749 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ = 7.22 (d, J = 8.5 Hz, 2H ArH), 6.82 (d, J = 8.5 Hz, 2H, ArH), 5.13 (s, 2H, CH_2), 3.72 (s, 3H, CH_3), 2.07 (s, 3H, OCH_3).

2-Chlorobenzyl formate: GC–MS (EI, 70 eV): m/z (%) = 170 42 $[M]^+$, 135 (98), 125 (100), 107 (66), 89

(95). IR (neat): 3066, 2928, 1726, 1596, 1477, 1443, 1167, 1058, 754 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): $d=5.24$ (s, 2H, CH_2), 7.26–7.30 (m, 2H, ArH), 7.40–7.45 (m, 2H, ArH), 8.14 (s, 1H, CHO).

2-Chlorobenzyl acetate: GC–MS (EI, 70 eV): m/z (%) = 184 4 $[\text{M}]^+$, 149 (100), 125 (54), 66 (11). IR (KBr): 3066, 2939, 1726, 1597, 1479, 1444, 1381, 1239, 1132, 900, 755 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): $d=7.35$ –7.31 (m, 2H, ArH), 7.23–7.19 (m, 2H, ArH), 5.15 (s, 2H, CH_2), 2.15 (s, 3H, OCH_3).

Conclusion

An efficient protocol for the formylation and acetylation of alcohols using solid acidic resin Amberlyst-15 as a catalyst was developed. The commercially available ethyl formate and ethyl acetate were used as formylating and acetylating agents, respectively. The developed method is chemoselective for the conversion of primary and secondary alcohols to their respective formates and acetates in the presence of phenols, thiols, and tertiary alcohols. However, electron-withdrawing nitro group at 2-position strongly affects the product yield. The present catalytic system has several advantages such as simple work-up, solvent-free reaction, noncorrosiveness, reusability, and high stability of the catalyst as compared with conventional protocols.

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