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Tandem synthesis of *N*,*N*′-alkylidenebisamides promoted by nano-$SnCl_4.SiO_2$

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Abstract. A highly efficient procedure for the preparation of *N*,*N*′-alkylidenebisamides in the presence of nano-$SnCl_4.SiO_2$ as a catalysis described. *N*,*N*′-alkylidenebisamides have been prepared via condensation reaction of various aldehydes and amides. All of the reactions proceeded in high yields and in moderately short reaction times.

Keywords. *N*,*N*′-alkylidenebisamides; aldehydes; amides; nano-$SnCl_4.SiO_2$.

1. Introduction

Bisamides are of considerable interest in the synthesis of peptidomimetic compounds.[1,2] They are key constituent of many biologically active and pharmaceutical compounds such as introduction of gem-diaminoalkyl residues in retro-inverso pseudopeptide derivatives by treating the corresponding amide with iodobenzenebistrifluoroacetate.[3,4]

Generally, symmetrical alkylidenebisamides are synthesized by the direct reaction of aldehydes with amides under suitable catalytic condition. In this topic, various catalysts such as triflic acid,[5] *p*-toluene sulphonic acid,[6] SiO_2-$MgCl_2$,[7] CC-activatd DMSO,[8] sulphamic acid,[9] phosphotungstic acid,[10] boric acid[11] and silica supported polyphosphoric acid (SiO_2-PPA)[12] have been examined. However, each method has certain restrictions with regards to scope and reaction conditions, for example, long reaction times, low yields, difficult work-up and harsh reaction conditions.

$SnCl_4{\cdot}SiO_2$[13–15] is bench-top catalyst which has many advantages such as simple preparation, reusability, easy handling and high efficiency. Because of the important role of solid acids in organic synthesis[16,17] and in continuation of our investigations on this area,[18–22] we have studied nano-$SnCl_4.SiO_2$ efficiency in the synthesis of *N*,*N*′-alkylidenebisamides under mild conditions.

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2. Experimental

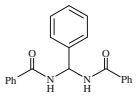
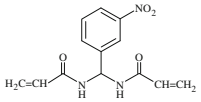
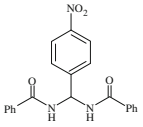
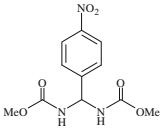
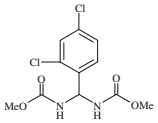
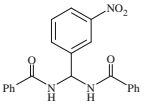
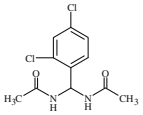
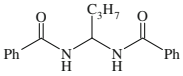
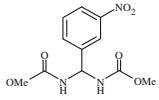
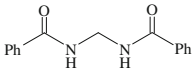
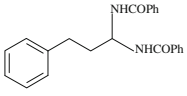
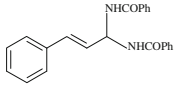
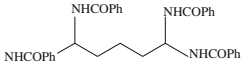
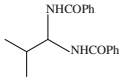
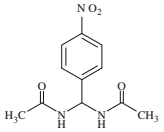
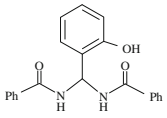
The chemicals were used without any additional purification. The products were characterized by FT-IR, ^{1}H-NMR, and a comparison of their physical properties with those reported in the literature. FT-IR spectra were run on a Bruker, Eqinox 55 spectrometer. A Bruker (DRX-400 Avance) NMR was used to record the ^{1}H NMR spectra. Melting points were determined by a Buchi melting point B-540 B.V.CHI apparatus. BANDELIN Sonopuls HD 3200 ultrasonic apparatus (20 kHz, 150 W) was used for sonication. The microwave oven Kenwood, 1300 W and Mixer Mill (MM 400) in 25 Hz frequency were used for running the described reactions. Elemental analyses were done by Costech ECS 4010 CHNS-O analyser.

2.1 *General procedure for the synthesis of N,N′-alkylidenebisamides*

A mixture of aldehyde (1 mmol), amide (2 mmol), *n*-hexane (5 ml) and nano-$SnCl_4.SiO_2$ (0.01 g) was refluxed for appropriate time. The progress of the reactions was monitored by TLC. After completion of the reaction, the mixture was cooled to room temperature and filtered to isolation of product and catalyst. The catalyst was separated from product by boiling ethanol. The crude solid product was purified by recrystallization in ethanol:water, 80:20, or ethanol.

2.1a *N,N′-(phenylmethylene)dibenzamide (table 1, entry 1)*: FT-IR: $\bar{U}$ (ATR, neat, cm^{-1}):3275 (N-H),

Table 1. Preparation of *N*,*N*′-alkylidenebisamides in the presence of nano-$SnCl_4.SiO_2$[a].

Entry	R^1	R^2	Product	Yield (%)[b]/time (h)	M.P. °C (Ref.)
1	C_6H_5	C_6H_5		90/2.1	213–215 (214–216)[11]
2	3-NO_2-C_6H_4	CH_2=CH-		86/4.9	224–225 (224–226)[11]
3	4-NO_2-C_6H_4	C_6H_5		94/1.9	240–241 (242–244)[11]
4	4-NO_2-C_6H_4	OCH_3		85/0.81	197–198
5	2,4-di-Cl-C_6H_3	OCH_3		91/0.9	249–251 (252–254)
6	3-NO_2-C_6H_4	C_6H_5		94/1.4	237–238
7	2,4-di-Cl-C_6H_3	CH_3		75/4.5	265–266
8	CH_3-CH_2-CH_2-	C_6H_5		80/2.3	171–172
9	3-NO_2-C_6H_4	OCH_3		91/2.1	184–185
10	1,3,5-trioxane	C_6H_5		89/6	124–125
11	Ph-CH_2-CH_2-	C_6H_5		71/4	247–249 (248–249)[6]
12	Ph-CH_2=CH_2-	C_6H_5		69/2	199–201
13	$CHOCH_2$-CH_2-CH_2-	C_6H_5		79/6.5	128–129
14	$(CH_3)_2$-CH-	C_6H_5		74/5.1	126–127
15	4-NO_2-C_6H_4	CH_3		96/4.8	235–237 (233–235)[7]
16	2-OH-C_6H_4	C_6H_5		72/5	178–179

[a]Reaction conditions: amide (2 mmol), aldehyde (1 mmol), nano-$SnCl_4.SiO_2$ (0.01 g)
[b]Isolated yields

1650 (C=O), 1480 (N-H), 715, 799; ^{1}H NMR (DMSO-d_6, ppm): δ 9.01 (d, J = 7.7 Hz, 2 H, N-H),7.92 (d, J = 7.8 Hz, 2 H),7.56 (t, J = 7.1 Hz, 1 H),7.49 (t, J = 7.5 Hz, 3 H),7.39 (t, J = 7.5 Hz, 1 H), 7.32 (t, J = 7.1 Hz, 1 H), 7.05 (t, J = 7.7 Hz, 1 H, CH). Elemental analysis. Found, %: C 76.55; H 5.38; N 8.38. $C_{21}H_{18}N_2O_2$. Calculated, %: C 76.34; H 5.49; N 8.48.

2.1b *N,N′-(3-nitrophenylmethylene)diacrylamide (table 1, entry 2)*: FT-IR: $\bar{\upsilon}$ (ATR, neat, cm^{-1}):3242 (N-H), 1664 (C=O), 1628, 1346, 1528, 1520, 966, 703, 667; ^{1}H NMR (DMSO-d_6, ppm): δ 9.22 (d, J = 7.4 Hz, 2 H, N-H), 8.20 (d, J = 1.7 Hz, 2 H), 7.82 (d, J = 7.8 Hz, 1 H), 7.70 (t, J = 8.0 Hz, 1 H), 6.74 (t, J = 7.5 Hz, 1 H, CH), 6.35 (dd, J = 17.1 and 10.2 Hz, 2 H), 6.17 (dd, J = 17.1 and 1.7 Hz, 2 H), 5.68 (dd, J = 10.2 and 1.7 Hz, 2 H). Elemental analysis. Found, %: C 56.56; H 4.58; N 15.38. $C_{13}H_{13}N_3O_4$. Calculated, %: C 56.72; H 4.76; N 15.27.

2.1c *N,N′-(4-nitrophenylmethylene)dibenzamide (table 1, entry 3)*: FT-IR: $\bar{\upsilon}$ (ATR, neat, cm^{-1}):3256 (N-H), 1649 (C=O), 1343, 1507, 1546, 852; ^{1}H NMR (DMSO-d_6, ppm): δ 9.2 (d, J = 5.0 Hz, 2 H, N-H), 8.26 (d, J = 6.9 Hz, 2 H), 7.93 (d, J = 5.6 Hz, 4 H), 7.75 (d, J = 6.9 Hz, 2 H), 7.58 (s, 2 H), 7.50 (s, 4 H), 7.09 (brs, 1 H, CH). ^{13}C-NMR (DMSO-d_6, ppm): 166.7, 134.4, 132.6, 129.2, 128.9, 128.4, 124.3. Elemental analysis. Found, %: C 66.99; H 4.78; N 11.15. $C_{21}H_{17}N_3O_4$. Calculated, %: C 67.19; H 4.56; N 11.19.

2.1d *N,N′-(4-nitrophenylmethylene)di-methylcarboxamide (table 1, entry 4)*: FT-IR: $\bar{\upsilon}$ (ATR, neat, cm^{-1}):3306 (N-H), 1706 (C=O), 1600, 1349, 1530, 1550, 1251, 1195, 871; ^{1}HNMR (DMSO-d_6, ppm): δ 8.2 (d, J = 7.5 Hz, 2 H), 8.1 (brs, 2 H, N-H), 7.6 (d, J = 7.6 Hz, 2 H), 6.24 (brs, 1 H, CH), 3.58 (s, 6 H, OMe); ^{13}C-NMR (DMSO-d_6, ppm): 156.6, 148.1, 147.9, 128.7, 124.3, 61.9, 52.5. Elemental analysis. Found, %: C 46.50; H 4.70; N 14.90. $C_{11}H_{13}N_3O_6$. Calculated, %: C 46.65; H 4.63; N 14.84.

2.1e *N,N′-(2,4-dichlorophenylmethylene)dimethylcarboxamide (table 1, entry 5)*: FT-IR: $\bar{\upsilon}$ (ATR, neat, cm^{-1}):3309 (N-H), 1708 (C=O), 1550, 720, 699, 643; ^{1}H NMR (DMSO-d_6, ppm): δ 8.04 (sbr, 2 H, N-H), 7.61 (d, J = 2 Hz, 1 H), 7.57 (d, J = 8.4 Hz, 1 H), 6.24 (dd, J = 8.4 and 1.9 Hz, 1H), 6.24 (t, J = 7.5 Hz, 1 H, CH), 3.55 (s, 6 H, OMe); ^{13}C-NMR (DMSO-d_6, ppm): 156.3, 137.5, 134.1, 133.8, 130.3, 129.5, 128.1, 59.8, 52.4. Elemental analysis. Found, %: C 42.92; H 3.90; N 9.08; Cl 23.02. $C_{11}H_{12}N_2O_4Cl_2$. Calculated, %: C 43.02; H 3.94; N 9.12; Cl 23.09.

2.1f *N,N′-(3-nitrophenylmethylene)dibenzamide (table 1, entry 6)*: FT-IR: $\bar{\upsilon}$ (ATR, neat, cm^{-1}):3250 (N-H), 1646 (C=O),1340 (N-H), 1339, 1533, 1505, 715, 695; ^{1}HNMR (DMSO-d_6, ppm): δ 9.2 (d, J = 7.4 Hz, 2 H, N-H), 8.35 (sbr, 1 H), 8.2 (dd, J = 6.9 and 1.37 Hz, 2 H), 7.96 (s, I H), 7.93 (d, J = 8.4 Hz, 4 H), 7.71 (t, J = 7.9 Hz, 1 H), 7.58 (t, J = 7.2 Hz, 2 H), 7.5 (t, J = 7.8 Hz, 4 H), 7.50 (s, 4 H), 7.09 (t, J = 7.3 Hz, 1 H, CH). Elemental analysis. Found, %: C 66.89; H 4.67; N 11.39. $C_{21}H_{17}N_3O_4$. Calculated, %: C 67.19; H 4.56; N 11.19.

2.1g *N,N′-(2,4-dichlorophenylmethylene)diacetamide (table 1, entry 7)*: FT-IR: $\bar{\upsilon}$ (ATR, neat, cm^{-1}):3285 (N-H), 1665 (C=O), 1425, 1518, 856, 749, 643; ^{1}H NMR (DMSO-d_6, ppm): δ 8.54 (d, J = 7.2 Hz, 2 H, N-H), 7.62 (d, J = 1.6 Hz, 1 H), 7.5 (m, 2 H), 6.6 (t, J = 7.5 Hz, 1 H, CH), 1.84 (s, 6H, CH_3). Elemental analysis. Found, %: C 47.90; H 4.48; N 10.08; Cl 25.62. $C_{11}H_{12}N_2O_2Cl_2$. Calculated, %: C 48.02; H 4.40; N 10.18; Cl 25.77.

2.1h *N,N′-(n-propylmethylene)dibenzamide (table 1, entry 8)*: FT-IR: $\bar{\upsilon}$ (ATR, neat, cm^{-1}):3232 (N-H), 1643 (C=O), 1484, 1600, 1530; ^{1}H NMR (DMSO-d_6, ppm): δ 8.52 (d, J = 7.6 Hz, 2 H, N-H), 7.86 (d, J = 7.1 Hz, 4 H), 7.55 (t, J = 7.1 Hz, 2 H), 7.47 (t, J = 7.7 Hz, 4 H), 5.85 (m, 1 H, CH), 1.85 (q, J = 7.2 Hz, 2 H, CH_2), 1.37 (m, 2 H, CH_2), 0.938 (t, J = 7.3 Hz, 3 H, CH_3). Elemental analysis. Found, %: C 73.09; H 6.57; N 9.39. $C_{18}H_{20}N_2O_2$. Calculated, %: C 72.95; H 6.80; N 9.45.

2.1i *N,N′-(3-nitrophenylmethylene)dimethylcarboxamide (table 1, entry 9)*: FT-IR: $\bar{\upsilon}$ (ATR, neat, cm^{-1}):3287 (N-H), 1701 (C=O), 1515, 1343, 1556, 1255, 1032, 674, 783, 809; ^{1}HNMR (DMSO-d_6, ppm): δ 8.24 (s, 1 H), 8.17 (d, J = 8.3 Hz, 1 H), 8.15 (sbr, 2 H, NH), 7.82 (d, J = 7.6 Hz, 1 H), 7.67 (t, J = 7.9 Hz, 1 H), 6.25 (t, J = 7.9 Hz, 1 H, CH), 3.61(s, 6 H, OMe). Elemental analysis. Found, %: C 46.82; H 4.56; N 14.28. $C_{11}H_{13}N_3O_6$. Calculated, %: C 46.65; H 4.63; N 14.84.

2.1j *N,N′-(methylene)dibenzamide (table 1, entry 10)*: FT-IR: $\bar{\upsilon}$ (ATR, neat, cm^{-1}):3308 (N-H), 1634 (C=O), 1487, 1578, 1526, 1448; ^{1}H NMR (DMSO-d_6, ppm): δ 9.03 (t, J = 5.5 Hz, 2 H, N-H), 7.9 (d, J = 7.1 Hz, 4 H), 7.55 (t, J = 7.1 Hz, 2 H), 7.48(t, J = 7.1 Hz, 4 H), 4.84(t, J = 5.5 Hz, 2 H, CH_2). Elemental analysis. Found, %: C 69.99; H 4.97; N 11.48. $C_{15}H_{14}N_2O_2$. Calculated, %: C 70.85; H 5.55; N 11.02.

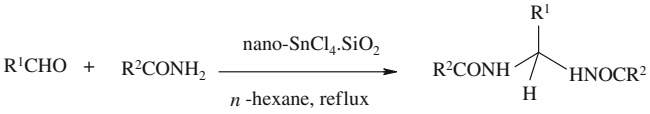
2.1k *N,N′-(2-phenylethylmethylene)dibenzamide (table 1, entry 11)*: FT-IR: $\bar{\upsilon}$ (ATR, neat, cm^{-1}):3299 (N-H), 1637 (C=O), 1508, 1579, 1545, 690, 756; ^{1}H NMR (DMSO-d_6, ppm): δ 8.64 (d, J = 7.5 Hz, 2 H, N-H), 7.88 (d, J = 7.2 Hz, 4 H), 7.54 (t, J = 7.3 Hz, 2 H), 7.48 (t, J = 7.7 Hz, 4 H), 7.28 (m, 4 H), 7.17 (m, 1 H), 5.85 (m, 1 H, CH), 2.69 (t, J = 8.2 Hz, 2 H, CH_2), 2.17 (dd, J = 15.4 and 7.3 Hz, 2 H, CH_2). Elemental analysis. Found, %: C 76.89; H 6.24; N 7.95. $C_{23}H_{22}N_2O_2$. Calculated, %: C77.07; H 6.19; N 7.82.

2.1l *N,N′-(3-phenyl-2-ene-propylene)dibenzamide (table 1, entry 12)*: FT-IR: $\bar{\upsilon}$ (ATR, neat, cm^{-1}):3274 (N-H), 1647 (C=O), 1484,1504, 1543, 690, 756; ^{1}H NMR (DMSO-d_6, ppm): δ 8.87 (d, J = 6.8 Hz, 2 H, N-H), 7.92 (d, J = 7.4 Hz, 4 H), 7.86 (t, J = 7.9 Hz, 2 H), 7.56 (t, J = 7.2 Hz, 2 H), 7.48 (m, 4 H), 7.35 (m, 2 H), 7.28 (t, J = 7.3 Hz, 1 H), 6.69 (d, J = 14.7 Hz, 1 H, CH), 6.65 (m, 2 H). Elemental analysis. Found, %: C 77.99; H 5.37; N 7.59. $C_{23}H_{20}N_2O_2$. Calculated, %: C 77.51; H 5.66; N 7.86.

2.1m *N,N,N′,N′-(1,5-pentylene)tetrabenzamide (table 1, entry 13)*: FT-IR: $\bar{\upsilon}$ (ATR, neat, cm^{-1}):3364, 3162 (N-H), 1655 (C=O), 1448, 1622, 1577, 683, 774; ^{1}H NMR (DMSO-d_6, ppm): δ 8.53 (d, J = 7.6 Hz, 4 H, N-H), 7.83 (m, 8 H), 7.53 (t, J = 7.3 Hz, 4 H), 7.44 (t, J = 7.4 Hz, 8 H), 5.86 (m, 2 H, CH), 1.94 (m, 4 H), 1.5 (m, 2 H). Elemental analysis. Found, %: C 72.49; H 5.67; N 10.39. $C_{33}H_{32}N_4O_4$. Calculated, %: C 72.24; H 5.88; N 10.21.

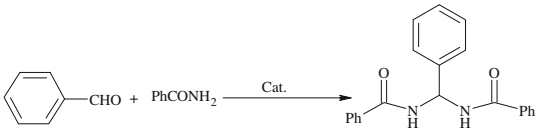
2.1n *N,N′-(iso-propylmethylene)dibenzamide (table 1, entry 14)*: FT-IR: $\bar{\upsilon}$ (ATR, neat, cm^{-1}):3234 (N-H), 1737 (C=O), 1480, 1643, 1561; ^{1}H NMR (DMSO-d_6, ppm): δ 8.40 (d, J = 8.2 Hz, 2 H, N-H), 7.85(d, J = 7.2 Hz, 4H), 7.54 (t, J = 7.2 Hz, 2 H), 7.48 (t, J = 7.7 Hz, 4 H), 5.67 (q, J = 8 Hz, 1 H, CH), 2.2 (m, 1 H, CH), 0.97 (d, J = 6.7 Hz, 6 H, CH_3). Elemental analysis. Found, %: C 66.89; H 6.8; N 9.45. $C_{18}H_{20}N_2O_2$. Calculated, %: C 72.95; H 6.8; N 9.45.

2.1o *N,N′-(2-hydroxyphenylmethylene)dibenzamide (table 1, entry 16)*: FT-IR: $\bar{\upsilon}$ (ATR, neat, cm^{-1}):3406-3268 (O-H and N-H), 1639 (C=O), 1425, 1126, 758; ^{1}H NMR (DMSO-d_6, ppm): δ 9.02 (d, J = 7.4 Hz, 2 H, N-H), 8.03 (d, J = 7.3 Hz, 2 H), 7.81 (d, J = 7.3 Hz, 3 H), 7.69 (m, 1 H), 7.52 (m, 3 H), 7.45 (m, 5 H),



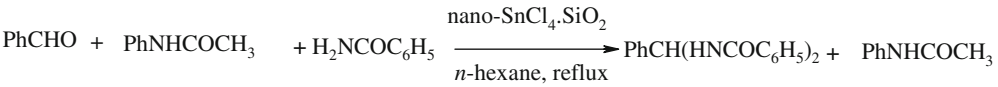
Scheme 1. Synthesis of *N,N′*-alkylidenebisamides in the presence of nano-$SnCl_4.SiO_2$.

Table 2. Synthesis of *N*, *N′*-(phenylmethylene)dibenzamides.

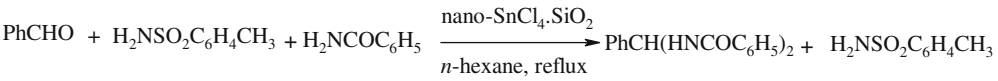


Entry	Catalyst (g)	Conditions	Time (h)/yield (%)[a]	Ref.
1	$SnCl_4.SiO_2$ (0.05)	S.F./Mixer Mill	1/5	
2	$SnCl_4.SiO_2$ (0.05)	S.F./M.W.	0.05/50	
2	$SnCl_4.SiO_2$ (0.05)	S.F./60°C	1/45	
4	$SnCl_4.SiO_2$ (0.05)	S.F./90°C	1/55	
5	$SnCl_4.SiO_2$ (0.05)	$CHCl_3$/reflux	7/81	-
6	$SnCl_4.SiO_2$ (0.05)	EtOAc/reflux	1/88	
7	$SnCl_4.SiO_2$ (0.05)	EtOAc/sonication	0.6/25	
8	$SnCl_4.SiO_2$ (0.05)	*n*-Hexane/reflux	1/94	-
9	$SnCl_4.SiO_2$ (0.05)	*n*-Hexane/sonication	0.5/40	
10	$SnCl_4.SiO_2$ (0.06)	*n*-Hexane/reflux	1/91	-
11	$SnCl_4.SiO_2$ (0.04)	*n*-Hexane/reflux	1/83	-
12	Nano-$SnCl_4.SiO_2$ (0.01)	*n*-Hexane/reflux	0.83/96	
13	Nano-$SnCl_4.SiO_2$ (0.01), 2nd run	*n*-Hexane/reflux	0.83/90	-
14	Nano-$SnCl_4.SiO_2$ (0.01), 3rd run	*n*-Hexane/reflux	0.83/75	-
15	SiO_2-$MgCl_2$ (0.025)	Solvent-free/100	3/73	7
16	CC (1.2 equiv)-activatd DMSO (7.0 equiv)	Toluene/70	1.5/71	8
17	Phosphortungstic acid (0.3 mmol)	Toluene/reflux	20/70	10
18	Boric acid (0.3 mmol)	Microwave	40 min/80	11

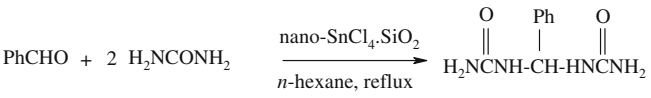
[a]Isolated yield



Scheme 2. Chemoselectivity in formation of *N,N′*-alkylidenebisamides for primary amides in the presence of secondary amides.



Scheme 3. Chemoselectivity in formation of *N,N′*-alkylidenebisamides for primary amides in the presence of sulfonamides.



Scheme 4. Formation of *N,N′*-alkylidenebisamides from urea.

7.35 (m, 1 H), 7.26 (t, $J = 7.3$ Hz, 1 H, CH). Elemental analysis. Found, %: C 72.99; H 5.17; N 7.99. $C_{21}H_{18}N_2O_3$. Calculated, %: C 72.82; H 5.24; N 8.09.

2.1p *N-benzylidene urea (scheme 1)*: FT-IR: $\bar{\upsilon}$ (ATR, neat, cm^{-1}):3272 (N-H), 1670 (C=O), 1467, 1268, 1060, 868. ^{1}H NMR (DMSO-d_6, ppm): 7.98 (d, $J = 5.7$ Hz, 2 H), 7.6 (d, $J = 6.5$ Hz, 1 H), 7.5 (t, $J = 6.4$ Hz, 2 H), 7.4 (d, $J = 6.5$ Hz, 2 H), 6.45 (t, $J = 5.8$ Hz, 1 H), 5.7 (brs., 2 H), 5.4 (brs., 2 H). Elemental analysis. Found, %: C 51.52; H 5.67; N 26.79. $C_9H_{12}N_4O_2$. Calculated, %: C 51.92; H 5.81; N 26.91.

3. Results and discussion

Our aim was to develop new synthetic methods using heterogeneous catalysts to reduce risks to humans and the environment. To prepare *N,N′*-alkylidenebisamides and find the best reaction conditions, the reaction of benzamide and benzaldehyde was examined under various conditions and different quantities of $SnCl_4.SiO_2$ or nano-$SnCl_4.SiO_2$ (table 2). The reaction proceeded efficiently in *n*-hexane under reflux condition using 0.05 g of $SnCl_4.SiO_2$ or 0.01 g of nano-$SnCl_4.SiO_2$ with 1 mmol of aldehyde and 2 mmol of amide (table 2, entries 8 and 12). The reusability of the nano-$SnCl_4{\cdot}SiO_2$ catalyst was also examined. After each run, CH_2Cl_2 was added and the product was filtered, the solvent evaporated and the residue (catalyst) was washed with CH_2Cl_2 and reused. Apparently, treatment with CH_2Cl_2 removes tar efficiently from the catalyst surface (table 2, entries 13 and 14). This catalyst was reusable, although a gradual decline in activity was observed.

Next, the scale of this procedure was explored using a wide range of aldehydes containing electron-donating or electron-withdrawing groups attaching to aromatic ring (table 1, scheme 1). In all cases, aromatic aldehydes containing electron-withdrawing groups gave higher yield of products in shorter time than benzaldehyde (table 1, entries 1 and 3).

Aromatic aldehydes have reacted in this protocol in lower times and higher yields, than aliphatic aldehydes (table 1, entries 1, 8, 10, 11) specially aliphatic aldehydes with steric hinders (table 1, entry 14) or conjugated aliphatic aldehydes (table 1, entry 12). 1,3,5-trioxane was used as formaldehyde source to produce *N,N′*-(methylene)dibenzamide (table 1, entry 10) and the both of aldehyde group in glutardialdehyde have reacted in this process and yield the tetra-amide derivative (table 1, entry 13). The aromatic aldehydes with electron-withdrawing group have reacted faster than aromatic aldehydes with electron-releasing group (table 1, entries 3 and 16). Aromatic amides have reacted with an active aldehyde with higher yield in lower time (table 1, entries 3 and 15). The OMe group in methyl carbamate caused higher yield of corresponding amide in lower time than acetamide (table 1, entry 5 and 7).

This protocol is special for primary amides and not for secondary amides or primary sulphonamides (schemes 2 and 3).

Reaction of benzaldehyde with urea produces corresponding bisamide with good yield (scheme 4).

Additional efforts about chemoselectivity of this protocol have shown that aromatic aldehydes versus aliphatic aldehydes or aromatic amides versus aliphatic amides have not shown any chemoselectivity.

4. Conclusion

We have demonstrated simple method for the synthesis of preparation of *N,N′*-alkylidenebisamides with using nano-$SnCl_4.SiO_2$ as highly efficient and reusable

catalyst. Short reaction times, high yields, a clean process, simple methodology and easy work-up conditions are some advantages of this protocol.

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