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A Highly Selective and Efficient Method for the Preparation of Amides from Carboxylic Acids and Amines Using Sodium Hydrogen Sulfate Adsorbed on Silica Gel †

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Abstract: The formation of amides from carboxylic acids and amines has been catalyzed efficiently with sodium hydrogen sulfate adsorbed on silica gel ($NaHSO_4.SiO_2$) at room temperature to give the products in high yields. The conversion carried out under reflux requires less reaction times and forms the products in higher yields. The reaction is highly selective as it has been found that either or both of the substrates should be aliphatic but it is failure when the acid as well as the amine is aromatic. The method has been utilized for the preparation of a natural phenethyl amide derivative and its analogues.

Keywords: Heterogeneous Catalysis, Carboxylic Acids, Amines, Amides, Nucleophilic Substitution

1. Introduction

Amides are useful intermediates in various reactions of carboxylic acids and amines in which it is desirable to protect these groups [1-3]. Amides can easily be hydrolyzed by acids or alkalis to generate the parent amines and carboxylic acids. Several amides are used in medicine as febrifuge [1]. The amide constituents isolated from nature have been found to possess various biological properties including anticancer activity [4-5]. The amides can also be converted into esters, amines and nitriles [1]. The former are generally prepared by the action of amines with acid chlorides, acid anhydrides or ester [1-6]. The direct conversion of esters into amides is a useful synthetic procedure but the aminolysis of esters generally requires high temperature and the catalyst used here may affect other functionalities. The one-step conversion of carboxylic acids into amides can also be effected with various reagents [7-24]. However, many of these reagents are not easily available and expensive. The preparation of these reagents also involves complex steps. Moreover, some of the reagents requires tedious experimental procedures and long reaction times and form the products with low yields. The selectivity of the amide formation by using these reagents has also been examined only in a few cases [21]. Thus there is a need to develop a simple, efficient and selective method for preparation of amides.

2. Experimental Section

2.1. Materials and Method

The spectra were recorded with the following instruments: IR: Perkin Elmer RX1 FT-IR spectrophotometer; NMR: Varian Gemini 200 MHz and ESI-MS: LC-MSD Trap SL spectrometer, Column Chromatography was carried out over silica gel (BDH 100-200 Mesh) and TLC was performed with silica gel GF 254 (Merck) plates.

2.2. General Experimental Procedure for Preparation of Amides

To a solution of an amine (1.2 mmol) dissolved in $CHCl_3$ or CH_2Cl_2 (10 ml) an acid (1 mmol) and the catalyst, $NaHSO_4.SiO_2$(100 mg) were added. The mixture was stirred at room temperature or under reflux. The reaction was monitored by TLC. After completion the solvent was removed and water (10 ml) was added. The mixture was extracted with EtOAc (3 x 10 ml) and the extract was dried, concentrated and subjected to column chromatography to obtain a pure amide.

3. Results and Discussion

In continuation of our work [26-33] on the application of silica gel supported sodium hydrogen sulfate ($NaHSO_4.SiO_2$) catalyst for synthesis of bioactive compounds as well as for developments of novel synthetic methodologies we have observed that the catalyst can efficiently be utilized for one-step preparation of amides from carboxylic acids and amines (Figure 1).

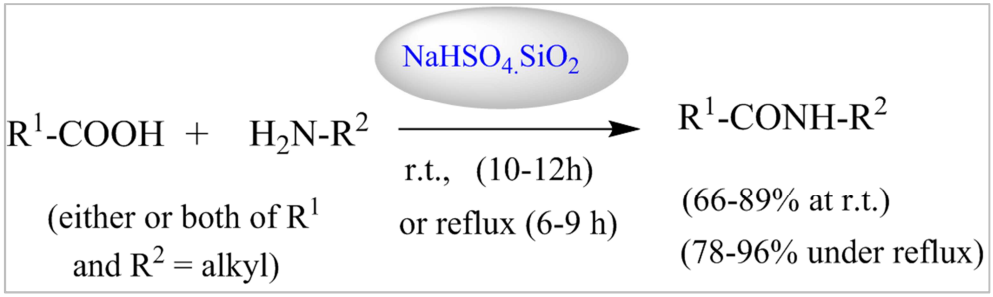

Figure 1. *One pot reaction of carboxylic acids and amines in the presence of sodium hydrogen sulphate adsorbed on silica gel at room temperature orunder reflux.*

A series of amides has been prepared by $NaHSO_4.SiO_2$catalyzed reaction of acids and amines at room temperature (Table 1). The yields of amides are high. When the conversion was carried out under reflux in $CHCl_3$ or toluene the time required for amide formation was less and the yields of the amides were higher (Table 1).

The amides were prepared from different aromatic and aliphatic acids and amines. The aromatic acids and anilines contained both electron-donating and electron-withdrawing groups. Long chain aliphatic acids also underwent the conversion smoothly. Various functional groups such as halogen, hydroxyl, ether and nitro remained intact. The structures of the amides were established from their spectral (IR, ^1H and ^{13}C NMR and MS) and analytical data.

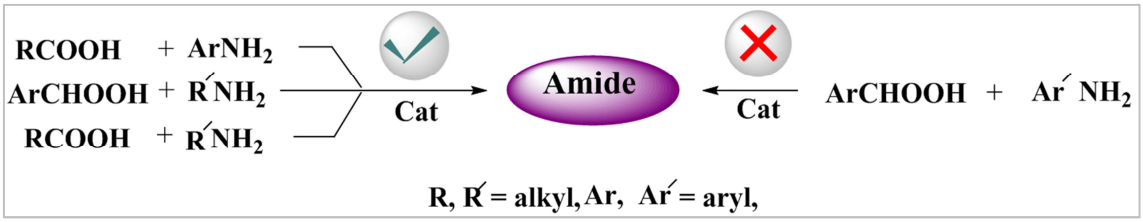

Figure 2. *Selectivity in the preparation of amides using $NaHSO_4.SiO_2$.*

The selectivity of the present conversion is interesting (Figure 2). It has been observed that at least one of the acid and amine should be aliphatic for the formation of an amide. However, if both are aromatic the reaction will not occur (Table 1)

Table 1. *Formation of amides from carboxylic acids and amines[a].*

Entry	Acid	Amine	At r.t.		Under reflux	
			Time (h)	Isolated yield (%)	Time (h)	Isolated yield (%)
1	CH_3CO_2H	$C_6H_5NH_2$	10	75	8	92
2	CH_3CO_2H	4-(F)$C_6H_4NH_2$	11	80	9	93
3	CH_3CO_2H	2,3-$(Cl)_2C_6H_3NH_2$	11	85	7	91
4	CH_3CO_2H	2,4,6-$(Cl)_3C_6H_2NH_2$	11	79	9	82
5	$CH_3CH_2CO_2H$	3-(Me)$C_6H_4NH_2$	12	82	8	91
6	$CH_3CH_2CO_2H$	2,3-$(Cl)_2C_6H_3NH_2$	10	69	8	87
7	$CH_3CH_2CO_2H$	2,6-$(Cl)_2$,4-$NO_2)C_6H_2NH_2$	12	68	9	78
8	$C_6H_5CH_2CO_2H$	$C_6H_5NH_2$	11	65	7	94
9	3-(Cl)$C_6H_4CH_2CO_2H$	2,3-$(Cl)_2C_6H_3NH_2$	12	69	8	96
10	$CH_3(CH_2)_8CO_2H$	2,3-$(Cl)_2C_6H_3NH_2$	12	69	9	80
11	$C_6H_5CO_2H$	CH_3NH_2	11	76	6	92
12	4-(OH)$C_6H_4CO_2H$	CH_3NH_2	12	79	7	84
13	2-(Cl)$C_6H_4CO_2H$	CH_3NH_2	11	78	8	83
14	2-(I)$C_6H_4CO_2H$	CH_3NH_2	10	69	8	78

Entry	Acid	Amine	At r.t.		Under reflux	
			Time (h)	Isolated yield (%)	Time (h)	Isolated yield (%)
15	4-$(NO_2)C_6H_4CO_2H$	CH_3NH_2	12	66	7	79
16	3,5-$(OH)_2C_6H_4CO_2H$	CH_3NH_2	12	78	9	84
17	3,5-$(Br)_2C_6H_4CO_2H$	CH_3NH_2	12	80	9	89
18	3,5-$(NO_2)_2C_6H_4CO_2H$	$C_6H_5CH_2NH_2$	11	75	9	81
19	$CH_3CH_2CO_2H$	CH_3NH_2	11	66	8	82
20	$CH_3CH_2CO_2H$	$CH_3(CH_2)_2NH_2$	11	77	9	81
21	$CH_3(CH_2)_8CO_2H$	CH_3NH_2	10	72	8	89
22	CH_3CO_2H	$C_6H_5CH_2NH_2$	11	77	8	82
23	$CH_3CH_2CO_2H$	4-$(OH)C_6H_5(CH_2)_2NH_2$	12	66	9	78
24	$CH_3CH_2CO_2H$	$C_6H_5(CH_2)_2NH_2$	11	80	9	90
25	$CH_3(CH_2)_8CO_2H$	$C_6H_5CH_2NH_2$	11	85	8	93
26	$CH_3CH(Cl)CO_2H$	$C_6H_5CH_2NH_2$	11	82	8	88
27	$C_6H_6CO_2H$	$C_6H_5NH_2$	12	0	9	0
28	$C_6H_6CO_2H$	2-$(NO_2)C_6H_4NH_2$	12	0	9	0
29	3-$(Cl)C_6H_4CO_2H$	4-$(OH)C_6H_4NH_2$	12	0	9	0
30	2-$(I)C_6H_4CO_2H$	4-$(Me)C_6H_4NH_2$	12	0	9	0
31	2-$(NH_2)C_6H_4CO_2H$	$C_6H_5NH_2$	12	0	9	0
32	4-$(NO_2)C_6H_4CO_2H$	$C_6H_5NH_2$	12	0	9	0
33	3,5-$(NO_2)C_6H_3CO_2H$	4-$(OMe)C_6H_4NH_2$	12	0	9	0

[a]The structures of the products were established from the spectral (IR, ^{1}H and ^{13}C NMR and MS) and analytical data.

The present method has been applied for the synthesis of natural tyramide, *N*- (4- hydroxyphenethyle) propionamide (Table 1, entry 23). The compound occurs in marine bacteria [34] and Myrmicine ants [35]. It has also been obtained as a metabolite of an endophytic *Stryptomyces*sp [36]. The starting material, 4-hydroxyphenethyle amine was prepared from 4-hydroxyphenyl methanol by converting it into the corresponding nitrile by treatment with NaCN in DMF [37] followed by reduction of the product with $NaBH_4/I_2$ system [38]. Treatment of 4-hydroxyphenethyl amine with propionic acid in the presence of $NaHSO_4.SiO_2$ at room temperature or under reflux afforded *N*- (4-hydroxphenethyl) propionamide. Some analogues of this compound (entry 20, 22, 24, 25 and 26) have also been prepared following the similar method.

The catalyst, $NaHSO_4.SiO_2$ works under heterogeneous conditions. In recent years heterogeneous catalysts have attracted much attention due to eco-economic benefits. The catalysts can easily be prepared [39] from its readily available ingredient, $NaHSO_4$ and silica gel (100-200 mesh). It can also easily be removed from the reaction mixture.

4. Conclusion

In conclusion, we have developed a novel and efficient methodology for one-pot preparation of amides from carboxylic acids and amines (both should not be aromatic) in the presence of $NaHSO_4.SiO_2$ as a catalyst. The procedure offers several advantages including mild reaction conditions, operational simplicity, high selectivity and utilization of a non-expensive and non-hazardous heterogeneous catalyst. The method will be useful for separation of aromatic carboxylic acids from a mixture containing aliphatic carboxylic acids as well as for separation of aromatic amines from a mixture containing aliphatic amines. The method has successfully been applied for the synthesis of natural tyramide, *N*- (4- hydroxyphenethyle) propionamide and its analogues.

The spectral and analytical data of some representative amides are given below:

N-m-Tolylpropionamide (Table 1, Entry 5):

IR (KBr): ν = 3305, 1662, 1607, 1547, 1437, 1217 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.36 – 7.21 (3H, m), 7.10 (1H, t, J = 8.0 Hz), 6.82 (1H, d, J = 8.0 Hz), 2.40 – 2.21 (5H, m), 1.10 (3H, t, J = 7.0 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 173.8, 138.2, 138.0, 128.4, 124.8, 121.0, 116.9, 30.1, 20.6; ESIMS: m/z 164 $[M+H]^+$, 186 $[M+Na]^+$; anal. Calcd for $C_{10}H_{13}NO$: C 73.62; H 7.98; N 8.59; found: C 73.71; H 7.92; N 8.53.

N-(2,3-Dichlorophenyl) propionamide (Table, Entry 6):

IR (KBr): ν = 3291, 1669, 1579, 1523, 1406, 1366, 1296 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.32 (1H, t, J = 8.0 Hz), 7.72 (1H, brs), 7.17 (2H, d, J = 8.0 Hz), 2.42 (2H, t, J = 7.0 Hz), 1.80-1.69 (2H, m) 1.41 – 1.20 (12H, m) 0.83 (3H, t, J = 7.0 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 171.7, 136.8, 133.0, 127.9, 125.0, 121.0, 119.9, 38.1, 32.2, 29.7, 29.0, 25.3, 22.6, 14.2; ESIMS: m/z 316, 318, 320 $[M+H]^+$, 338, 340, 342 $[M+Na]^+$; anal. Calcd for $C_{16}H_{23}Cl_2NO$: C 60.76; H 7.28; N 4.43; found: C 60.84; H 7.32; N 4.47.

2-(2-Chlorophenyl)-*N*-(2,3-dichlorophenyl) acetamide (Table 1, Entry 9):

IR (KBr): ν = 3293, 1645, 1550, 1453, 1368, 1281cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.32 (1H, dd, J = 8.0, 2.0 Hz), 7.80 (1H, brs), 7.51 – 7.40 (3H, m), 7.38 – 7.30 (2H, m), 7.19 (2H, d, J = 8.0 Hz), 3.92 (1H, s); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 168.0, 136.7, 135.0, 132.1, 132.0, 130.2, 130.0, 127.9, 125.4, 119.5, 42.7, ESIMS: m/z 314, 316, 318, 320 $[M+H]^+$, 336, 340, 342 $[M+Na]^+$; anal. Calcd for $C_{14}H_{10}Cl_3NO$: C 53.42; H 3.18; N 4.45; found: C 53.51; H 3.22; N 4.51.

2-Iodo-*N*-Methylbenzamide (Table 1, Entry 14):

IR (KBr): ν = 3436, 1654, 1565, 1510, 1440 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.98 (1H, d, J = 8.0 Hz) 7.58 (1H, brs), 7.40 (1H, t, J = 8.0 Hz), 6.67 (1H, d, J = 8.0 Hz), 6.59 (1H, t, J = 8.0 Hz), 2.94 (3H, s); ^{13}C NMR (50 MHz,

$CDCl_3$): δ = 167.9, 131.8, 130.1, 129.5, 127.8, 125.3, 119.2, 42.9; ESIMS: m/z 128 $[M+H]^+$; anal. Calcd for C_8H_8INO: C 36.78; H 3.07; N 5.36; found: C 36.86; H 3.12; N 5.27.

2,6-Dibromo-*N*-methylbenzamide (Table 1, Entry 17):

IR (KBr): *v* = 3425, 1662, 1590, 1450, 1416, 1364 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 8.02 (2H, s), 7.63 (1H, s), 6.12 (1H, brs), 2.49 (3H, S); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 167.0, 139.4, 133.9, 130.0, 121.0, 23.5; ESIMS: m/z 292, 294, 296 $[M+H]^+$; anal. Calcd for $C_8H_7Br_2NO$: C 32.76; H 2.39; N 4.78; found: C 32.68; H 2.42; N 4.83.

N-Methylpropionamide (Table 1, Entry 21):

IR (KBr): *v* = 3300, 1638, 1563, 1416, 1375, 1290 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 6.12 (1H, brs), 2.79 (3H, s), 2.12 (2H, t, *J* = 7.0 Hz), 1.67 – 1.52 (2H, m), 1.38 – 1.20 (12H, m), 0.88 (3H, t, *J* = 7.0 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 173.8, 36.9, 32.2, 29.8, 29.3, 26.2, 26.0, 20.9, 14.1; ESIMS: m/z 186 $[M+H]^+$, 208 $[M+Na]^+$; anal. Calcd for $C_{11}H_{23}NO$: C 71.35; H 12.43; N 7.57; found: C 71.44; H 12.48; N 7.49.

N-Benzylacetamide (Table 1, Entry 22):

IR (KBr): *v* = 3293, 1647, 1551, 1454, 1375, 1281cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 7.28 – 7.15 (5H, m), 6.83 (1H, brs), 4.30 (2H, s), 1.92 (3H, S); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 170.8, 137.9, 128.4, 127.5, 127.2, 43.4, 22.6; ESIMS: m/z 150 $[M+H]^+$, 172 $[M+Na]^+$; anal. Calcd for $C_9H_{11}NO$: C 72.48; H 7.38; N 7.40; found: C 72.57; H 7.43; N 7.34.

N-(4-Hydroxyphenethyl) propionamide (Table 1, Entry 23):

IR (KBr): *v* = 3417, 1646, 1551, 1456, 1275 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 9.54 (1H, brs), 7.01 (2H, d, *J* = 8.0 Hz), 6.71 (2H, d, *J* = 8.0 Hz), 5.42 (1H, brs), 3.49 (2H, q, *J* = 7.0 Hz) 2.80 (2H, t, *J* = 7.0 Hz), 2.11 (2H, q, *J* = 7.0 Hz), 1.10 (3H, t, *J* = 7.0 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 170.2, 155.8, 133.1, 129.5, 115.7, 40.8, 35.6, 22.9, 20.9; ESIMS: m/z 194 $[M+H]^+$, 216 $[M+Na]^+$; anal. Calcd for $C_{11}H_{15}NO_2$: C 68.39; H 7.77; N 7.25; found: C 68.28; H 7.83; N 7.17.

N-Phenethylacetamide (Table 1, Entry 24):

IR (KBr): *v* = 3284, 1652, 1554, 1451, 1369, 1296 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 7.30 – 7.09 (5H, m), 6.31 (1H, brs), 3.41 (2H, q, *J* = 7.0 Hz), 2.79 (2H, t, *J* = 7.0 Hz), 1.90 (3H, s); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 170.2, 138.9, 128.7, 128.5, 126.4, 40.8, 35.6, 22.9; ESIMS: m/z 164 $[M+H]^+$, 186 $[M+Na]^+$; anal. Calcd for $C_{10}H_{13}NO$: C 73.62; H 7.98; N 8.59; found: C 73.73; H 7.92; N 8.65.

N-Benzylpropionamide (Table 1, Entry 25):

IR (KBr): *v* = 3293, 1613, 1553, 1459, 1381, 1239 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 7.37 – 7.11 (5H, m), 5.65 (1H, brs), 4.33 (2H, s), 2.11 (2H, t, *J* = 7.0 Hz), 1.62 – 1.53 (2H, m), 1.29 – 1.14 (12H, m), 0.83 (3H, t, *J* = 7.0 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 171.5, 127.8, 127.5, 128.7, 128.6, 127.4, 127.3, 65.1, 44.6, 43.6, 36.8, 31.8, 29.5, 29.3, 25.8, 22.7, 14.1; ESIMS: m/z 262 $[M+H]^+$; anal. Calcd for $C_{17}H_{27}NO$: C 78.16; H 10.35; N 5.36; found: C 78.25; H 10.41; N 5.42.

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