Available online at www.sciencedirect.com
ScienceDirect
Journal of Molecular Catalysis A: Chemical 263 (2007) 143–148
JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL
www.elsevier.com/locate/molcata

Short communication

A novel environmentally friendly process for carbon–sulfur bond formation catalyzed by montmorillonite clays

Gaurav Sharma, Raj Kumar, Asit K. Chakraborti *

Department of Medicinal Chemistry, National Institute of Pharmaceutical Education and Research (NIPER), Sector 67, S.A.S. Nagar, Punjab 160062, India

Received 5 July 2006; received in revised form 5 August 2006; accepted 8 August 2006
Available online 15 August 2006

Abstract

Montmorillonite clays are reported as efficient, inexpensive, and reusable catalysts for carbon–sulfur bond formation by conjugate addition of thiols to α,β-unsaturated ketones/ester/nitrile. The reaction of aryl and aryl alkyl thiols with cyclic/acyclic α,β-unsaturated ketones/ester afforded excellent yields after 5 min to 20 h. The reaction rate was found to be influenced by the (i) size of the ring in case of cyclic enone, (ii) electronic nature of the thiol, and (iii) presence of aryl/alkyl substituent at the β position of the acyclic α,β-unsaturated ketone/nitrile. The conjugate addition of thiols took place at faster rates for five-membered and acyclic α,β-unsaturated ketones than the six-membered analogue. Aryl thiols reacted at faster rates than aryl alkyl and alkane thiols and the differential reaction rates were attributed to the relative acidic strength of the thiols. The reaction of α,β-unsaturated ketones having an aryl/alkyl group at the β-carbon took longer times and higher temperature. The difference in the reactivity between six and five membered enones and various thiols was utilized to demonstrate selective thia-Michael addition reaction during intermolecular competition studies.

Keywords: Montmorillonite K 10; Montmorillonite KSF; Catalysts; Thiols; α,β-Unsaturated ketones; α,β-Unsaturated ester; α,β-Unsaturated nitrile; thia-Michael addition; Carbon–sulfur bond formation; Selectivity

1. Introduction

Carbon–sulfur bond formation by conjugate addition of thiols to α,β-unsaturated carbonyl compounds, has versatile applications in chemistry and biology as it plays critical roles in the (i) biosynthesis [1], (ii) synthesis of bioactive compounds [2], (iii) protection of the olefinic double bond of conjugated enones [3] (due to the ease of regeneration of the double bond by copper(I)-induced [4] and oxidative [3] elimination of the sulfur moiety), and (iv) generation of β-acylvinyl cation [5] and homoenolate anion [6] equivalents.

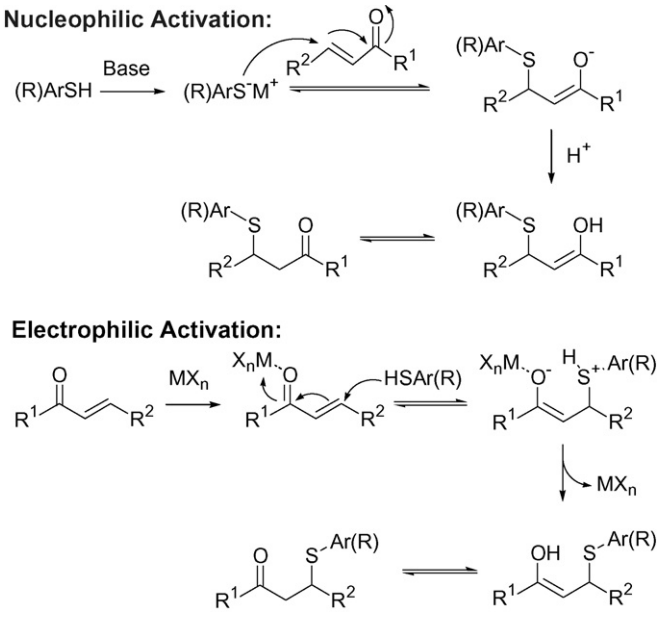
These have generated interest to organic/medicinal chemists to search for newer methodologies for thia-Michael addition reaction. Two strategies have been adopted for this purpose: (i) nucleophilic activation and (ii) electrophilic activation (Scheme 1). Under nucleophilic activation strategy, a base is used that abstracts proton from the sulfhydryl group of the thiol to generate thiolate anion which reacts at the β-carbon of the α,β-unsaturated carbonyl compound. In electrophilic activation strategy, a Lewis acid is used that coordinates with the oxygen atom of the carbonyl group of the α,β-unsaturated carbonyl compound rendering it more susceptible to nucleophilic attack at the β-carbon by the sulfur atom of the thiol. Various organic [7] and inorganic [8] bases have been used for nucleophilic activation of the thiol for the desired transformation. The methodologies developed for synthesis of β-sulfido carbonyl compounds following electrophilic activation strategy includes the use of various Lewis acid catalysts [9]. Other methods involve the use of ionic liquids [10] and β-cyclodextrine [11]. The reported methodologies have various disadvantages such as long reaction times, use of halogenated solvents, difficulty in recovery of high boiling solvents, high temperatures, special efforts required for preparation of catalysts, use of costly catalysts, moderate yields, use of toxic chemical, etc. These necessitate the development of a better method and encouraged us to develop new methodologies for thia-Michael addition [12–14].

2. Results and discussion

While designing a new methodology under the present investigation, we kept in mind the tight legislation on maintenance of

* Corresponding author. Tel.: +91 172 2214683/686; fax: +91 172 2214692.
E-mail address: akchakraborti@niper.ac.in (A.K. Chakraborti).

1381-1169/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2006.08.021



Scheme 1. Nucleophilic and electrophilic activation during thia-Michael addition reaction.

greenness in synthetic pathways and processes that demands to prevent waste, avoid use of auxiliary substances (e.g. solvents, additional reagents) and minimise energy requirement [15]. The role of catalysis in the design, development, and implementation of green chemistry has been well recognized [16,17]. Therefore, we focused our attention towards the electrophilic activation strategy (Scheme 1) and were influenced by the awareness of the use of solid acids as environmentally friendly catalysts in organic synthesis [18]. We noticed that only a few methodologies are reported for thia-Michael addition reaction using solid acids (heterogeneous catalysts) [19]. However, these catalysts are not available commercially and special efforts are required for their preparation that need additional reagents and involve tedious process such as calcination at 700–1100 °C [19b–d], treatment at 110 °C for 14 days [19a], etc. The natural abundance of clay minerals, their high surface area, sorptive and ion-exchange properties have attracted attention for catalytic applications [20] and encouraged us to exploit the catalytic activity of commercially available montmorillonite clays for the opening of epoxide rings by amines [21] and formation of *N*-*tert*-butyloxycarbonylation of amines [22]. Herein we report that montmorillonite clays (K 10 and KSF) are efficient and reusable catalysts for carbon–sulfur bond formation by conjugate addition of thiols to α,β-unsaturated carbonyl compounds.

The reaction of cyclic (six and five membered) and acyclic α,β-unsaturated ketones and α,β-unsaturated ester with various aryl and aryl alkyl thiols were carried out under the catalytic influence of montmorillonite K 10 and KSF (Table 1). The desired thia-Michael adducts were obtained in good to excellent yields. The catalyst was recovered and reused after activation without any significant detrimental effect on the catalytic activity. The reaction rate was found to be influenced by the (i) size of the ring in case of cyclic enone, (ii) electronic nature of the thiol, and (iii) presence of aryl/alkyl substituent at the β position

Table 1
Montmorillonite K 10 and KSF catalyzed carbon–sulfur bond formation by conjugate addition of thiols to various α,β-unsaturated carbonyl compounds[a,b]

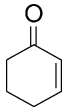
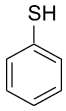
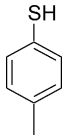
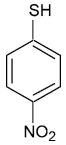
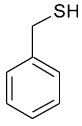
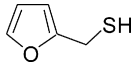
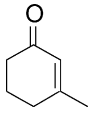
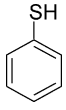
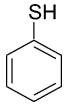
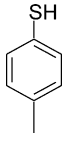
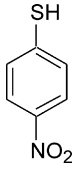
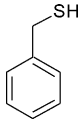
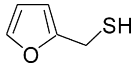
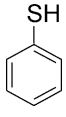
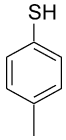
Entry	α,β-Unsaturated carbonyl compound	Thiol	Time (min)	Yield (%)[c,d]
1			15 (30)	80 (90)
2			30 (30)	82 (80)
3			10 (15)	85 (89)
4			40 (60)	91[e] (85)[e]
5			180	85[e]
6			6 h (6 h)	65[f] (60)[f]
7			5 (5)	90 (92)[g]
8			5	85
9			5 (10)	85 (82)
10			15 (25)	80 (85)
11			15	82
12			10 (15)	92 (88)
13			10	90

Table 1 (*Continued*)

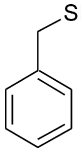
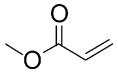
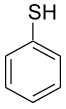
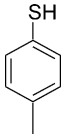
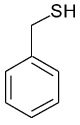
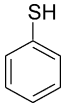
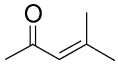
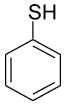
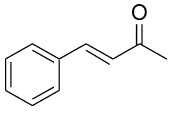
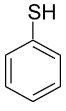
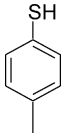
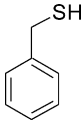
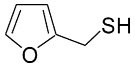
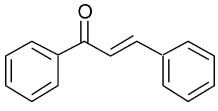
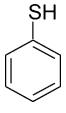
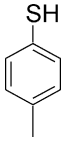
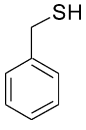
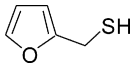
Entry	α,β-Unsaturated carbonyl compound	Thiol	Time (min)	Yield (%)[c,d]
14			20	87
15			15 (10)	92 (82)
16			15	90
17			15	95
18			20 (35)	80 (72)
19			12 h (12 h)	70[f] (65)[f]
20			120 (180)	90[h] (83)[h]
21			12 h	75[h]
22			12 h	90[h]
23			20 h	65[h]
24			5 h (6 h)	80[h] (82)[h]
25			10 h	75[h]
26			8 h	90[h]

Table 1 (*Continued*)

Entry	α,β-Unsaturated carbonyl compound	Thiol	Time (min)	Yield (%)[c,d]
27			12 h	80[h]

[a] The α,β-unsaturated carbonyl compound (2.5 mmol) was treated with the thiol (1.1 equiv.) in presence of montmorillonite K 10/KSF (10%, w/w) at room temperature (30–35 °C).

[b] The figures in parentheses are the corresponding data for montmorillonite KSF catalyzed reactions.

[c] Isolated yield of the corresponding product.

[d] Products were characterized by IR and NMR.

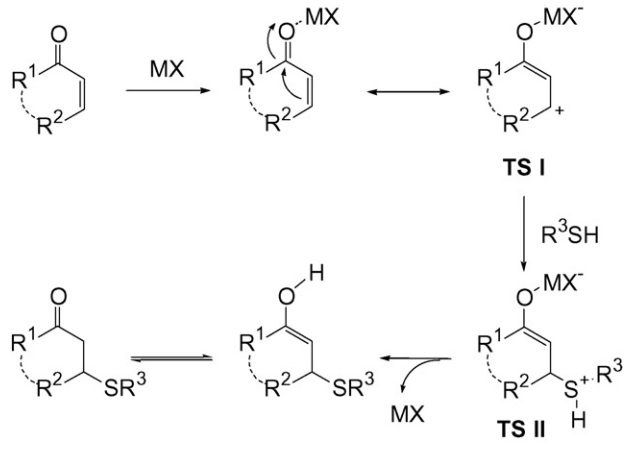
[e] The reaction was carried out at 80 °C.

[f] The reaction was carried out at 50 °C.

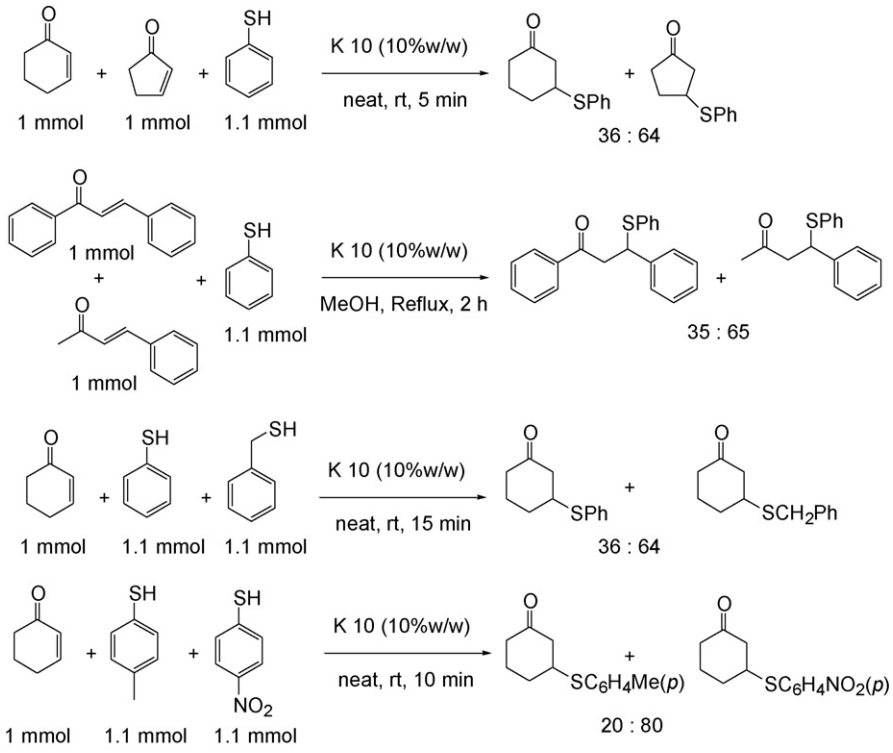
[g] The thia-Michael adduct was formed in 5% yield when the reaction was carried out for 1 h at room temperature in the absence of any catalyst.

[h] The reaction was carried out in methanol under reflux.

of the α,β-unsaturated ketone. The conjugate addition of thiols took place at faster rates for five-membered and acyclic α,β-unsaturated ketones than the six-membered analogue (compare entries 1–5 with 7–11 and 12–14, Table 1). During the reaction with a particular α,β-unsaturated carbonyl compound, aryl thiols reacted at faster rates compared to aryl alkyl thiols (compare entries 1–3 with 4 and 5, entries 7–9 with 10 and 11, entries 12 and 13 with 14, entries 20 and 21 with 22 and 23, and entry 24 with entries 26 and 27, Table 1). In case of aryl thiols, the rate of reaction was influenced by the pK_a of the SH proton rather than the relative nucleophilicity of the corresponding sulfur atom. Thus, the reactions of thiophenol were faster than those of 4-methylthiophenol with a common Michael acceptor (compare entries 1 with 2, 20 with 21, and 24 with 25, Table 1). Similarly reaction of 4-nitrothiophenol with cyclohexenone was faster than the corresponding reaction involving 4-methylthiophenol (compare entries 2 and 3, Table 1). The presence of an aryl or alkyl group at the β-position of the α,β-unsaturated ketones reduced the rate of thia-Michael addition significantly and for such substrates the reactions were carried out either on heating at 50 °C under neat condition or under reflux in MeOH (compare



Scheme 2. The role of the catalyst in the carbon–sulfur bond formation via thia-Michael addition.



Scheme 3. Selectivity in carbon–sulfur bond formation via thia-Michael addition reaction during intermolecular competition studies.

entry 1 with 6, entry 12 with 19, entries 12–14 with 20–22 and 24–26, Table 1).

These observations can be explained by the tentative mechanism depicted in Scheme 2 that describes the role of the catalyst in promoting the thia-Michael addition reaction. Coordination of the metal cationic site of the catalyst with the carbonyl oxygen atom of the α,β-unsaturated carbonyl compound induces electrophilic activation and makes the β-carbon atom electron deficient (TS I). Nucleophilic attack at the electron deficient β-carbon atom of the α,β-unsaturated carbonyl compound by the sulfur atom of the thiol generates the TS II which on intramolecular proton transfer from the sulfonium moiety to the oxyanionic site liberates the catalyst and forms the enol of the resultant Michael adduct. Therefore, structural modification on the Michael acceptor that can reduce the electrophilic character of the β-carbon atom of the α,β-unsaturated carbonyl compound should retard the rate of the conjugate addition reaction. Since an aryl or alkyl group can decrease the positive charge developed at the β-carbon atom of the α,β-unsaturated carbonyl compound due to the resonance effect, 3-aryl/alkyl substituted enones required elevated temperature. Apart from the electronic effect of the 3-aryl/alkyl substituent, the steric factor also contributes to the overall decrease in the rate of Michael addition for such acceptors. As the liberation of the catalyst depends on the efficiency of the proton transfer in TS II, thiols with stronger acidic property are expected to react at faster rates. Hence, aryl thiols took shorter times compared to aryl alkyl thiols during the reaction with a common substrate as the SH proton of aryl thiols are more acidic than that of the aryl alkyl thiols. The greater acidic property the SH proton of thiophenol compared to that of 4-methylthiophenol makes the former thiol to react at a faster rate. Although the sulfur atom of 4-nitrothiophenol is expected to be less nucleophilic than that of 4-methylthiophenol, the former thiol reacted at a faster rate due to more efficient proton exchange in the TS II formed during the reaction of cyclohexenone with 4-nitrothiophenol as 4-nitrothiophenol is a stronger proton donor than 4-methylthiophenol.

The difference in the rate of reaction between cyclohexenone and cyclopentenone encouraged us to carry out selective carbon–sulfur bond formation via the thia-Michael addition during inter-molecular competition studies (Scheme 3). The treatment of an equimolar mixture of cyclohexenone and cyclopentenone with thiophenol (1.1 equiv.) afforded the corresponding thia-Michael adducts in a ratio of 36:64 (GCMS) after 5 min at RT under neat condition. The difference in the rate of reaction 1,3-diphenylpropenone and 4-phenyl-3-butene-2-one resulted in a 35:65 selectivity (GCMS) when an equimolar mixture of 1,3-diphenylpropenone and 4-phenyl-3-butene-2-one was treated with thiophenol in MeOH under reflux for 2 h. In the following representative examples the difference in the reactivity of thiols with a common Michael acceptor was exploited to demonstrate selectivity during inter-molecular competition reactions. Thus, when cyclohexenone was treated with an equimolar mixture of thiophenol and α-toluenethiol for 15 min at RT under neat condition, a 64:36 selectivity (GCMS) was observed in favour of the Michael adduct formation with the aryl thiol. The corresponding reaction of cyclohexenone with an equimolar mixture of 4-nitrothiophenol and 4-methylthiophenol afforded an 80:20 selectivity (GCMS) after 10 min at RT under neat condition.

3. Conclusion

We have described herein commercially available montmorillonite K 10 and KSF as efficient and reusable catalysts for chemoselective carbon–sulfur bond formation by conjugate addition of thiols to α,β-unsaturated carbonyl compounds. The advantages include, (i) the use of a cheap, easy to handle, and reusable catalyst, (ii) ease of product isolation by filtration, (iii) excellent selectivity, and (iv) high yields.

4. Experimental

The ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance DPX 300 (300 MHz) spectrometer in $CDCl_3$ using TMS as internal standard. The IR spectra were recorded on Nicolet Impact 400 spectrometer as KBr pellets for solid and neat for liquid samples. The reactions were monitored by TLC (silica gel-G) and Shimadzu QP 5000 GCMS. Evaporation of solvents was performed at reduced pressure, using a Büchi rotary evaporator.

4.1. Typical procedure for carbon–sulfur bond formation by thia-Michael addition

4.1.1. Method A

Montmorillonite K 10 (25 mg, 10% (w/w)) was added to a magnetically stirred mixture of cyclohexenone **1** (0.24 g, 2.5 mmol) and thiophenol **2** (0.303 g, 2.75 mmol, 1.1 equiv.) at room temperature (30–35 °C). The mixture was stirred until completion of reaction (TLC, 30 min), diluted with EtOAc (10 mL) and filtered through a plug of cotton. The residue was washed with EtOAc (2 × 5 mL) and the combined filtrates were concentrated under reduced pressure to afford an oil which on passing through a column of silica-gel and elution with EtOAc-hexane afforded β-phenylthiocyclohexanone **3** (0.473 g, 92%) as colourless oil, identical (IR, NMR and MS) with an authentic sample. The cotton plug containing the catalyst was dipped into EtOAc (15 mL) in a beaker (25 mL) when the montmorillonite K 10 settled down to the bottom of the beaker. The cotton was removed and the EtOAc decanted off. The recovered catalyst after being air dried and treated at 100 °C for 2 h under reduced pressure (5 mm Hg) was reused to afford **3** in 89% yields during a fresh batch of reaction of **1** with **2**.

4.1.2. Method B

Treatment of **1** (0.24 g, 2.5 mmol) with **2** (0.303 g, 2.75 mmol, 1.1 equiv.) in the presence of montmorillonite KSF (25 mg, 10% (w/w)) at room temperature (30–35 °C) followed by usual work-up as described for Method A afforded **3** (0.463 g, 90%, entry 1, Table 1), identical (IR, ^{1}H and ^{13}C NMR, and EIMS) to an authentic sample. The catalyst was recovered and used after being reactivated as described in method A providing **3** in 85% yields during a fresh batch of reaction of **1** with **2**.

The remaining reactions were carried out following these general procedures (Methods A or B). The physical data (mp, IR and NMR) of known compounds were found to be identical with those of authentic samples. Unknown compounds were characterized by spectral (IR and NMR) and elemental analyses.

4.2. Typical procedure for selective thia-Michael addition reaction during intermolecular competition studies

Montmorillonite K 10 (10 mg, 10% (w/w)) was added to a magnetically stirred mixture of **1** (96 mg, 1 mmol), 4-methylthiophenol (136.4 mg, 1.1 mmol) and 4-nitrothiophenol (170.5 mg, 1.1 mmol) at room temperature (30–35 °C). The mixture was stirred for 10 min, diluted with EtOAc (3 mL) and filtered through a plug of cotton. The residue was washed with EtOAc (2 × 2 mL) and the combined filtrates were concentrated under reduced pressure to afford the crude mixture of products (345 mg, 92%) was found to contain 3-(4-methylphenylsulfanyl)cyclohexanone and 3-(4-nitrophenylsulfanyl)cyclohexanone in a ratio of 20:80 (GCMS).

4.3. 3-(Furan-2-ylmethylsulfanyl)-cyclopentanone (entry 9, Table 1)

IR (Neat) cm^{-1}: 2927, 1742, 1151; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.27 (s, 1H), 6.32 (s, 1H), 6.20 (s, 1H), 3.84–3.73 (m, 2H), 3.45–3.36 (m, 1H), 2.61–2.52 (m, 1H), 2.47–2.28 (m, 2H), 2.24 (m, 2H), 1.97–1.93 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 217.12, 151.85, 142.76, 111.09, 108.05, 46.01, 40.70, 37.76, 30.10, 28.47. Elemental Anal. $(CHNS)_{Cal}$: C = 61.20%, H = 6.16%, S = 16.34%; $(CHNS)_{obs}$: C = 61.23%, H = 6.18%, S = 16.32%.

4.4. 3-(4-Nitro-phenylsulfanyl)-cyclopentanone (entry 10, Table 1)

Mp: 64–66 °C; IR (KBr) cm^{-1}: 1742; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.15 (d, 2H, J = 8.6 Hz), 7.40 (d, 2H, J = 8.6 Hz), 4.18–4.13 (m, 1H), 2.84–2.75 (m, 1H), 2.56–2.47 (m, 2H), 2.39–2.28 (m, 2H), 2.17–2.11 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 215.55, 146.16, 128.43, 126.93, 124.96, 45.37, 42.00, 37.12, 29.69. Elemental Anal. $(CHNS)_{Cal}$: C = 55.68%, H = 4.67%, N = 5.90%, S = 13.51%; $(CHNS)_{obs}$: C = 55.64%, H = 4.64%, N = 5.92%, S = 13.54%.

References

[1] E. Fujita, Y. Nagao, Bioorg. Chem. 6 (1977) 287–309.
[2] (a) A.L. Fluharty, in: S. Patai (Ed.), The Chemistry of the Thiol Group, Wiley–Interscience, New York, 1974, p. 589, Part 2;
(b) A. Kumar, R.V. Salunkhe, R.A. Rane, S.Y. Dike, J. Chem. Soc., Chem. Commun. (1991) 485–486.
[3] B.M. Trost, D.E. Keeley, J. Org. Chem. 40 (1975) 2013.
[4] T. Cohen, A.J. Mura Jr., D.W. Shull, E.R. Fogel, R.J. Ruffner, J.R. Falck, J. Org. Chem. 41 (1976) 3218–3219.
[5] P. Bakuzia, M.L.F. Bakuzis, J. Org. Chem. 46 (1981) 235–239.
[6] J.P. Cherkauskas, T. Cohen, J. Org. Chem. 57 (1992) 6–8.
[7] (a) C.D. Hurd, L.L. Gershbein, J. Am. Chem. Soc. 69 (1947) 2328–2335;
(b) H. Hiemstra, H. Wynberg, J. Am. Chem. Soc. 103 (1981) 417–430;
(c) J. Skarzewski, M. Zielinska-Blajet, I. Turowska-Tyrk, Tetrahedron Asymm. 12 (2001) 1923–1928;
(d) V. Athawale, N. Manjrekar, Tetrahedron Lett. 42 (2001) 4541–4543;

(e) P. McDaid, Y. Chen, L. Deng, Angew. Chem. Int. Ed. Engl. 41 (2002) 338–340;
(f) A. Kamimura, N. Murakami, K. Yokota, M. Shirai, H. Okamoto, Tetrahedron Lett. 43 (2002) 7521–7523;
(g) B.N. Naidu, M.E. Sorenson, T.P. Connolly, Y. Ueda, J. Org. Chem. 68 (2003) 10098;
(h) P. Bernal, J. Tamariz, Tetrahedron Lett. 47 (2006) 2905–2909.

[8] (a) I. Kuwajima, T. Murofushi, E. Nakamura, Synthesis (1976) 602–604;
(b) K. Nishimura, M. Ono, Y. Nagaoka, K. Tomioka, J. Am. Chem. Soc. 119 (1997) 12974–12975;
(c) E. Emori, T. Arai, H. Sasaki, M. Shibasaki, J. Am. Chem. Soc. 120 (1998) 4043–4044;
(d) A. Kamimura, F. Kawahara, Y. Omata, N. Murakami, R. Morita, H. Otake, H. Mitsudera, M. Shirai, A. Kakehi, Tetrahedron Lett. 42 (2001) 8497–8500;
(e) M. Ménand, V. Dalla, Synlett (2005) 95–98;
(f) L. Yang, L.-W. Xu, C.-G. Xia, Tetrahedron Lett. 46 (2005) 3279.

[9] (a) CdI_2: M. Saito, M. Nakajima, S. Hashimoto, Tetrahedron 56 (2000) 9589;
(b) $InBr_3$: M. Bandini, P.G. Cozzi, M. Giacomini, P. Melchiorre, S. Selva, A. Umani-Ronchi, J. Org. Chem. 67 (2002) 3700–3704;
(c) $Hf(OTf)_3$: S. Kobyashi, C. Ogawa, M. Kawamura, M. Sugiura, Synlett (2001) 983–985;
(d) $Bi(NO_3)_3$: N. Srivastava, B.K. Banik, J. Org. Chem. 68 (2003) 2109–2114;
(e) $Bi(OTf)_3$: M.M. Alam, R. Varala, S.R. Adapa, Tetrahedron Lett. 44 (2003) 5115–5119;
(f) I_2: C.-M. Chu, S. Gao, M.N.V. Sastry, C.-F. Yao, Tetrahedron Lett. 46 (2005) 4971–4974;
(g) $InCl_3$: B.C. Ranu, S.S. Dey, S. Samanta, ARKIVOC (iii) (2005) 44–50;
(h) SDS: H. Firouzabadi, N. Iranpoor, A.A. Jafari, Adv. Synth. Catal. 347 (2005) 655.

[10] (a) J.S. Yadav, B.V.S. Reddy, G. Baishya, J. Org. Chem. 68 (2003) 7098–7100;
(b) B.C. Ranu, S.S. Dey, A. Hajra, Tetrahedron 59 (2003) 2417–2421;
(c) B.C. Ranu, S.S. Dey, Tetrahedron 60 (2004) 4183–4188.

[11] N.S. Krishnaveni, K. Surendra, K.R. Rao, Chem. Commun (2005) 669.

[12] S.K. Garg, R. Kumar, A.K. Chakraborti, Tetrahedron Lett. 46 (2005) 1721–1724.

[13] S.K. Garg, R. Kumar, A.K. Chakraborti, Synlett (2005) 1370–1374.

[14] G.L. Khatik, R. Kumar, A.K. Chakraborti, Org. Lett. 8 (2006) 2433–2436.

[15] J.H. Clark, Green Chem. (1999) 1–8.

[16] P.T. Anastas, L.B. Bartlett, M.M. Kirchhoff, T.C. Williamson, Catal. Today 55 (2000) 11–22.

[17] J.H. Clark, Pure Appl. Chem. 73 (2001) 103–111.

[18] K. Wilson, J.H. Clark, Pure Appl. Chem. 72 (2000) 1313–1319.

[19] (a) Zeolites: R. Sreekumar, P. Rugmini, R. Padmakumar, Tetrahedron Lett. 38 (1997) 6557–6560;
(b) $Na_2CaP_2O_7$: M. Zahouily, Y. Abrouki, A. Rayadh, Tetrahedron Lett. 43 (2002) 7729–7730;
(c) KF-NP: Y. Abrouki, M. Zahouily, A. Rayadh, B. Bahlaouan, S. Sebti, Tetrahedron Lett. 43 (2002) 8951–8953;
(d) Fluorapatite: M. Zahouily, Y. Abrouki, A. Rayadh, S. Sebti, H. Dhimane, M. David, Tetrahedron Lett. 44 (2003) 2463–2465;
(e) Nafion® SAC-13: T.C. Wabnitz, J.-Q. Yu, J.B. Spencer, Synlett (2003) 1070–1072;
(f) $H_3PW_{12}O_{40}$: H. Firouzabadi, N. Iranpoor, A.A. Jafari, Synlett (2005) 299–303.

[20] R.S. Verma, Tetrahedron 58 (2002) 1235–1255.

[21] A.K. Chakraborti, A. Kondaskar, S. Rudrawar, Tetrahedron 60 (2004) 9085–9091.

[22] S.V. Chankeshwara, A.K. Chakraborti, J. Mol. Catal. A: Chem. 253 (2006) 198–202.