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AN EFFICIENT SYNTHESIS OF 1-ACYL-3-ARYLIMIDAZOLIDINES CATALYZED BY MONTMORILLONITE K-10 CLAY UNDER MICROWAVE IRRADIATION

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Abstract – The synthesis of 1-acyl-3-arylimidazolidines were performed by reaction of *N*-acyl-*N*´-arylethylenediamines with formaldehyde and Montmorillonite clay K-10 as a catalyst under microwave irradiation.

INTRODUCTION

Tetrahydroimidazoles (imidazolidines) are cyclic aminals of pharmacological interest due to the bioactivity shown by some members which is closely related to the substitution type. The most studied compounds are those *N*,*N*´-disubstituted ones with alkyl or aryl groups, functionalized sometimes. Accordingly, a large number of these compounds with diverse properties such as strogenic activity[1] and mammary tumor inhibition,[2] anti inflammatory and analgesic activity[3] have been described in the literature. Fungicide, bactericide and antiviral activities had also been reported.[3,4] On the other hand, due to the hydrophobic nature of imidazolidines they can be used to increase the bioavailability of biologically active precursors in the form of a pro-drug and they had been employed as carriers of pharmacologically active ethylenediamines[5] or carbonyl compounds.[6] They are also closely related to the coenzyme N^5,N^{10}-methylenetetrahydrofolic acid, which participate in single carbon transfer at the oxidation level of formaldehyde.[7] Synthesis and study of this type of compounds present interest from a chemical point of view, as synthetic intermediates of cyclic and acyclic compounds with the ethylenediamine structural unit. Thus, dehydrogenation of imidazolidines leads to 4,5-dihydro-1*H*-imidazolium salts[8] and their selective reduction to *N*,*N*,*N*´-trisubstituted ethylenediamines.[9] The imidazolidine system has been widely employed as protecting group of vicinal diamines in peptide synthesis, due to its easy cleavage in mild acid medium.[10] Besides, imidazolidines were also employed as heterocyclic chiral auxiliaries in asymmetric synthesis.[11] Opposite to compounds

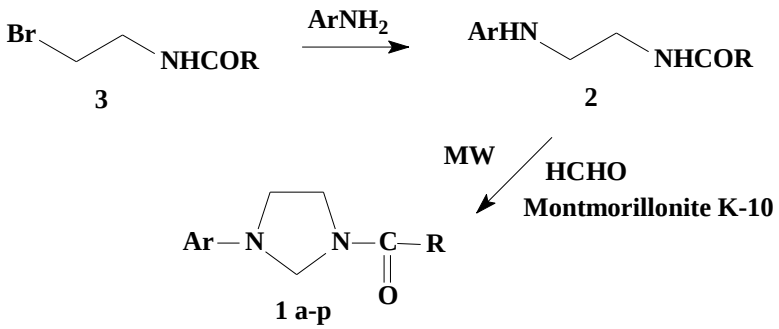
mentioned above, *N*-acylimidazolidines have been less studied. 1,3-Dialkanoyl imidazolidines were reported with antimycotic activity;[12] more recently 1-acetyl-2,3-dimethylimidazolidine has been reported as a new organic reductant for aldehydes and imines.[13]

The classic synthesis of imidazolidines involves the condensation of adequately substituted ethylenediamines with carbonyl compounds. Stable 1,3-disubstituted imidazolidines with alkyl or aryl substituents are obtained from *N,N´*-disubstituted ethylenediamines and aldehydes, whatever substituents are present in reactants.[14] Instead, only a few reports on the preparation of *N*-acylimidazolidines by cyclization of the corresponding *N,N´*-diacylethylenediamine and aldehydes in acid catalyzed reactions were found.[12] These were commonly prepared by acylation of the unsubstituted or *N*-monosubstituted imidazolidine.[15a,b,c,d] Simultaneous reduction and acylation of imidazole was also reported.[15e]

The use of solid acid catalysts such as clays, ion-exchange resins and zeolites has received considerable attention in different areas of organic synthesis.[16] Montmorillonite clay specially, a class of inexpensive and noncorrosive solid, exhibit high surface acidity which has been used to perform useful organic transformations. Particularly in heterocyclic synthesis, Montmorillonite clay has been used as an efficient catalyst in synthesis of dihydropyrimidinones,[17] benzodiazepines,[18] fluorined spiro heterocycles[19] and quinolines[20] among others. On the other hand, microwave-assisted organic synthesis has received increasing attention in recent years as a valuable technique for accelerating chemical reactions.[21] Condensation reactions leading to heterocyclic products are particularly prone to microwave irradiation enhancements.[22] In connection with our ongoing work on synthesis and study of imidazolidines[23,8a] we now report a simple and efficient method for the preparation of novel 1-acyl-3-arylimidazolidines **1**.

RESULTS AND DISCUSSION

Compounds (**1a-p**) were obtained from *N*-acyl-*N´*-arylethylenediamines (**2**) and formaldehyde. Precursors (**2**) were obtained by aminolysis of *N*-(2-bromoethyl)amides (**3**) (Scheme 1).



Scheme 1

Due to the low nucleophilicity of both aminoamide nitrogens, cyclocondensation of compounds (**2**) with

formaldehyde does not proceed in the absence of acid catalyst. When reactions are carried out in THF with aqueous formaldehyde and activated Montmorillonite K-10 (1 h, 120°) as the catalyst, under continuous stirring at rt, desired products are obtained in times varying from 3-12 hours with yields of 55-70%. Under conventional heating the reactions times can be shortened to 1-4 h with moderated yields (45-65%). In order to decrease reaction times and improve cyclization yields, we assayed them in a domestic microwave oven adapted for reflux heating. Reactions were conducted under intermittent microwave irradiation[24] at a lower irradiation power (180W). In such conditions, reaction times dramatically decreased to 3-5 minutes and yields increased to 75-98%. 1-Acyl-3-arylimidazolidines shown in Table 1 were obtained.

Table 1. Summary of reactions (**2** → **1**) using conventional heating and microwave irradiation.

Compound **1**	Ar	R	Conventional heating Time (h)/yields (%)	Mocrowave irradiation (180 W) Time (min)/ yields (%)
a	C_6H_5	C_6H_5	1 / 62	2 / 94
b	4-HOC_6H_4	C_6H_5	1.5/ 65	2 / 92
c	4-ClC_6H_4	C_6H_5	2.5 / 51	3 / 98
d	4-MeC_6H_4	C_6H_5	1.5 / 60	2 / 91
e	2-$C_6H_5OC_6H_4$	C_6H_5	1.5 / 52	2 / 85
f	4-$NO_2C_6H_4$	C_6H_5	4 / 54	5 / 89
g	4-$NO_2C_6H_4$	4-$NO_2C_6H_4$	3.5 / 62	5 / 88
h	3,4-$Cl_2C_6H_3$	C_6H_5	4 / 59	5 / 89
i	C_6H_5	4-ClC_6H_4	3.5 / 52	5 / 85
j	4-MeC_6H_4	Me	2 / 58	3 / 79
k	4-$MeOC_6H_4$	Me	1/ 58	2 / 81
l	C_6H_5	Et	2.5 / 61	3 / 79
m	4-MeC_6H_4	Et	2.5 / 49	3 / 77
n	4-ClC_6H_4	Et	3 / 51	3 / 78
o	4-MeC_6H_4	*i*-Pr	3.5 / 62	3 / 97
p	4-ClC_6H_4	*i*-Pr	3.5 / 60	4 / 95

Results were satisfactory for *N*-alkanoyl and *N*-acyl groups. In general, longer reaction times were required for derivatives having electron withdrawing groups on *N*-aryl moiety.

When at least one of the *ortho* positions of the arylamine is substituted (2-NO_2, 2-Cl, 2-Me) or when aryl group is a α-naphtyl, cyclization reaction does not occur. An exception to this is the *o*-phenoxy derivative which evidently presents a minor steric hindrance and a more nucleophilic nitrogen.

Structure of compounds (**1**) was confirmed by elemental analysis and spectroscopic methods. The ^{1}H NMR spectra of compounds suggest that the molecules exist in two conformationally non-equivalent structures (two sets of signals in different proportion) as a result of restricted rotation about the N-CO bond. ^{1}H NMR spectra of the preferred diastereomer are detailed in Table 2.

Table 2. Data for products (**1a-p**)

Product	mp (ºC)	^{1}H NMR (Cl_3CD/TMS).δ, *J* (Hz) * overlapped signals of both diastereomers	IR (KBr), cm^{-1}
1a	138-140	3.50-3.52* (m, CH_2NAr), 3.85 (t, CH_2NCO, *J*= 6.3, 2 H), 5.00 (s, NCH_2N, 2 H), 6.60-6.80* (m, aromatics), 7.15-7.50* (m, aromatics), 7.60 (d, aromatics, *J*= 7.3)	2853, 1625, 1520, 1436, 1242, 748, 715
1b	179-180	3.39-3.50* (m, CH_2NAr), 3.81 (t, CH_2NCO, *J*= 6.4, 2 H), 4.90 (s, NCH_2N, 2 H), 6.59 (d, aromatics, *J*= 8.0, 2 H), 6.70-6.82* (m, aromatics), 7.40-7.50* (m, aromatics), 7.51-7.53* (m, aromatics)	3495, 2910, 1610, 1450, 1377, 1244, 821, 720
1c	157-158	3.40-3.52* (m, CH_2NAr), 3.92 (t, CH_2NCO, *J*= 6.4, 2 H), 5.0 (s, NCH_2N, 2 H), 6.60 (d, aromatics, *J*= 7.8, 2 H), 7.35-7.45* (m, aromatics), 7.50-7.52* (m, aromatics)	2983, 1615, 1600, 1425, 1378, 1088, 841, 750, 689
1d	156-157	2.27 (s, Me, 3 H), 3.40-3.58* (m, CH_2NAr), 3.71 (bs, CH_2NCO, 2 H), 4.95 (s, NCH_2N, 2 H,), 6.65 (d, aromatics, *J*= 7.2, 2 H), 6.99-7.10* (m, aromatics), 7.40-7.51* (m, aromatics), 7.53-7.56* (m, aromatics)	2848, 1630, 1525, 1447, 1244, 802, 724, 700
1e	88-90	3.48-3.52* (m, CH_2NAr), 3.65 (t, CH_2NCO, *J*= 6.4, 2 H), 5.05 (s, NCH_2N, 2 H), 6.60-6.70* (m, aromatics), 6.80-7.10* (m, aromatics), 7.15-7.60* (m, aromatics)	2975, 1635, 1489, 1421, 1225, 750, 717, 692
1f	225-227	3.60-3.69* (m, CH_2NAr), 4.01 (bs, CH_2NCO, 2H), 5.15 (s, NCH_2N, 2 H), 6.50-6.55* (m, aromatics), 6.60 (m, aromatics, 4 H), 7.40-7.50* (m, aromatics), 7.51-7.60* (m, aromatics), 8.20* (bs, aromatics)	3056, 1599, 1308, 1113, 826, 753, 701

1g	195-196	3.62-3.78* (m, CH_2NAr), 3.95 (bs, CH_2NCO, 2 H), 5.18 (s, NCH_2N, 2 H), 6.50-6.65* (bs, artomatics), 7.75 (dd, aromatics, ^1J= 7.1, ^2J= 2.1), 8.15* (bs, aromatics), 8.38 (dd, aromatics, ^1J= 7.1 Hz, ^2J= 2.1, 2 H)	3435, 2980, 1641, 1599, 1522, 1341, 1111, 852, 752
1h	163-164	3.40-3.52* (m, CH_2NAr), 3.92 (bs, CH_2NCO, 2 H), 4.95 (s, NCH_2N, 2 H), 7.30-7.40* (m, aromatics), 7.49-7.54* (m, aromatics)	2861, 1634, 1599, 1487, 1417, 1381, 1098, 715
1i	165-167	3.49-3.59* (m, CH_2NAr), 3.85 (bs, CH_2NCO, 2 H), 5.02 (s, NCH_2N, 2 H), 6.60-6.69*(m, aromatics), 7.49-7.59* (m, aromatics)	2987, 1630, 1603, 1415, 1380, 1088, 827, 751, 692
1j	oil	2.12 (s, Me, 3 H), 2.26 (s, Me, 3 H), 3.54 (t, CH_2NAr, J= 6.6, 2 H), 3.80-3.84* (m, CH_2NCO), 4.73 (s, NCH_2N, 2 H), 6.58-6.64* (m, aromatics), 7.09-7.15* (m, aromatics)	2852, 1634, 1527, 1445, 1241, 809, 716, 702
1k	oil	2.14 (s, Me, 3 H), 3.60 (t, CH_2NAr, J= 6.7, 2 H), 3.78 (s, OMe, 3 H), 3.80-3.85* (m, CH_2NCO), 4.73 (s, NCH_2N, 2 H), 6.65-6.72* (m, aromatics), 6.90-6.95* (m, aromatics)	2833, 1625, 1515, 1427, 1246, 812, 715
1l	118-119	1.22 (t, Me, J= 7.4, 3 H), 2.37 (q, CH_2CO, J= 7.4, 2 H), 3.60 (t, CH_2NAr, J= 6.5, 2 H), 3.79-3.89* (m, CH_2NCO), 4.80 (s, NCH_2N, 2 H), 6.64-6.70* (m, artomatics), 6.85-6.87* (m, aromatics), 7.23-7.33* (m, aromatics)	2818, 1643, 1446, 745, 692
1m	106-108	1.19-1.23* (m, Me), 2.27(s, Me, 3 H), 2.31-2.36* (m, CH_2CO), 3.54 (t, CH_2NAr, J= 6.6, 2 H), 3.76-3.85* (m, CH_2NCO), 4.74 (s,NCH_2N, 2 H), 6.60* (m, aromatics), 7.07-7.13* (m, aromatics)	2971, 1645, 1524, 1441, 800
1n	118-119	1.20 (t, Me, J= 7.5, 3 H), 2.38 (q, CH_2CO, J= 7.5, 2 H), 3.54 (t, CH_2NAr, J= 6.5, 2 H), 3.77-3.87* (m, CH_2NCO), 4.74 (s, NCH_2N, 2 H), 6.56-6.59* (m, aromatics), 6.97-7.05* (m, aromatics)	2972, 1652, 1505, 1443, 1259, 1025, 807
1o	109-110	1.18 (d, Me, J= 6.9, 6 H), 2.27 (s, Me, 3 H), 2.67 (m, CH, J= 6.9, 1 H), 3.56 (t, CH_2NAr, J=6.6, 2 H), 3.81-3.87*(m, CH_2NCO), 4.74 (s,NCH_2N, 2 H), 6.59* (m, aromatics), 7.10* (m, aromatics)	2969, 1652, 1520, 1446, 800
1p	91-92	1.20 (d, Me, J= 6.6, 6 H), 2.70 (m, CH, J= 6.6, 1 H), 3.60 (t, CH_2NAr, J= 6.6, 2 H), 3.85-3.93* (m, CH_2NCO), 4.75 (s, NCH_2N, 2 H), 6.55-6.60* (m, aromatics), 7.20-7.30* (m, aromatics)	2974, 1634, 1434, 1379, 1087, 822, 808, 743

In conclusion we report a simple and efficient method for the synthesis of 1-acyl-3-arylimidazolidines (**1a-p**) from *N*-acyl-*N´*-arylethylenediamines (**2**) and formaldehyde under microwave irradiation using Montmorillonite K-10 activated as a solid catalyst. The coupling of microwave irradiation with the use of Montmorillonite as efficient heterogeneous catalyst provides a clean methodology for this type of condensations. High yields, low reaction times and easy work-up are the common advantages of this method.

EXPERIMENTAL

Melting points were taken on a Büchi capillary apparatus and are uncorrected. The ^{1}H spectra were recorded on a Bruker MSL 300 MHz in $CDCl_3$. Standard concentration of the samples was 20 mg/mL. Chemical shifts are quoted in parts per million (δ) downfield from an internal TMS reference. The presence of exchangeable protons was confirmed by use of deuterium oxide. MS (EI) were performed on a MS Shimadzu QP-1000 spectrometer operating at 70 eV. The IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer. Reactions under MW irradiation were conducted in a domestic MW BGH 16260. Analytical TLC was carried out on aluminum sheets Silica Gel 60 F_{254}. Reagents, solvents and starting materials were purchased from standard sources and purified according to literature procedures. Experiments performed with toxic or severely irritant substances were carried out in an efficient cupboard.

N-Acyl-*N´*-arylethylenediamines (2)

Compounds (**2**) were prepared from *N*-(2-bromoethyl)amides (**3**) and the corresponding arylamine following literature procedure.[25] Precursor *N*-(2-bromoethyl)amides (**3**) were prepared by reaction of *N*-(2-bromoethyl)amine hydrobromide with a suitable acylating agent (benzoyl chloride, acetic, propionic or isobutiric anhydrides) under Schotten-Baumann conditions.[25]

Compounds (**2a,f**)[25] (**2b,c,d,g**)[26] and (**2i**)[9a] were previously described. The physical data and elemental analyses of new compounds are as follows.

N-Benzoyl-*N´*-(2-phenoxyphenyl)ethylenediamine (2e)

Yield: 77 %. mp 190-193 °C (EtOH). ^{1}H NMR: δ= 3.40 (t, *J*= 5.7 Hz, 2 H, CH_2N), 3.69 (q, *J*= 5.7 Hz, 2 H, CH_2N), 4.15 (bs, 1 H, NH), 6.50 (bs,1 H, NH), 6.71-7.70 (m, 14 H, aromatics). MS: *m/z:* 332 (M^+). IR (KBr): 3333, 3061, 2936, 1631, 1489, 1220, 846, 747, 739 cm^{-1}. Anal. Calcd for $C_{21}H_{20}N_2O_2$: C; 75.88, H; 6.06, N; 8.43. Found: C; 75.69, H; 6.10, N; 8.38.

N-Benzoyl-*N´*-(3,4-dichlorophenyl)ethylenediamine (2h)

Yield: 84%. mp 59-61 °C (EtOH). ^{1}H NMR: δ= 3.41 (t, *J*= 5.6 Hz, 2 H, CH_2N), 3.72 (q, *J*=5.6 Hz, 2 H,

CH_2N), 4.35 (bs, 1 H, NH), 6.52 (bs, 1 H, NH), 6.53-6.70 (m, 3 H, aromatics), 7.48 (m, 3 H, aromatics), 7.72 (dd, *J*= 8.1 Hz, *J*= 1.7 Hz, 2 H, aromatics). MS: *m/z*: 308, 310 (M^+). IR (KBr): 3389, 2997, 2923, 1620, 1479, 1085, 836, 747, 720 cm^{-1}. Anal. Calcd for $C_{15}H_{14}Cl_2N_2O$: C; 58.27, H; 4.56, N; 9.06. Found: C; 58.45, H; 4.50, N; 8.95.

***N*-Acetyl-*N´*-(4-methylphenyl)ethylenediamine (2j)**

Yield: 65%; oil (column chromatography, EtOAc). ^1H NMR: δ= 2.01 (s, 3 H, Me), 2.25 (s, 3 H, Me), 3.22 (t, *J*= 5.7 Hz, 2 H, CH_2N), 3.47 (q, *J*= 5.7 Hz, 2 H, CH_2N), 4.02 (bs, 1 H, NH), 6.10 (bs, 1 H, NH), 6.55 (d, *J*= 8.5 Hz, 2 H, aromatics), 6.98 (t, *J*= 8.5 Hz, 2 H, aromatics). IR (film): 3312, 2922, 1659, 1522, 1452, 1378, 807 cm^{-1}. MS: *m/z*: 192 (M^+). Anal. Calcd for $C_{11}H_{16}N_2O$: C; 68.72, H; 8.39, N; 14.57. Found: C; 68.68, H; 8.45, N; 14.50.

***N*-Acetyl-*N´*-(4-methoxyphenyl)ethylenediamine (2k)**

Yield: 64%. mp 45-46 °C. ^1H NMR: δ= 1.97 (s, 3 H, Me), 3.22 (t, *J*= 5.7 Hz, 2 H, CH_2N), 3.46 (q, *J*= 5.7 Hz, 2 H, CH_2N), 3.73 (s, 3 H, Me), 4.01 (bs, 1 H, NH), 5.95 (bs, 1 H, NH), 6.59 (d, *J*=8.9 Hz, 2 H, aromatics), 6.77 (d, *J*= 8.9 Hz, 2 H, aromatics). MS: *m/z* : 208 (M^+). IR (film): 3301, 2938, 1651, 1514, 1463, 1237, 824 cm^{-1}. Anal. Calcd. for $C_{11}H_{16}N_2O_2$: C; 63.44, H; 7.74, N; 13.45. Found: C; 63.54, H; 7.67, 13.51.

***N*-Phenyl-*N´*-propionylethylenediamine (2l)**

Yield: 78%; oil (column chromatography, EtOAc). ^1H NMR: δ= 1.13 (t, *J*= 7.5 Hz, 3 H, Me), 2.20 (q, *J*= 7.5 Hz, 2 H, CH_2), 3.24 (t, *J*= 5.6 Hz, 2 H, CH_2N), 3.48 (q, *J*= 5.6 Hz, 2 H, CH_2N), 4.30 (bs, 1 H, NH), 6.30 (bs, 1 H, NH), 6.59 (dd, *J*= 8.7, *J*= 1.03 Hz, 2 H, aromatics), 6.68 (tt, *J*= 7.4, *J*= 1.03 Hz, 1 H, aromatic), 7.15 (dd, *J*= 8.7, *J*= 7.4 Hz, 2 H, aromatics). MS: *m/z*: 192 (M^+). IR (film): 3300, 2978, 1649, 1463, 1182, 750, 694 cm^{-1}. Anal. Calcd. for $C_{11}H_{16}N_2O$: C; 68.72, H; 8.39, N; 14.57. Found: C; 68.69, H; 8.46, N; 14.67.

***N*-(4-Methylphenyl)-*N´*-propionylethylenediamine (2m)**

Yield: 78%; oil (column chromatography, EtOAc). ^1H NMR: δ= 1.15 (t, *J*= 7.4 Hz, 3 H, Me), 2.17 (q, *J*= 7.4 Hz, 2 H, CH_2), 2.23 (s, 3 H, Me), 3.22 (t, *J*= 5.8 Hz, 2 H, CH_2NH), 3.45 (q, *J*= 5.8 Hz, 2 H, CH_2H), 4.15 (bs, 1 H, NH), 6.14 (bs, 1 H, NH), 6.52 (d, *J*= 8.3 Hz, 2 H, aromatics), 6.98 (d, *J*= 8.3 Hz, 2 H, aromatics). MS: *m/z:* 206 (M^+). IR (film): 3307, 2939, 1645, 1519, 1463, 1254, 810 cm^{-1}. Anal. Calcd. for $C_{12}H_{18}N_2O$: C; 69.87, H; 8.79, N; 13.58. Found: C; 69.74, H; 8.89, N; 13.47.

***N*-(4-Chlorophenyl)-*N´*-propionylethylenediamine (2n)**

Yield: 72 %; oil (column chromatography, EtOAc). ^1H NMR: δ= 1.10 (t, *J*= 7.6 Hz, 3 H, Me), 2.20 (q, *J*= 7.6 Hz, 2 H, CH_2), 3.22 (t, *J*= 5.6 Hz, 2 H, CH_2N), 3.56 (q, *J*= 5.6 Hz, 2 H, CH_2N), 4.20 (bs, 1 H, NH), 5.90 (bs, 1 H, NH), 6.50 (d, *J*= 8.9 Hz, 2 H, aromatics), 7.05 (d, *J*= 8.9 Hz, 2 H, aromatics). MS: *m/z* :

226, 228 (M^+). IR (film): 2981, 1662, 1510, 1440, 1241, 1025, 806 cm^{-1}. Anal. Calcd. for $C_{11}H_{15}ClN_2O$: C; 58.28, H; 6.67, N; 12.36. Found: C; 58.15, H; 6.73, N; 12.42.

***N*-(4-Methylphenyl)-*N´*-(2-methylpropionyl)ethylenediamine (2o)**

Yield: 75%; oil (column chromatography, EtOAc). ^{1}H NMR: δ= 1.10 (d, *J*= 6.9 Hz, 6 H, Me), 2.20 (s, 3 H, Me), 2.31 (m, 1 H, CH), 3.25 (t, *J*= 5.9 Hz, 2 H, CH_2N), 3.50 (q, *J*= 5.9 Hz, 2 H, CH_2N), 4.42 (bs, 1 H, NH), 5.85 (bs, 1 H, NH), 6.55 (d, *J*= 8.4 Hz, 2 H, aromatics), 7.00 (d, *J*= 8.4 Hz, 2 H, aromatics). MS: *m/z*: 220 (M^+). IR (film): 3306, 2970, 1645, 1548, 1249, 813 cm^{-1}. Anal. Calcd. for $C_{13}H_{20}N_2O$: C; 70.87, H; 9.15, N; 12.72. Found: C; 70.74, H; 9.23, N; 12.65.

***N*-(4-Chlorophenyl)-*N´*-(2-methylpropionyl)ethylenediamine (2p)**

Yield: 79%. mp 69-70 °C (EtOH). ^{1}H NMR: δ= 1.10 (d, *J*=7.0 Hz, 6 H, Me), 2.30 (sep, *J*= 7.0 Hz, 1 H, CH), 3.20 (t, *J*= 6.4 Hz, 2 H, CH_2N), 3.50 (q, *J*= 6.4 Hz, 2 H, CH_2N), 4.06 (bs, 1 H, NH), 5.90 (bs, 1 H, NH), 6.64 (d, *J*=8.8 Hz, 2 H, aromatics), 7.10 (d, *J*= 8.8 Hz, 2 H, aromatics). MS: *m/z*: 240, 242 (M^+). IR (KBr): 3334, 2971, 1660, 1470, 1434, 1252, 1137, 816 cm^{-1}. Anal. Calcd. for $C_{12}H_{17}ClN_2O$: C; 59.87, H; 7.12, N; 11.64. Found: C; 59.76, H; 7.20, N; 11.55.

Imidazolidines (1a-p): General Procedure

To a solution of *N*-acyl-*N´*-arylethylenediamine (**2**) (1 mmol) in anhydrous THF (5 mL) was added Montmorillonite K-10 actived 1 h/ 120 °C (500 mg) followed by aqueous 37% formaldehyde (3 mmol). To the reaction mixture , a 30 s of irradiation at 180 W and a 20 s without irradiation were repeated alternately until the starting material disappeared as monitored by TLC. After filtration, the solvent was removed in vacuo and the residue was crystallized from EtOH except compounds (**1j,k**) which were purified by column chromatography (EtOAc).

Melting points, ^{1}H-NMR and IR data are given in table 2. Elemental analyses and MS data are as follows.

1-Benzoyl-3-phenylimidazolidine (1a)

MS: *m/z:* 252 (M^+). Anal. Calcd for $C_{16}H_{16}N_2O$: C; 76.16, H; 6.39, N; 11.10. Found: C; 76.22, H; 6.28, N; 11.15.

1-Benzoyl-3-(4-hidroxyphenyl)imidazolidine (1b)

MS (EI, 70eV): *m/z:* 268 (M^+). Anal. Calcd for $C_{16}H_{16}N_2O_2$: C; 71.62, H; 6.01, N, 10.44. Found: C; 71.50, H; 5.91, N; 10.51.

1-Benzoyl-3-(4-chlorophenyl)imidazolidine (1c)

MS: *m/z :* 286, 288 (M^+). Anal. Calcd for $C_{16}H_{15}ClN_2O$: C; 67.02, H; 5.27, N; 9.77. Found: C; 67.13, H; 5.31, N; 9.65.

1-Benzoyl-3-(4-methylphenyl)imidazolidine (1d)

MS: *m/z:* 266 (M^+). Anal. Calcd for $C_{17}H_{18}N_2O$: C; 76.66, H; 6.81, N; 10.52. Found: C; 76.54, H; 6.70, N; 10.65.

1-Benzoyl-3-(2-phenoxyphenyl)imidazolidine (1e)

MS: *m/z:* 344 (M^+). Anal. Calcd for $C_{22}H_{20}N_2O_2$: C; 76.72, H; 5.85, N; 8.13. Found: C; 76.65, H; 5.91, N; 8.07.

1-Benzoyl-3-(4-nitrophenyl)imidazolidine (1f)

MS: *m/z:* 297 (M^+). Anal. Calcd for $C_{16}H_{15}N_3O_3$: C; 64.64, H; 5.09, N; 14.13. Found: C; 64.72, H; 5.20, N; 14.25.

1-(4-Nitrobenzoyl)-3-(4-nitrophenyl)imidazolidine (1g)

MS: *m/z*: 342 (M^+). Anal. Calcd for $C_{16}H_{14}N_4O_5$: C; 56.14, H; 4.12, N; 16.37. Found: C; 56.23, H; 4.05, N; 16.29.

1-Benzoyl-3-(3,4-dichlorophenyl)imidazolidine (1h)

MS: *m/z* : 320, 322 (M^+). Anal. Calcd for $C_{16}H_{14}Cl_2N_2O$: C; 59.83, H; 4.39, N; 8.72. Found: C; 59.96, H; 4.42, N; 8.68.

1-(4-Chlorobenzoyl)-3-phenylimidazolidine (1i)

MS: *m/z*: 286, 288 (M^+). Anal. Calcd for $C_{16}H_{15}ClN_2O$: C; 67.02, H; 5.27, N; 9.77. Found: C; 67.10, H; 5.29, N; 9.69.

1-Acetyl-3-(4-methylphenyl)imidazolidine (1j)

MS: *m/z :* 204 (M^+). Anal. Calcd for $C_{12}H_{16}N_2O$: C; 70.56, H; 7.89, N; 13.71. Found: C; 70.47, H; 7.95, N; 13.65.

1-Acetyl-3-(4-methoxyphenyl)imidazolidine (1k)

MS: *m/z:* 220 (M^+). Anal. Calcd for $C_{12}H_{16}N_2O_2$: C; 65.43, H; 7.32, N; 12.72. Found: C; 65.32, H; 7.39, N; 12.68.

1-Phenyl-3-propionylimidazolidine (1l)

MS: *m/z:* 204 (M^+). Anal. Calcd for $C_{12}H_{16}N_2O$: C; 70.56, H; 7.89, N; 13.71. Found: C; 70.48, H; 7.95, N; 13.65.

1-(4-Methylphenyl)-3-propionylimidazolidine (1m)

MS: *m/z:* 218 (M^+). Anal. Calcd for $C_{13}H_{18}N_2O$: C; 71.53, H; 8.31, N; 12.83. Found: C; 71.67, H; 8.39, N; 12.72.

1-(4-Chlorophenyl)-3-propionylimidazolidine (1n)

MS: *m/z*: 238, 240 (M^+). Anal. Calcd for $C_{12}H_{15}ClN_2O$: C; 60.38, H; 6.33, N; 11.73. Found: C; 60.45, H; 6.28, N; 11.79.

1-(4-Methylphenyl)-3-(2-methylpropionyl)imidazolidine (1o)

MS: *m/z :* 232 (M^+). Anal. Calcd for $C_{14}H_{20}N_2O$: C; 72.38, H; 8.68, N; 12.06. Found: C; 72.27, H; 8.75,

N; 12.13.

1-(4-Chlorophenyl)- 3-(2-methylpropionyl)imidazolidine (1p)

MS: *m/z*: 252, 254 (M^+). Anal. Calcd for $C_{13}H_{17}ClN_2O$: C; 61.78, H; 6.78, N; 11.08. Found: C; 61.67, H; 6.59, N; 11.13.

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