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ORIGINAL ARTICLE

One-pot preparation of *N,N′*-alkylidene bisamide derivatives catalyzed by silica supported polyphosphoric acid (SiO_2-PPA)

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KEYWORDS

Amide;
N,N′-Alkylidene bisamide;
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Alkyne

Abstract Silica supported polyphosphoric acid (SiO_2-PPA) as an efficient heterogeneous catalyst was found to be effective for the one-pot three-component condensation reaction of phenyl acetylene/1-hexyne, aromatic aldehyde and benzamide/acetamide to produce a series of *N,N′*-alkylidene bisamides. The desired products were obtained in good to high yields. The assistance of alkynes has been confirmed by using thin layer chromatographic (TLC) studies. All the reactions were done at 100 °C using 0.025 g of catalyst. The developed method is valid for either substituted aldehyde, thus it constitutes a general synthetic method for these kinds of compounds. In all the cases aromatic aldehydes containing electron-withdrawing groups gave shorter time than that with electron-donating groups. Additionally, the reaction of butyraldehyde with benzamide failed to have any product in the presence of phenyl acetylene but with 1-hexyne the product was formed in moderate yield.

1. Introduction

Amide and bisamide functionalized groups represent important biological and medicinal scaffolds. For example, in this interest the amide skeleton is present in the protein molecules that play a major role in the development and composition of biological and pharmacological systems (Bode, 2006; Shaterian et al., 2008). They can be easily transformed into other useful materials (such as gem-diaminoalkyl and aminoalkyl groups) and are of considerable interest in the synthesis of pharmacological materials such as peptidomimetic compounds (Dingermann et al., 2004; Shen et al., 1992; Al'-Assar et al, 2002; Pallai et al., 1985; Sechi et al., 2008; Aleman and Puiggali, 1995).

In the past, the compounds containing bisamide functionalized groups were commonly prepared via direct reaction of aldehydes with the corresponding carboxamide using a strong acid catalyst, such as sulfuric acid, hydrochloric acid, phosphotungstic acid, triflic acid and/or chlorosulfonic acid or by the reaction of aldehydes with nitrils (Magat et al., 1951; Zhu et al., 1999; Pernak et al., 1994; Fernández et al., 1996; Selvam et al., 2008; Harichandran et al., 2011; Mosslemin

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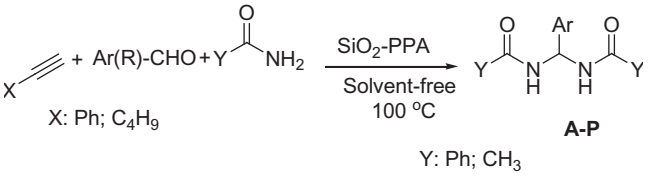


Scheme 1 preparation of *N,N′*-alkylidene bisamide derivatives using SiO_2-PPA as catalyst.

et al., 2010; Anary-Abbasinejad et al., 2009). However, these methods require the presence of corrosive homogeneous liquid acid catalyst (especially in a large amount of acid) and considering the fact that most of the organic reagents involved in fine chemical synthesis are sensitive to harsh conditions, it is desirable to choose catalysts which can catalyze organic transformations under mild conditions.

The discovery of new synthetic methodologies to facilitate the preparation of organic compounds is a fundamental main point of research activity in the field of modern organic, bioorganic and medicinal chemistry. Thus, the present study has been established to report the development of a new, mild and convenient protocol, which encompasses a broad range of new derivatives of *N,N′*-alkylidene bisamides via the reaction of alkyne, aromatic aldehydes and amides in the presence of SiO_2-PPA (Aoyama et al., 2004) as catalyst under thermal, solvent-free conditions (Scheme 1). To the best of our knowledge, these new compounds have not been previously described.

2. Experimental

All reagents were purchased from Merck and Aldrich and used without further purification. All yields refer to isolated products after purification. The NMR spectra were recorded on a Bruker Avance DPX 300 MHz instrument. The NMR spectra were measured in DMSO-d_6 (25 °C) relative to TMS (0.00 ppm). IR spectra were recorded on a Perkin-Elmer 781 spectrophotometer. Melting points were determined in open capillaries with a BUCHI 510 melting point apparatus. TLC was performed on silica gel polygram SIL G/UV 254 plates.

2.1. Preparation of SiO_2-PPA

In a 250 ml flask, PPA (2.1 g) was dissolved in $CHCl_3$ (100 ml) with stirring at 50 °C for 1 h, SiO_2 4.9 g (Silica gel 60 for column chromatography; 230 mesh) was added to the solution, and the mixture was stirred for another 1 h. $CHCl_3$ was removed with a rotary evaporator and the resulting solid was dried in vacuo at room temperature for 3 h. This powder was kept in an oven at 100 °C for 30 min for more activation of the catalyst.

Table 1 Optimization of the amount of SiO_2-PPA and the reaction temperature.

Entry	Catalyst (g)	*T* (°C)	Time (min)	Yield (%)[a]
1	0.025	rt	400	–
2	0.025	80	150	59
3	0.1	100	40	53
4	0.05	100	60	67
5	0.025	100	70	75
6	0.01	100	95	70

[a] Isolated yield (based on phenyl acetylene (1 mmol), benzaldehyde (1 mmol) and benzamide (2.2 mmol).

2.2. Typical procedure

To a mixture of benzaldehyde (1 mmol), benzamide (2.2 mmol) and phenyl acetylene (1 mmol) was added SiO_2-PPA (0.025 g) and the mixture was heated at 100 °C in an oil bath for appropriate time (Table 1). The progress of the reaction was monitored by TLC. After completion of the reaction, the mass was cooled to 25 °C and the mixture was dissolved in boiling ethanol. The catalyst was removed by simple filtration. The solvent was concentrated and the solid product was purified by recrystallization procedure in appropriate solvent (ethanol 40% or diethyl ether).

2.2.1. N-Benzoylamino(phenyl)methyl benzamide (*A*)

^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.05 (t, J = 7.7 Hz, 1H), 7.29–7.58 (m, 11H), 7.92 (d, J = 7.1 Hz, 4H), 9.03 (d, J = 7.7 Hz, 2H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ = 59.6, 127.4, 128.4, 128.5, 129.2, 132.5, 134.7, 141.1, 166.5 ppm; IR (KBr, cm^{-1}): 3285, 3088, 1651, 1543, 1497, 1342, 1269, 1137, 1047, 875, 802, 702. Found: C, 76.39; H, 5.55; N, 8.51; $C_{21}H_{18}N_2O_2$ requires C, 76.34; H, 5.49; N, 8.48%.

2.2.2. N-Benzoylamino(4 -(1,1-dimethylethyl)phenyl)methyl benzamide (*B*)

^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.29 (s, 9H), 7.03 (t, J = 7.6 Hz, 1H), 7.36–7.58 (m, 10H), 7.93 (d, J = 7.8 Hz, 4H), 9.02 (d, J = 7.7 Hz, 2H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ = 32.0, 35.1, 59.4, 125.9, 127.1, 128.1, 128.4, 129.2, 132.4, 134.7, 138.3, 166.4 ppm; IR (KBr, cm^{-1}): 3271, 3060, 2965, 1646, 1601, 1579, 1555, 1511, 1352, 1271, 1136, 1075, 871, 833, 710. Found: C, 77.80; H, 6.89; N, 7.29; $C_{25}H_{26}N_2O_2$ requires C, 77.69; H, 6.78; N, 7.25%.

2.2.3. N-Benzoylamino(4-methoxyphenyl)methyl benzamide (*C*)

^{1}H NMR (300 MHz, DMSO-d_6): δ = 3.74 (s, 3H), 6.93–6.99 (m, 3H), 7.39–7.55 (m, 8H), 7.91 (d, J = 7.3 Hz, 4H), 8.97 (d, J = 7.3 Hz, 2H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ = 56.0, 59.3, 114.5, 128.3, 128.6, 129.2, 132.4, 133.3, 134.8, 159.7, 166.3 ppm; IR (KBr, cm^{-1}): 3273, 3068, 2958, 1648, 1546, 1511, 1280, 1249, 1177, 1065, 815, 765, 703. Found: C, 73.37; H, 5.65; N, 7.89; $C_{22}H_{20}N_2O_3$ requires C, 73.32; H, 5.59; N, 7.77%.

2.2.4. N-Benzoylamino(4-fluorophenyl)methyl benzamide (*D*)

^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.19 (t, J = 6.9 Hz, 1H), 7.36–7.69 (m, 10H), 7.94 (d, J = 7.2 Hz, 4H), 9.11 (d, J = 7.0 Hz, 2H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ = 58.1, 127.9, 128.2, 128.5, 129.0, 129.3, 129.6, 130.3, 130.4, 132.4, 133.4, 134.7, 138.2, 166.6 ppm; IR (KBr, cm^{-1}): 3277, 3065, 3026, 1643, 1521, 1480, 1350, 1275, 1141, 1072, 1037, 800, 753, 699. Found: C, 72.49; H, 4.98; N, 8.11; $C_{21}H_{17}FN_2O_2$ requires C, 72.40; H, 4.92; N, 8.04%.

*2.2.5. N-Benzoylamino(2,4-dichlorophenyl)methyl benzamide (**E**)*
^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.14 (t, J = 6.8 Hz, 1H), 7.45–7.68 (m, 9H), 7.93 (d, J = 7.1 Hz, 4H), 9.13 (d, J = 6.8 Hz, 2H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ = 57.9, 128.0, 128.5, 129.1, 129.7, 130.7, 132.4, 134.1, 134.4, 134.6, 137.4, 166.7 ppm; IR (KBr, cm^{-1}): 3290, 3214, 3066, 3028, 1639, 1602, 1579, 1543, 1514, 1364, 1330, 1261, 1145, 1078, 1043, 860, 827, 744, 698. Found: C, 63.19; H, 4.08; N, 7.05; $C_{21}H_{16}Cl_2N_2O_2$ requires C, 63.17; H, 4.04; N, 7.02%.

*2.2.6. N-Benzoylamino(4-nitrophenyl)methyl benzamide (**F**)*
^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.08 (t, J = 7.3 Hz, 1H), 7.47–7.60 (m, 6H), 7.75 (d, J = 8.6 Hz, 2H), 7.93 (d, J = 7.1 Hz, 4H), 8.26 (d, J = 8.7 Hz, 2H), 9.22 (d, J = 7.4 Hz, 2H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ = 59.4, 124.4, 128.5, 128.9, 129.2, 132.6, 134.4, 147.9, 148.4, 166.8 ppm; IR (KBr, cm^{-1}): 3264, 3085, 3028, 2963, 1650, 1633, 1608, 1579, 1548, 1486, 1345, 1295, 1277, 1201, 1143, 1083, 1055, 875, 852, 794, 718, 695. Found: C, 67.36; H, 4.60; N, 11.26; $C_{21}H_{17}N_3O_4$ requires C, 67.19; H, 4.56; N, 11.19%.

*2.2.7. N-Benzoylamino(3-nitrophenyl)methyl benzamide (**G**)*
^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.11 (t, J = 7.3 Hz, 1H), 7.47–7.60 (m, 6H), 7.71 (t, J = 7.9 Hz, 1H), 7.94–7.96 (m, 5H), 8.21 (d, J = 8.1 Hz, 2H), 8.36 (s, 1H), 9.27 (d, J = 7.3 Hz, 2H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ = 59.5, 122.3, 123.6, 128.5, 129.2, 130.8, 132.6, 134.4, 134.6, 143.3, 148.7, 166.8 ppm; IR (KBr, cm^{-1}): 3313, 3259, 3086, 2969, 1649, 1602, 1581, 1534, 1505, 1340, 1271, 1211, 1140, 1054, 873, 736, 716. Found: C, 67.32; H, 4.65; N, 11.29; $C_{21}H_{17}N_3O_4$ requires C, 67.19; H, 4.56; N, 11.19%.

*2.2.8. N-Benzoylamino(2-nitrophenyl)methyl benzamide (**H**)*
^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.41–7.61 (m, 8H), 7.76–7.81 (m, 2H), 7.91 (d, J = 7.0 Hz, 4H), 7.98 (d, J = 8.1 Hz, 1H), 9.19 (d, J = 6.9 Hz, 2H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ = 56.7, 125.3, 128.6, 129.1, 129.7, 130.1, 132.5, 133.9, 134.4, 134.6, 149.4, 166.9 ppm; IR (KBr, cm^{-1}): 3275, 3073, 3030, 1648, 1610, 1531, 1481, 1347, 1274, 1189, 1146, 1086, 1059, 854, 796, 703. Found: C, 67.26; H, 4.63; N, 11.24; $C_{21}H_{17}N_3O_4$ requires C, 67.19; H, 4.56; N, 11.19%.

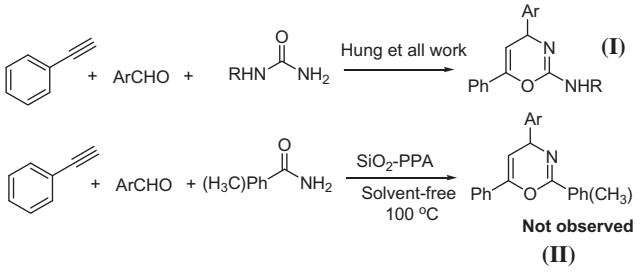
*2.2.9. N-Benzoylamino(2-chlorophenyl)methyl benzamide (**I**)*
^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.01 (t, J = 7.5 Hz, 1H), 7.18–7.24 (m, 2H), 7.46–7.59 (m, 8H), 7.91 (d, J = 7.1 Hz, 4H), 9.05 (d, J = 7.6 Hz, 2H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ = 58.1, 117.3, 117.7, 128.3, 129.2, 129.5, 129.8, 132.5, 134.6, 137.5, 164.1, 166.5 ppm; IR (KBr, cm^{-1}): 3280, 3092, 1649, 1547, 1506, 1343, 1274, 1228, 1146, 1062, 830, 790, 703. Found: C, 69.19; H, 4.81; N, 7.72; $C_{21}H_{17}ClN_2O_2$ requires C, 69.14; H, 4.70; N, 7.68%.

*2.2.10. N-Acetylamino(phenyl)methyl acetamide (**J**)*
^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.86 (s, 6H), 6.52 (t, J = 7.8 Hz, 1H), 7.26–7.38 (m, 5H), 8.57 (d, J = 7.8 Hz, 2H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ = 23.3, 58.1, 127.2, 128.4, 129.1, 141.4, 169.4 ppm; IR (KBr, cm^{-1}): 3278, 3119, 3060, 3029, 2932, 1663, 1563, 1517, 1371, 1273, 1094, 848, 749, 696. Found: C, 64.16; H, 6.91; N, 13.66; $C_{11}H_{14}N_2O_2$ requires C, 64.06; H, 6.84; N, 13.58%.

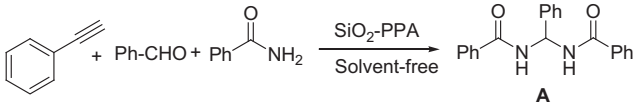
*2.2.11. N-Acetylamino(4-fluorophenyl)methyl acetamide (**K**)*
^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.86 (s, 6H), 6.48 (t, J = 7.7 Hz, 1H), 7.19 (t, J = 8.8 Hz, 2H), 7.32–7.37 (dd, J = 5.6, 8.4 Hz, 2H), 8.53 (d, J = 7.7 Hz, 2H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ = 23.3, 57.6, 115.7, 116.0, 129.2, 129.3, 137.5, 137.6, 160.8, 164.0, 169.4 ppm; IR (KBr, cm^{-1}): 3276, 3124, 3016, 2957, 1665, 1555, 1515, 1369, 1237, 1093, 1028, 861, 823. Found: C, 59.01; H, 5.95; N, 12.56; $C_{11}H_{13}FN_2O_2$ requires C, 58.92; H, 5.84; N, 12.49%.

*2.2.12. N-Acetylamino(4-nitrophenyl)methyl acetamide (**L**)*
^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.88 (s, 6H), 6.56 (t, J = 7.7 Hz, 1H), 7.58 (d, J = 8.4 Hz, 2H), 8.23 (d, J = 8.5 Hz, 2H), 8.71 (d, J = 7.6 Hz, 2H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ = 23.3, 57.8, 124.3, 128.6, 147.8, 148.7, 169.7 ppm; IR (KBr, cm^{-1}): 3270, 3116, 2999, 2949, 1670, 1605, 1563, 1518, 1353, 1273, 1089, 1017, 852, 825, 772. Found: C, 52.63; H, 5.30; N, 16.83; $C_{11}H_{13}N_3O_4$ requires C, 52.59; H, 5.22; N, 16.73%.

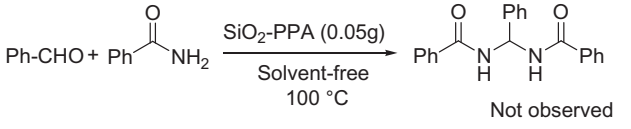
*2.2.13. N-Benzoylamino butyl benzamide (**P**)*
^{1}H NMR (300 MHz, DMSO-d_6): δ = 0.93 (t, J = 7.3 Hz, 3H), 1.37 (six, J = 7.4 Hz, 2H), 1.82 (q, J = 7.6 Hz, 2H), 5.88 (quin, J = 7.4 Hz, 1H), 7.43–7.55 (m, 6H), 7.86 (d, J = 7.0 Hz, 4H), 8.57 (d, J = 7.6 Hz, 2H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ = 14.5, 19.3, 37.2, 57.7, 128.2, 129.1,



Scheme 2 Synthesis of 2-substituted 4*H*-1,3-oxazine derivatives.



Scheme 3 Synthesis of *N*-benzoylamino(phenyl)methyl benzamide via the reaction of phenyl acetylene, benzaldehyde and benzamide.



Scheme 4 preparation of *N*-benzoylamino(phenyl)methyl benzamide in the absence of phenyl acetylene.

Table 2 preparation of *N*,*N*′-alkylidene bisamide derivatives (Scheme 1).

Entry	Aldehyde	Y	X	Product	Time (min)	Yield (%)[a]	Mp (°C)
1	Benzaldehyde	Ph	Ph	**A**	70	75	238–240
2	4-(1,1-Dimethyl ethyl) benzaldehyde	Ph	Ph	**B**	140	69	214–216
3	4-Methoxybenzaldehyde	Ph	Ph	**C**	180	66	228–230
4	4-Flourobenzaldehyde	Ph	Ph	**D**	40	82	207–209
5	2,4-Dichlorobenzaldehyde	Ph	Ph	**E**	120	81	198–200
6	4-Nitrobenzaldehyde	Ph	Ph	**F**	27	83	260–262
7	3-Nitrobenzaldehyde	Ph	Ph	**G**	37	72	236–238
8	2-Nitrobenzaldehyde	Ph	Ph	**H**	70	61	257–259
9	2-Chlorobenzaldehyde	Ph	Ph	**I**	75	67	242–244
10	Benzaldehyde	CH_3	Ph	**J**	120	66	252–254
11	4-Flourobenzaldehyde	CH_3	Ph	**K**	180	70	259–261
12	4-Nitrobenzaldehyde	CH_3	ph	**L**	90	76	233–235
13	4-Nitrobenzaldehyde	Ph	C_4H_9	**M**	30	83	248–250
14	Benzaldehyde	Ph	C_4H_9	**N**	35	71	211–213
15	Butyraldehyde	Ph	ph	**O**	240	–	–
16	Butyraldehyde	Ph	C_4H_9	**P**	10	70	212–214

[a] Isolated yields. All the products were characterized by IR, ^{1}H NMR and ^{13}C NMR spectra.

132.2, 135.1, 166.4 ppm; IR (KBr, cm^{-1}): 3237, 3106, 2966, 2927, 1648, 1557, 1518, 1483, 1365, 1333, 1288, 1134, 1079, 1053, 995, 844, 809, 764. Found: C, 73.00; H, 6.89; N, 9.55; $C_{18}H_{20}N_2O_2$ requires C, 72.95; H, 6.80; N, 9.45%.

3. Results and discussion

The first method for the multi-component reaction of phenyl acetylene, aromatic aldehyde and urea has been reported previously by Hung et al. that they used a mixture of acetic acid/trifluoroacetic acid as catalyst and acetonitrile as solvent leading to the formation of 4*H*-[1,3]oxazines (Scheme 2(**I**)) (Huang et al., 2005). At first our aim was trying to develop new synthetic methods, reaction conditions and uses of heterogeneous catalysts that reduce risks to humans and the environment to prepare a series of new compounds of 4*H*-[1,3]oxazine derivatives. Thus, the reaction of phenyl acetylene, benzaldehyde and benzamide in the presence of SiO_2-PPA as catalyst under thermal, solvent-free conditions were investigated (Schemes 2 and 3). As can be seen from Schemes 2 and 3 our trying for the observation of 2-phenyl(methyl)-4*H*-1,3-oxazine (Scheme 2(**II**)) failed and *N*-benzoylamino(phenyl)methyl benzamide was formed as the only product.

To continue, we are trying to investigate the structures of bisamide and need of an alkyne for the formation of bisamides, but, the reaction including benzaldehyde, benzamide and a catalytic amount of SiO_2-PPA under heating at 100 °C failed to give the correlative product in the absence of phenyl acetylene, which indicated that phenyl acetylene plays an important role in the reaction process (Scheme 4). Chromatographic studies (TLC indicating) confirm that the alkyne was completely disappearing when the product was formed.

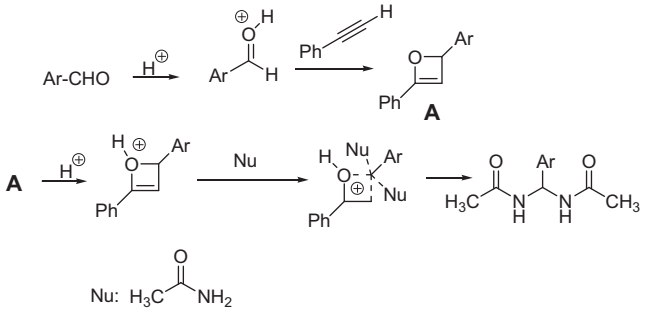
To shows the utility of SiO_2-PPA as catalyst, a model reaction of phenyl acetylene, benzaldehyde and benzamide has been established. As revealed from our investigations, in the absence of catalyst no product was obtained and the use of catalyst is unavoidable for this transformation.

Finally, the reaction of phenyl acetylene (1 mmol), benzaldehyde (1 mmol) and benzamide (2.2 mmol) in the presence SiO_2-PPA as catalyst was chosen as a model to optimize the yield and the reaction condition. No product was observed when the reaction was carried out at room temperature. The reaction proceeded smoothly with increasing the temperature and better results were obtained at 100 °C.

Encouraged by these results, we started to study the effects of amount of the catalyst on the reaction condition. Decreasing the amount of SiO_2-PPA to 0.025 g resulted in an improved reaction rate and yield (Table 1).

Next, the scope and limitations of this process were explored using a wide range of aromatic aldehyde containing both electron-donating and electron-withdrawing groups attached to the aromatic ring (Table 2, entries 1–9). In all the cases aromatic aldehydes containing electron-withdrawing groups (such as nitro-) gave shorter time than that with electron-donating groups (such as methoxy-). Though *meta*- and *para*-substituted aromatic aldehydes gave good results, *ortho*-substituted aromatic aldehydes (such as 2-nitrobenzadehyde) gave lower yields and longer reaction time because of the steric effects. These good results were also obtained in the case of 1-hexyne (Table 2, entries 13, 14 and 16). As a result the reaction of butyraldehyde with benzamide failed to have any product in the presence of phenyl acetylene but with 1-hexyne the product was formed in moderate yield (Table 2, entries 15 and 16).

Encouraged by the results obtained with benzamide, we turned our attention to acetamide (Table 2). As shown in Table 2, the reactions of phenyl acetylene and aryl aldehyde with acetamide under the mentioned reaction conditions was progressing smoothly but in longer reaction times and the desired products were obtained in good yields. (Table 2, entries 10 and 12).



Scheme 5 Proposed mechanism for the formation of *N*,*N*′-alkylidene bisamides.

To explain the formation of bisamides via the one-pot multi-component reaction, we have proposed a plausible reaction mechanism, which is illustrated in Scheme 5. Firstly, the protonation of aldehyde by Brønsted acid occurred to form a cation intermediate. To continue, as has been reported in the literature, the formation of a highly strained oxetene intermediate (**A**) resulting from the cyclo-condensation of protonated aldehyde with phenyl acetylene was established (Hayashi et al., 1995; Friedrich and Lam, 1981; Martino and Shevlin, 1980; Friedrich and Bower, 1973; Harding and Stanford, 1989; Harding and King, 1992; Sisko et al., 1992; Yadav et al., 2008; Oblin et al., 1998). The formation of oxete and oxetane from the cyclo-addition of triple and double bonds is well documented as Paterno–Buchi reaction (Li and Corey, 2004). The second step is the addition of two molecules of amide to **A** that protonated and converting to bisamide as the product by the attack of amide.

In conclusion, a practical method for the environmentally friendly preparation of *N,N′*-alkylidene bisamides in a one-pot procedure has been developed. The work-up procedure is very clear-cut; that is the products were isolated and purified by simple filtration and crystallization from aqueous ethanol (or diethyl ether). Our protocol avoids the use of SiO_2-PPA as heterogeneous non-toxic Lewis acid catalyst and dry media during the reaction process, making it superior to the reactions that use solvent.

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