Available online at www.sciencedirect.com
ScienceDirect
Journal of Molecular Catalysis A: Chemical 266 (2007) 109–113
JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL
www.elsevier.com/locate/molcata

Highly efficient, one-pot, solvent-free synthesis of tetrasubstituted imidazoles using $HClO_4$–SiO_2 as novel heterogeneous catalyst

Srinivas Kantevari *, Srinivasu V.N. Vuppalapati, Dhanraj O. Biradar, Lingaiah Nagarapu

Organic Chemistry Division-II, Indian Institute of Chemical Technology, Uppal Road, Hyderabad 500007, India

Received 18 September 2006; received in revised form 24 October 2006; accepted 24 October 2006
Available online 10 November 2006

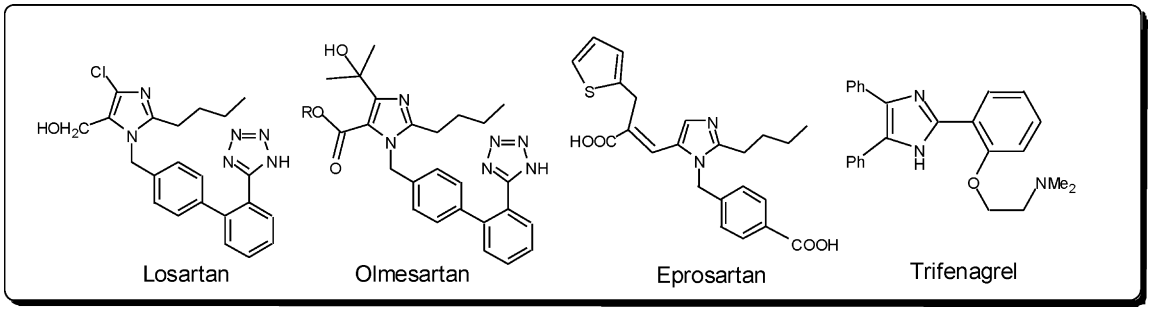
Abstract

Highly efficient, one-pot, four-component synthesis of 1,2,4,5-tetrasubstituted imidazoles was reported the condensation of various aldehydes, benzil, aliphatic or aromatic primary amines and ammonium acetate under solvent free conditions using perchloric acid adsorbed on silica gel ($HClO_4$–SiO_2) as catalyst in excellent yields. $HClO_4$–SiO_2 exhibited remarkable catalytic activity with respect to the reaction time (2–20 min), amount of catalyst. Present protocol with $HClO_4$–SiO_2 catalyst is convincingly superior to the recently reported catalytic methods.

Keywords: Imidazoles; Four-component reaction; One-pot synthesis; MCRs; Silica-supported perchloric acid

1. Introduction

The development of simple, efficient and environmentally benign chemical process or methodologies for widely used pharmacophores from readily available reagents and catalysts are the major challenges for chemists' world over. [1] The imidazole, being a core molecule in many biological systems[2] viz. Histidine, Histamine and biotin, an active component in several drug molecules[3] (for eg. Losartan, Olmesartan, Eprosartan and Trifenagrel) and pesticides [4] has attracted attention in recent years. Different substituted imidazoles show variable biological activities such as anti-inflammatory activity, [5] anti-allergic activity [6] and analgesic activity.[7] In particular, 4,5-diaryl substituted imidazoles have been identified as potential inhibitors of p38 MAP kinase [8] and thus have rekindled our interest in obtaining tetrasubstituted imidazoles. Despite the availability of wide variety of synthetic routes towards imidazoles, [9] only few studies exist for the synthesis of 1,2,4,5-tetrasubstituted imidazoles, which are most widely performed via multi-step routes [8,10] or via trisubstituted *1H* -imidazole in which the nitrogen is substituted in the final step [7,11].



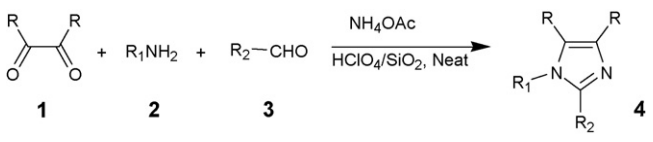
For the past decade very efficient way to access heterocycles is by using Multicomponent reactions (MCRs). [12] In this type of reactions three or more components are reacted to form ideally one product, which incorporates essentially all the atoms present in the initial reactants. For the synthesis of imidazoles,

* Corresponding author.
E-mail address: Kantevari@yahoo.com (S. Kantevari).

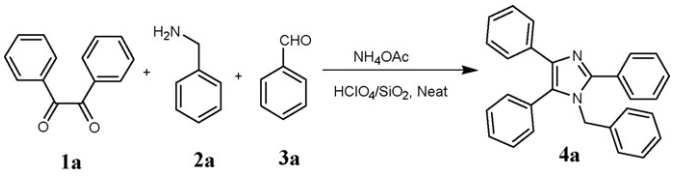
1381-1169/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2006.10.048

mostly, variations of the method first reported by Radziszewski, [13a] later modified by Drefahl and Herma [13b] were used. For highly substituted imidazoles, the mostly used methods in the last decade are: condensation of benzoin or benzoin acetate with aldehydes, primary amines, ammonia in the presence of copper acetate; [14a] condensation of β-carbonyl-*N*-acyl-*N*-alkylamines with ammonium acetate in refluxing acetic acid; [14b] four-component condensation of diones, aldehydes, primary amines and ammonium acetate in acetic acid under reflux conditions; [14c] cyclization of sulfonamides with mesoionic 1,3-oxazolium-5-olates; [14d] conversion of *N*-(2-oxo)amides with ammonium trifluoroacetate under neutral conditions; [14e] condensation of benzonitrile, benzil and alkyl amine using silica gel and Zeolite HY as heterogeneous catalysts under solvent free microwave conditions. [14f,g] Although these methods has lot of potential, the reactions suffer from low yields, longer reaction times, use of expensive reagents, use of solvents and toxic agents associated with mixture of products, lack of generality and were not suitable for, or were not applied for the synthesis of structurally diverse imidazoles. Hence, the development of clean, high-yielding and environmental benign approaches is still desirable and much in demand.

The leading contenders for environmentally acceptable processes are supported reagents. Use of silica-supported reagents in one-pot multi-component construction of heterocycles has received considerable importance in organic synthesis. [15] In particular, perchloric acid adsorbed on silica gel ($HClO_4/SiO_2$) [16a] has immerged as an extremely useful catalyst in various organic transformations, including acylation of alcohols, [16a] acylation of aldehydes, [16b,c] 1,3-dithiolane/dithiane formation, [16d] tetrahydropyrany lation, [16e] thio-acetalization, [16e] Ferrier rearrangement, [16f,g] Michael addition, [16h] cleavage of ketals and benzylidene acetals, [16i,j] the Hantzsch condensation, [16k] Synthesis of bis-indolylmethanes, [16l] glycosylation of sugars [16m] and *N*-*tert*-butoxycarbonylation of amines. [16n] In view of its inherent properties like environmental compatibility, greater selectivity, operational simplicity, moisture-insensitive, non-corrosive nature and ease of isolation, it is therefore, interest to us to find out the behavior of the reagent system, $HClO_4$ supported on silica gel (230–400 mesh) in the synthesis of imidazole derivatives. To the best of our knowledge, there are no examples on the use of perchloric acid adsorbed on silica gel ($HClO_4/SiO_2$), for the synthesis of tetrasubstituted imidazoles. In continuation of our work on the development of efficient protocols for the synthesis 2-(*n*-butyl)-5-chloro-3*H*-imidazole-4-carboxaldehyde, [17] an intermediate for the preparation of an anti-hypertensive drug, Losartan-K, and in view of importance of heterogeneous acid catalysts in organic synthesis, we now wish to report perchloric acid adsorbed on



Scheme 1.



Scheme 2.

silica gel ($HClO_4/SiO_2$) catalyzed highly efficient synthesis of tetrasubstituted imidazoles using one-pot four-component condensation of 1,2-diketones with wide variety of aldehydes, aliphatic or aromatic primary amines and ammonium acetate under solvent free conditions (Scheme 1).

2. Results and discussion

For our investigations, $HClO_4$–SiO_2 was prepared according to the literature procedure. [16a] In order to determine the most appropriate reaction conditions and evaluate the catalytic efficiency of $HClO_4$–SiO_2 catalyst; initially a model study was carried out on the synthesis of 1-benzyl-2,4,5-triphenylimidazole (**4a**, Scheme 2). Among the tested solvents such as methanol, ethanol, isopropanol, DMF, DMSO, chloroform, dichloromethane and solvent-free system, condensation of benzil, benzaldehyde, benzyl amine, and ammonium acetate is more facile and proceeded to gave highest yield, under solvent free conditions (Table 1). To evaluate and optimize the catalytic system, four-component condensation of benzil, benzaldehyde, benzyl amine, and ammonium acetate (Scheme 2) was examined with solid acid and supported Lewis/protic acid catalysts (Table 2).

Interestingly, it is found that $HClO_4$ supported on silica gel with low loading (0.025 mmol/50 mg, 1 mol%) is an efficient catalyst and gave exclusively 1-benzyl-2,4,5-triphenylimidazole **4a** in 96% yield in 6 min under solvent free conditions. Formation of bi-product 2,4,5-triphenyl-1*H*-imidazole was not observed. The claim is justified through a few representative examples in which the efficiency of has been compared with those recently reported supported Lewis/protic acid catalysts. [18] (Table 2) Blank experiments have shown that the silica gel alone cannot bring about this transformation. The aqueous perchloric acid also brings the reaction to form imidazoles after longer hours (2.5 h). From these experiments it was clearly demonstrated that the silica-supported perchloric acid is indeed an effective catalyst and is convincingly superior to the reported procedures [18]

Table 1
Synthesis of 1-benzyl-2,4,5-tripehnylimidazole **4a** using $HClO_4$–SiO_2 catalyst (0.025 mmol) in the different solvents

Entry	Solvent	Temperature (°C)	Time	Yield (%)
1	Methanol	65	4 h	46
2	Ethanol	75	4 h	48
3	Isopropanol	82	4 h	45
4	Dichloromethane	45	12 h	>10
5	DMF	110	2 h	62
6	DMSO	110	2 h	70
7	Solvent-free	140	6 min	96

Table 2
Synthesis of 1-benzyl-2,4,5-triphenylimidazole **4a** using different catalysts and reaction conditions

Serial no.	Catalyst	Solvent	Temperature (°C)	Time	Yield (%)	Ref.
1	No catalyst	Solvent free	140	24 h	–	–
2	SiO_2 (200 mg/mmol)	Solvent free	140	14 h	40	–
3	Aq. $HClO_4$ (0.05 mmol)	Solvent free	140	2.5 h	85	–
4	$HClO_4$–SiO_2					
(50 mg, 0.025 mmol)	Solvent free	140	6 min	96	–	
5	$NaHSO_4$–SiO_2	Solvent free	140	120 min	92	[18c]
6	Al_2O_3	Solvent free	MWI	20 min	80	[18i]
7	Wang resin	Acetic acid	100	4.0 h	95	[18j]
8	Heteropoly acid	Ethanol	Reflux	8 min	88	[18d]
9	Acetic acid	Chloroform	160, MWI	15 min	90	[18e]
10	Acetic acid	NMP/*n*-pentanol	120	118 min	90	[18f]
11	Molecular Iodine	Ethanol	75	10 min	96	[18h]

MWI: microwave irradiation.

with respect reaction time; amount of catalyst and yields and under solvent free conditions.

In order to evaluate the generality of the process, several diversified examples illustrating the present method for the synthesis of 1,2,4,5-tetrasubstituted imidazoles **4** was studied (Table 3). The reaction of benzil **1** with various aromatic aldehydes **3** bearing electron withdrawing groups (such as nitro, halide) or electron releasing groups (such as *N*,*N*-dimethylamino, methyl, hydroxyl; mono, di, or tri methoxy groups), benzyl amine or cyclohexyl amine or *sec*-butyl amine, aniline derivatives **2** and ammonium acetate was carried out in the presence of $HClO_4$–SiO_2 as catalyst. The yields obtained were good to excellent without formation of any side products such as 2,4,5-trisubstituted imidazoles, which are normally observed under the influence of strong acids. [18] The reaction of aromatic aldehydes having electron withdrawing groups reacted very well at faster rate compared with aromatics aldehydes substituted with electron releasing groups. The results obtained in the current method are illustrated in Table 3. All the products obtained were fully characterized by spectroscopic methods such as IR, ^{1}H NMR, ^{13}C NMR and mass spectroscopy and also by comparison with the reported [18] spectral data.

The simplicity, together with the use of inexpensive, non-toxic and environmentally benign nature of $HClO_4$–SiO_2 catalyst under solvent free condition is other remarkable feature of the procedure. Acetone was added to the reaction mixture, the catalyst was filtered and the filtrate was concentrated to give crude residue, which was crystallized in acetone–water (10:1) to

Table 3
$HClO_4$–SiO_2 catalyzed Solvent free synthesis of 1,2,4,5-tetrasubstituted imidazoles **4a-y**

Entry	*R*	R_1	R_2	Product	Reaction time (min)	Yield[a,b] (%)	m.p. (°C)	Ref.
1	C_6H_5	$C_6H_5CH_2$	C_6H_5	4a	6	96	165–167	[7,18a,b]
2	C_6H_5	$C_6H_5CH_2$	4-MeC_6H_4	4b	6	90	165–168	[7,18a,c]
3	C_6H_5	$C_6H_5CH_2$	3-OMeC_6H_4	4c	8	88	128–130	[7]
4	C_6H_5	$C_6H_5CH_2$	3,4,5-$(OMe)_3C_6H_2$	4d	15	94	184–186	
5	C_6H_5	$C_6H_5CH_2$	3-ClC_6H_4	4e	10	90	146–148	[7,18c]
6	C_6H_5	$C_6H_5CH_2$	4-ClC_6H_4	4f	8	94	162–165	[7,18c]
7	C_6H_5	$C_6H_5CH_2$	4-OMeC_6H_4	4g	10	96	157–160	[7,18b]
8	C_6H_5	$C_6H_5CH_2$	4-BrC_6H_4	4h	8	98	170–172	[7]
9	C_6H_5	$C_6H_5CH_2$	2-ClC_6H_4	4i	8	96	140–142	[7]
10	C_6H_5	$C_6H_5CH_2$	4-N$(Me)_2C_6H_4$	4j	15	90	150–152	[7]
11	C_6H_5	$C_6H_5CH_2$	4-OHC_6H_4	4k	20	75	134–135	[7,18b]
12	C_6H_5	$C_6H_5CH_2$	2-$NO_2C_6H_4$	4l	3	93	152–155	[7]
13	C_6H_5	*iso*-Butyl	3,4,5-$(OMe)_3C_6H_2$	4m	20	80	112–115	
14	C_6H_5	3-Me$C_6H_4CH_2$	4-OH-3-$OMeC_6H_3$	4n	15	86	205–210	
15	C_6H_5	*iso*-Butyl	4-MeC_6H_4	4o	15	90	151–153	[18a,c]
16	C_6H_5	$C_6H_5CH_2$	*iso*-Propyl	4p	15	86	129–130	[18f,e]
17	C_6H_5	$C_6H_5CH_2$	2-Furyl	4q	20	78	156–157	[7]
18	C_6H_5	4-MeC_6H_4	3-$NO_2C_6H_4$	4r	5	90	149–151	[18c]
19	C_6H_5	4-MeC_6H_4	4-$NO_2C_6H_4$	4s	2	98	219–220	[18c]
20	C_6H_5	C_6H_5	C_6H_5	4t	10	91	216	[18a,f]
21	C_6H_5	$C_6H_5CH_2CH_2$	4-MeC_6H_4	4u	12	89	125–126	[18b]
22	C_6H_5	3-$NO_2C_6H_4$	4-N$(Me)_2C_6H_4$	4v	10	84	239–240	[18b]
23	C_6H_5	Cyclohexyl	4-MeC_6H_4	4w	18	90	164	[18b]
24	CH_3	$C_6H_5CH_2$	*iso*-Propyl	4x	20	56	104–105	[18f,e]
25	CH_3	*iso*-Butyl	C_6H_5	4y	20	60	Oil	[18e]

[a] Yield of the corresponding isolated and purified product.
[b] All compounds were fully characterized by IR, NMR and mass spectroscopy.

give pure 1,2,4,5-tetrasubstituted imidazoles **4a–y** in excellent yields.

3. Conclusion

We described herein perchloric acid adsorbed on silica gel ($HClO_4$–SiO_2) catalyzed highly efficient, one-pot, four-component protocol for the synthesis of 1,2,4,5-tetrasubstituted imidazoles by the condensation of an aldehyde, benzil, aliphatic or aromatic primary amines and ammonium acetate under solvent free conditions in excellent yields. The remarkable catalytic activity of $HClO_4$–SiO_2 exhibited is convincingly superior to the recently reported other catalytic methods with respect reaction time (2–20 min), amount of catalyst and the pure products were obtained by simple crystallization. Easy work up, inexpensive, ready availability of the catalyst makes the procedure an attractive alternative to the existing methods for the synthesis of tetrasubstituted imidazoles **4a–y**.

4. Experimental

4.1. General

Perchloric acid ($HClO_4$) aqueous solution (70%) was purchased from Loba Chemie, India and silica gel (230–400 mesh) from spectrochem India Pvt. Ltd. India. All the commercial reagents and solvents used without further purification unless otherwise stated. Melting points were recorded on Buchi 535 melting point apparatus and are uncorrected. All the reactions were monitored by thin layer chromatography performed on precoated silica gel $60F_{254}$ plates (Merck). Compounds were visualized with UV light at 254 nm and 365 nm, iodine and heating plates after dipping in 2% phosphomolybdic acid in 15% aq. H_2SO_4 solution. IR spectra were recorded on Perkin-Elmer 683 or 1310 FT-IR spectrometer with KBr pellets. NMR spectra were recorded on Varian Unity-400 MHz and BRUKER AMX 300 MHz spectrometers using tetra methyl silane as an internal standard. ^{13}C NMR was recorded on Varian Unity 100 MHz using $CDCl_3$ as internal standard. Mass spectra were recorded on a VG Micromass 7070H and Finnigan Mat 1020B mass spectrometers operating at 70 eV.

4.2. Preparation of $HClO_4/SiO_2$ catalyst

Seventy percent aqueous perchloric acid (1.8 g, 12.5 mmol) was added to a suspension of SiO_2 (230–400 mesh, 23.7 g) in ether (70 ml). The mixture was concentrated and the residue was heated at 100 °C for 72 h under vacuum to give $HClO_4$–SiO_2 (0.5 mmol/g) as free flowing powder (50 mg = 0.025 mmol of $HClO_4$).

4.3. General experimental procedure for the preparation of tetrasubstituted imidazoles

To a mixture of benzil (2.5 mmol), aldehyde (2.5 mmol) primary amine (2.5 mmol), ammonium acetate (2.5 mmol) and $HClO_4$–SiO_2 (50 mg, 0.025 mmol, 1 mol%) were heated at 140 °C with stirring for 2–20 min. After completion of reaction (monitored by TLC) the mixture was cooled to room temperature, acetone (50 ml) was added. The catalyst was filtered, solid was washed with acetone (10 ml), combined acetone solution was concentrated in vacuum to afford crude product. The crystalline pure product was obtained by further recrystalization in Acetone: water (10:1). All the products obtained were fully characterized by spectroscopic methods such as IR, ^1H NMR, ^{13}C NMR and mass spectroscopy and have been identified by the comparison of the reported spectral data. The spectral and analytical data for the selected compounds are presented below.

*4.4. 1-Benzyl-2-(3,4,5-trimethoxyphenyl)-4, 5-diphenylimidazole **4d***

IR (KBr, ν_{max}, cm^{-1}): 3059, 2956, 2933, 1960, 1640, 1582, 1520, 1443, 1361, 1255, 1182, 1071, 921. ^1H NMR (400 MHz, DMSO-d_6) δ_H: 3.62 (s, 6H), 3.75 (s, 3H), 5.12(s, 2H), 6.80(s, 2H), 6.98 (d, J = 7.3 Hz, 2H), 7.36-7.07 (m, 11H), 7.52 (d, J = 7.3 Hz, 2H). ^{13}C NMR (DMSO-d_6, 100 MHz) δ_c: 59.2, 62.1 62.8, 105.8, 109.0, 111.7, 120.8, 124.6, 125.4, 127.6, 127.8, 128.2, 128.5, 129.1, 129.5, 129.9, 130.5, 130.9, 132.5, 135.6, 140.2, 143.4, 150.5, 152.2. Anal. Calcd. for $C_{31}H_{28}N_2O_3$: C, 78.13; H, 5.92; N, 5.88; found C, 78.18; H, 5.98; N, 5.92%.

*4.5. 2-(4-Dimethylaminophenyl)-1-(3-nitrophenyl)-4, 5-diphenylimidazole **4v***

IR (KBr, ν_{max}, cm^{-1}): 2926, 1623, 1560, 1503, 1494; ^1H NMR (300 MHz, DMSO-d_6) δ_H: 2.95 (s, 6H, CH_3), 6.77-7.94 (m, 18H, Ar). ^{13}C NMR (DMSO-d_6, 100 MHz) δ_c: 111.8, 117.9, 121.8, 125.6, 126.4, 127.3, 127.6, 127.9, 128.5, 129.0, 129.4, 129.9, 130.5, 130.8, 131.5, 135.5, 141.4, 145.4, 150.1. Anal. Calcd. for $C_{29}H_{24}N_4O_2$, C, 75.63; H, 5.25; N, 12.17; found C, 75.68; H, 5.18; N, 12.20%.

*4.6. 1-Benzyl-2-isopropyl-4,5-dimethylimidazole **4x***

IR (KBr, ν_{max}, cm^{-1}): 2960, 1655, 1617, 1494, 1436, 1360, 1328, 1302. ^1H NMR (300 MHz, $CDCl_3$) δ_H: 1.24 (d, J = 6.8 Hz, 6H), 2.01 (s, 3H), 2.16 (s, 3H), 2.90 (septet, J = 6.8 Hz, 1H), 5.02(s, 2H), 6.90(d, J = 6.6 Hz, 2H), 7.20–7.35 (m, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz) δ_c: 8.9, 12.8, 22.1, 26.2, 44.5, 121.8, 125.4, 127.6, 129.0, 132.0, 136.9, 151.6. Anal. Calcd. for $C_{15}H_{20}N_2$: C, 78.90; H, 8.83; N, 12.27; found: C, 78.83; H, 8.88; N, 12.19%.

Acknowledgement

We thank Dr. J.S. Yadav, Director, IICT, Hyderabad for his constant encouragement and support.

References

[1] (a) C. Hulme, V. Gore, Curr. Med. Chem. 10 (2003) 51;
(b) M.R. Grimmett, Imidazole and Benzimidazole Synthesis (Best Synthetic Methods), Academic Press, London, 1997.

[2] (a) M.R. Grimmett, in: A.R. Katritzky, C.W. Rees (Eds.), Comprehensive Heterocyclic Chemistry, vol. 5, Pergamon Press, London, 1984, p. 374;
(b) M.R. Grimmett, Advances in Heterocyclic chemistry, vol. 12, Academic Press, New York, 1980, p. 241;
(c) S.A. Laufer, W. Zimmermann, K.J. Ruff, J. Med. Chem. 47 (2004) 6311.
[3] (a) H. Koike, T. Konse, T. Sada, T. Ikeda, A. Hyogo, D. Hinman, H. Saito, Yanagisawa, Ann. Rep. Sankyo Res. Lab. 55 (2003) 1;
S.L. Abrahams, R.J. Hazen, A.G. Batson, A.P. Phillips, J. Pharmacol. Exp. Ther. 249 (1989) 359;
(c) C. Leister, Y. Wang, Z. Zhao, C.W. Lindsley, Org. Lett. 6 (2004) 1453.
[4] A.M.M. Mjalli, S. Sarshar, U.S. patent (1997) US 5700826, 19 pp. Chemical abstract, 128 (1998) 88918a.
[5] M. Misono, Chem. Commun. (2001) 1141.
[6] J.W. Blank, G.J. Durant, J.C. Emmett, C.R. Ganellin, Nature 248 (1974) 65.
[7] U. Ucucu, N.G. Karaburun, I. Iskdag, Il Farmaco 56 (2001) 285.
[8] J.A. Murry, Curr. Opin. Drug Discov. Dev. 6 (2003) 945.
[9] G.W. Gribble, J.A. Joule, T.L. Gilchrist (Eds.), Progress in Heterocyclic Chemistry, vol. 13–17, Elsvier, Oxford, 2001–2005.
[10] (a) W. Li, Y. Lam, J. Comb. Chem. 7 (2005) 644;
Y.M. Losksha, A.A. El-Barbary, M.A. El-Badawi, C. Nielson, E.B. Pederson, Bioorg. Med. Chem. 13 (2005) 4209;
(c) O.A. Attanasi, L. De Crescentini, G. Favi, P. Filippone, F. Mantellini, S. Santeusanio, Synlett (2004) 549.
[11] (a) P. Deprez, E. Mandine, A. Vermond, D. Lesuisse, Bioorg. Med. Chem. Lett. 12 (2002) 1287;
(b) J. Sisko, M. Mellinger, Pure Appl. Chem. 74 (2002) 1349.
[12] (a) J. Zhu, H. Bienayme (Eds.), For Recent Monograph, See Multi Component Reactions, Wiley-VCH, Weinheim, 2005;
(b) For special issue in MCRs, see Tetrahedron, 61 (2005) 11299;
(c) D.J. Ramon, M. Yus, Angew. Chem. Int. Ed. 44 (2005) 1602;
(d) J. Zhu, Eur. J. Org. Chem. (2003) 1133;
(e) R.V. Orru, M. de Greef, Synthesis (2003) 1471.
[13] (a) B. Radziszewski, Chem. Ber. 15 (1882) 1493;
(b) G. Drefahl, H. Herma, Chem. Ber. 93 (1960) 486.
[14] (a) B.H. Lipshutz, M.C. Morey, J. Org. Chem. 48 (1983) 3745;
(b) D.A. Evans, K.M. Lundy, J. Am. Chem. Soc. 114 (1992) 1495;
(c) B. Krieg, G.Z. Manecke, Naturforschung 22b (1967) 132;
(d) R. Consonni, P.D. Croce, R. Ferraccioli, C.L. Rosa, J. Chem Res. (S) 188 (1991);
(e) C.F. Claiborne, N.J. Liverton, K.T. Nguyen, Tetrahedron Lett. 39 (1998) 8939;
(f) S. Balalaie, M.M. Hashemi, M. Akhbari, Tetrahedron Lett. 44 (2003) 1709;
(g) S. Balalaie, A. Arabanian, M.s. Hashtroudi, Monatsh. Chem. 131 (2000) 945.
[15] A. Corma, H. Garcia, Adv. Synth. Catal. 348 (2006) 1391.
[16] (a) A.K. Chakraborthi, R. Gulhane, Chem. Commun. (2003) 1896;
(b) V.T. Kamble, V.S. Jamode, N.S. Joshi, A.V. Biradar, R.Y. deshmukh, Tetrahedron Lett. 47 (2006) 5573;
(c) A.T. Kahan, L.H. Choudhury, S. Ghosh, J. Mol. Catal. A: Chem. 255 (2006) 230;
(d) S. Rudrawar, R.C. Besra, A.K. Chakraborti, Synthesis (2006) 2767;
(e) A.T. Khan, T. Pravin, L.H. Choudhury, Synthesis (2006) 2497;
(f) A. Agarwal, Y.D. Vankar, Carbohydr. Res. 340 (2005) 1661;
(g) A. Agarwal, S. Rani, Y.D. Vankar, J. Org. Chem. 69 (2004) 6140;
(h) A.T. Khan, S. Ghosh, L.H. Choudhury, Eur. J. Org. Chem. (2006) 2226;
(i) G. Agnihotri, A.K. Misra, Tetrahedron Lett. 47 (2006) 3653;
(j) P. Tiwari, A.K. Misra, Tetrahedron Lett. 47 (2006) 3573, 2345;
(k) M. Maheswara, V. Siddaiah, G.L.V. Damu, C.V. Rao, ARKIVOC (2006) 201;
(l) V.T. Kamble, K.R. Kadam, N.S. Joshi, D.B. Muley, Catal. Commun. 8 (2007) 498–502;
(m) Y. Du, G. Wei, S. Cheng, Y. hua, R.J. Linhardt, Tetrahedron Lett. 47 (2006) 307;
(n) A.K. Chakraborthi, S.V. Chankeshwara, Org. Biomol. Chem. 4 (2006) 2769.
[17] (a) S. Kantevari, C.K.S. Nair, M. Pardhasaradhi, Synthesis (2004) 506;
(b) S. Kantevari, C.K.S. Nair, M. Pardhasaradhi, J. Heterocycl. Chem. 43 (2006) 1353–1356.
[18] Recent publications on the synthesis of 1,2,4,5-tetrasubstituted imidazoles:
(a) S. Balalaie, A. Arabanian, Green Chem. 2 (2000) 274;
(b) Y. Xu, Y.-Z. Liu, L. Rui, L. Liu, Q.-X. Guo, Heterocycles 63 (2004) 87;
(c) A.R. Karimi, Z. Alimohammadi, J. Azizian, A.A. Mohammadi, M.R. Mohammadizadesh, Catal. Commun. 7 (2006) 728;
(d) M.M. Heravi, F. Derikvand, F.F. Bamoharram, J. Mol. Catal. A: Chem. 263 (2006) 112–114;
(e) E. Gelens, F.J.J. De Kanter, R.F. Schmitz, L.A.J.M. Sliedregt, B.J. Van Steen, C.G. Kruse, R. Leurs, M.B. Groen, R.V.A. Orru, Mol. Div. 10 (2006) 17;
(f) D.R.J. Acke, R.V.A. Orru, C.V. Stevens, QSAR Comb. Sci. 25 (2006) 474;
(g) M. Kidwai, S. Saxena, Ruby, S. Rastogi, Bull. Korean Chem. Soc. 26 (2005) 2051;
(h) M. Kidwai, P. Mothsra, Tetrahedron Lett. 47 (2006) 5029;
(i) A.Y.U. Usyatinsky, Y.L. Khmelnitsky, Tetrahedron Lett. 41 (2000) 5031;
(j) S. Sarshar, D. Siev, A.M.M. Mjalli, Tetrahedron Lett. 37 (1996) 835.