Available online at www.sciencedirect.com

ScienceDirect

Tetrahedron Letters 47 (2006) 7375–7380

Tetrahedron Letters

The iron(III) chloride-mediated 1,4-addition of mercaptans to α,β-unsaturated ketones and esters under solvent free conditions

Cheng-Ming Chu, Wan-Ju Huang, Chaowei Lu, Pohsi Wu, Ju-Tsung Liu and Ching-Fa Yao*

Department of Chemistry, National Taiwan Normal University, 88, Sec. 4, Tingchow Road, Taipei 116, Taiwan, ROC

Received 28 May 2006; revised 27 July 2006; accepted 31 July 2006
Available online 28 August 2006

Abstract—The 1,4-addition of various thiols to α,β-unsaturated ketones was completed rapidly in the presence of a catalytic amount (2–3 mol %) of anhydrous iron(III) chloride under solvent free conditions and an air atmosphere. Anhydrous iron(III) chloride is more active than that of other ferric salts. With more reactive and/or less steric reagents (**1a**–**c** and/or **2a**–**2c**), expeditious conditions (short reaction times at room temperature) could be employed. With less reactive and/or steric reagents (**1d**–**g** and/or **2d**–**e**), a slight increase in reaction time was required, but high yields were obtained. The $FeCl_3$ catalyst causes preferential interactions with α,β-unsaturated ketones present in the reaction.

1. Introduction

The base catalyzed 1,4-addition of thiols to α,β-unsaturated carbonyl compounds to form carbon–sulfur bonds constitutes a key reaction in a variety of biosynthetic processes as well as in organic synthesis.[1,2] Traditionally, the 1,4-addition of mercaptans is catalyzed by strong bases such as alkali metal alkoxides, hydroxides,[3] and amines.[4,5] Alternatively, these reactions can also proceed using different Lewis acids such as $Hf(OTf)_3$,[6a] $InBr_3$,[6b] $Bi(NO_3)_3$,[6c] $Bi(OTf)_3$,[6d] $InCl_3$,[6e] $Cu(BF_4)_2$.[6f] and $Zn(ClO_4)_2{\cdot}6H_2O$.[6g] However the use of either strongly acidic or basic conditions frequently leads to the formation of undesirable side products owing to competing reactions, such as polymerization, self-condensation and rearrangements.[7] Chakraborti et al. recently reported on the conjugate addition of thiols to α,β-unsaturated carbonyl compounds in water at room temperature without the use of any metal catalyst leading to the easy and highly efficient synthesis of α-sulfido carbonyl compounds. However, there has been no straightforward synthesis of these uncomplicated enones and methyl acrylate to confirm the preparation of typical enones (e.g., chalcone and *trans*-4-phenyl-3-butene-2-one, etc.), which cannot react in water even under forcible conditions.[8]

In addition to the above description, these reactions can also be conducted with zeolites and other heterogeneous systems.[9] Since organosulfur compounds have become increasingly useful and important in the synthesis of biologically active compounds such as the calcium antagonist diltiazem,[10] the development of simple, convenient and environmentally benign approaches are highly desirable.

Iron has enormous practical advantages as a catalyst due to its low cost, ample supply, environmental friendliness and lack of toxicity. Iron catalysis therefore is currently being intensively studied to achieve a controlled organic synthesis, especially in the vinylogous Michael reaction and cross-coupling reactions.[11] Considerable progress in this field has recently been made by Nakamura[12] and others.[13] Iron catalysis not only improves many known catalytic processes but also brings about new possibilities in synthesis. Thus, our goal was to evaluate the catalytic efficiency of various commercially available ferric mediated catalysts as a new and efficient catalyst for thia-Michael addition reactions.

2. Results and discussion

In a typical reaction, *trans*-4-phenyl-3-butene-2-one **1d** was used as a representative of α,β-unsaturated ketone

---

Keywords: 1,4-Addition; Anhydrous iron(III) chloride; α,β-Unsaturated ketones; Solvent free.

* Corresponding author. Tel./fax: +886 2 29309092; e-mail: cheyaocf@scc.ntnu.edu.tw

0040-4039/$ - see front matter © 2006 Published by Elsevier Ltd.
doi:10.1016/j.tetlet.2006.07.151

1. Initially, endeavours were mainly focused on the efficiency of the uncatalyzed reaction. Several blank reactions were conducted at this stage between **1d** and 1.1 equiv of thiophenol **2a** under solvent free conditions under different atmospheres. Only a slight conversion of **1d** to **3da** was observed, suggesting that the rate of the uncatalyzed reaction is not favourable for 1,4-addition. No significant change was observed in the reaction mixture, when the reactions were conducted under different atmospheres such as Ar, air and pure oxygen.

When **1d** was treated with thiophenol **2a** under neat conditions in the absence or presence of $FeCl_3$ at room temperature, the reactions were monitored by ^{1}H NMR and the yields were confirmed by GC and the optimum results are shown in Table 1.

The best result was observed when the reaction was carried out in the presence of 2 mol % of anhydrous Fe(III)Cl_3 to quantitatively afford the desired conjugate addition product **3aa** after 10 min (entries 4–5 of Table 1). The poor catalytic activity of Fe(II) can probably be explained by its lower oxidation state so that the oxophilicity of Fe(II) ion significantly decreased compared to that of Fe(III) ion. The parallel of the catalytic activity of the metal chloride was also observed in metal nitronate-catalyzed and sulfonate-catalyzed reactions. However, the inferior results obtained for Fe(III)$(NO_3)_3$·$9H_2O$ and Fe(III)$(SO_4)_3(NH_4)_2SO_4$·$24H_2O$ (entries 7 and 8) are probably due to the poor electron-withdrawing nature, which makes the central metal ion more oxophilic. Thus, Fe(III) salts are susceptible to hydrolytic decomposition in the presence of trace amounts of moisture and lose their catalytic properties.

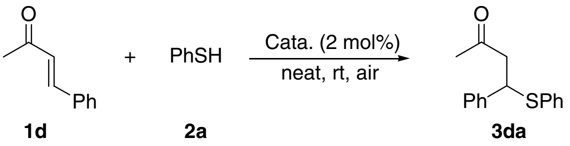
A solvent effect was observed in the reaction of **1d** with **2a** in the presence of a catalytic amount of anhydrous Fe(III)Cl_3 (Table 2). The catalyst was compatible with various solvents, affording high yields of **3da**.

The results indicate that anhydrous Fe(III)Cl_3 retained its catalytic activity in solvents with poor and weak coordinating properties, irrespective of the high polarity ($\varepsilon = 37$) of a hydroxylic solvent such as DMF (entry 8). In the presence of 2 mol % anhydrous iron(III) chloride, the reaction in an aprotic solvent such as in acetone and DMF gave only 84% and 28% yields of **3da**, respectively, along with some unreacted **1a** after 96 h (entries 3 and 8). The inferior results are probably due to its specific affinity towards the cation, which interferes with the formation of a coordinate bond between the carbonyl oxygen atom and the Fe^{3+} ion. Although a similar interference of coordination between the carbonyl substrate and the Fe^{3+} ion would be expected to take place in a protic solvent such as MeOH, the hydrogen bonding effect of MeOH probably compensates for this. It is noteworthy that the treatment of **1d** with **2a** in 2 mol % of anhydrous Fe(III)Cl_3, in a solvent free system, afforded the corresponding Michael adduct **3da** in quantitative yield within 10 min at ambient temperature (entry 2 of Table 1).

In this reaction, the efficiency of the metallic catalyst was strongly influenced by the nature of the metal ion. The reactivity of various thiols and enones was examined in anhydrous $FeCl_3$ and the results are presented in Eq. 1 and Table 3.

Among the above reagents, anhydrous $FeCl_3$ was found to be superior in terms of conversion. The yields are always very high (>90%) and the product is formed within a few minutes. For example, the treatment of 2-cyclohexen-1-one **1a** with **2a** in a solvent free system in the presence of 2 mol % of anhydrous $FeCl_3$ gave the corresponding 1,4-adduct in 94% yield (entry 1 of

Table 1. Reaction of **2a** with **1d** in the presence of various ferrous catalyst under air atmosphere



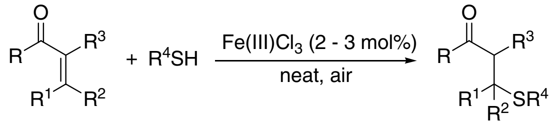
Entry	Catalyst[a]	Time	**3da**[b] (%)	Recovered **1d** (%)[b]
1	Non-additive[c]	3 h	tr	99
2	Non-additive	3 h	2	98
3	Non-additive[d]	3 h	4	96
4	Fe(III)Cl_3[c]	10 min	98	tr
5	Fe(III)Cl_3	10 min	99	—
6	Fe(III)Cl_3[d]	10 min	99	—
7	Fe(III)$(NO_3)_3$·$9H_2O$	8 h	99	tr
8	Fe(III)$(SO_4)_3(NH_4)_2SO_4$·$24H_2O$	72 h	92	8
9	Fe(II)Cl_2	72 h	61	39
10	Fe(II)SO_4·$7H_2O$	72 h	68	32
11	Fe(II)$SO_4(NH_4)_2SO_4$·$6H_2O$	72 h	75	25

[a] All reactions were performed by using 2 mmol of **1d** and 2.2 mmol of **2a** in the presence of different ferrous catalyst under air atmosphere.

[b] The crude mixture was worked up in ice cold brine solution and then extracted with diethyl ether, the yield was measured by GC by using naphthalene as the internal standard.

[c] The reaction was carried out under argon atmosphere.

[d] The reaction was carried out under oxygen atmosphere.



(1)

1 **2** **3**

1a: R + R^1 = $-(CH_2)_3-$, R^2 = R^3 = H
1b: R + R^1 = $-(CH_2)_2-$, R^2 = R^3 = H
1c: R = Me, R^1 = R^2 = R^3 = H
1d: R = Me, R^2 = Ph, R^1 = R^3 = H
1e: R = Ph, R^2 = Ph, R^1 = R^3 = H
1f: R = Ph, R^1 = R^2 = Me, R^3 = H
1g: R = Me, R^2 + R^3 = $-(CH_2)_4-$, R^1 = H

2a: R^4 = Ph
2b: R^4 = c-C_6H_{11}
2c: R^4 = $C_6H_5CH_2$
2d: R^4 = C_3H_7
2e: R^4 = CH_2=$CHCH_2$

Table 3). The reaction proceeded rapidly and was complete at room temperature within 5 min without the necessity of any acid or base catalyst. The product also could be easily isolated by simple extraction with diethyl ether. Encouraged by the result using **1a** and **2a**, we turned our attention to various thiols and enones. Interestingly, numerous cyclic and acyclic enones including benzilideneacetone **1d** underwent a 1,4-addition with a range of thiols under mild reaction conditions to afford the corresponding Michael adducts (Table 3).

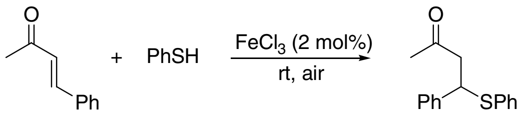
It is noteworthy that the highly steric cyclohexanethiol **2b** and the unstable allyl mercaptan **2e** also afforded the 1,4-adduct in 96% and 91% yield, respectively, after isolation (entries 13 and 16). Sterically hindered enones **1e–g** also gave the desired 1,4-adducts in excellent yields (entries 17–19, Table 3). Furthermore, the bonding resonance effect of the β-phenyl substituent in **1d** and **1e** makes these enones less electrophilic compared to **1a–c**. The combined steric and resonance effects of the β-phenyl substituent make conjugate addition reactions of **1d** and **1e**, with particular thiols, less active compared to those of **1a–c** (entries 1–17 of Table 3). The similarity of the results for **1d**, **1e** and **1f** suggest that the α,β-unsaturated ketone exhibited electronic effects in controlling the conjugate addition. The resonance effect of the methyl group in **1d** (R = Me) increased the electron density at the carbonyl oxygen and enhanced the coordinating ability of the compound with Fe^{3+}. On the contrary, the phenyl group in **1e** and **1f** (R = Ph), decreased the electron density at the carbonyl oxygen by inductive and resonance effects. Therefore, the reaction of **1e** and **1f** with **2a** required a longer time and a higher temperature compared to the corresponding reaction of **1d** (entries 12–18, Table 3). It is noteworthy that no byproducts resulting from 1,2-addition or bis-addition were observed by ^{1}H NMR and GC. Moreover, the reactions were clean, high yielding and sometimes quantitative. Compared to conventional methods, enhanced reaction rates, improved yields and excellent 1,4-selectivity are features observed in catalysis by anhydrous Fe(III)Cl_3.

One plausible mechanism for this reaction is proposed and is based on the oxidizing characteristics of Fe(III), which is shown as Scheme 1. The use of a strong oxidizing catalyst such as Fe(III)Cl_3 could easily form a strong coordinate bond with the carbonyl oxygen of the α,β-unsaturated ketone, which in turn, increases the electrophilicity of the β-carbon in assisting the conjugate addition reaction to proceed under mild conditions with short reaction times.

The excellent results obtained for $FeCl_3$ in promoting the addition of various thiols to different enones encouraged us to design and optimize synthetic strategies for α,β-unsaturated ester catalyzed processes. The 1,4-addition of thiophenol **2a** to the resulting 1,4-adduct ester took place smoothly as shown by the data in Table 4.

It is noteworthy that increased catalytic amounts (15 mol %) of anhydrous Fe(III)Cl_3 and an extended reaction time are necessary for a complete reaction. The reaction is dependent on sterically hindered and electronic effects of the esters for achieving good yields (entries 1, 2 and 4 of Table 4) except for the *trans*-ethyl cinnamate (entry 3), in which case the reaction was very difficult. This torpor is presumably due to the presence of

Table 2. Reaction of **1a** with **2a** in various solvents under the catalytic influence of $FeCl_3$[a]



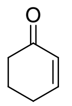
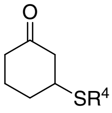
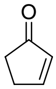
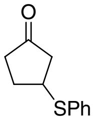
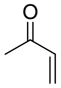
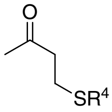
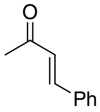
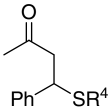
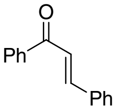
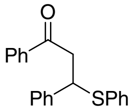
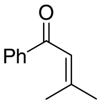
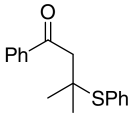
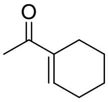
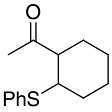
1d **2a** **3da**

Entry	Solvent[a]	Time (h)	**3da**[b] (%)	Recovered **1d**[b] (%)
1	CH_2Cl_2	4	100	—
2	MeCN	2.5	100	—
3	Me_2CO	96	84	16
4	Et_2O	2.5	100	—
5	$CH_3(CH_2)_4CH_3$	2	100	—
6	MeOH	28	100	—
7	EtOAc	2	100	—
8	DMF	96	28	44

[a] All reactions were performed by using 2 mmol of **1d** and 2.2 mmol of **2a** in 2 mL of argon degassed solvent under air atmosphere.

[b] The crude mixture was worked up in ice cold brine solution and then extracted with diethyl ether, the yield was measured by GC by using naphthalene as the internal standard.

Table 3. Fe(III)Cl$_3$-Catalyzed conjugate addition of thiols to α,β-unsaturated ketones[a]

Entry	**1**	**2**	Temp (°C)/time	Product **3**		Yield[b] (%)
1		**2a**	rt/5 min		**3aa**	94
2		**2b**	rt/5 min		**3ab**	93
3		**2c**	rt/5 min		**3ac**	95
4		**2d**	rt/5 min		**3ad**	94
5		**2e**	rt/5 min		**3ae**	93
6		**2a**	rt/5 min		**3ba**	90
7		**2a**	rt/5 min		**3ca**	92
8		**2b**	rt/5 min		**3cb**	92
9		**2c**	rt/5 min		**3cc**	93
10		**2d**	rt/5 min		**3cd**	90
11		**2e**	rt/5 min		**3ce**	91
12		**2a**	rt/10 min		**3da**	94
13		**2b**	rt/10 min		**3db**	96
14		**2c**	rt/10 min		**3dc**	93
15		**2d**	rt/10 min		**3dd**	92
16		**2e**	rt/10 min		**3de**	91
17[c]		**2a**	50/10 min		**3ea**	96
18[d]		**2a**	50/20 min		**3fa**	94
19		**2a**	50/12 min		**3ga**	92 (98:1)[e]

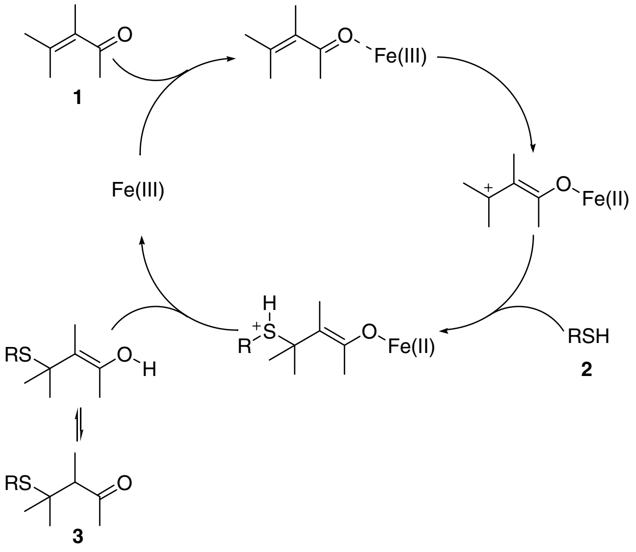
[a] All reactions were performed by using 1 equiv (2 mmol) of enones **1** and 1.1 equiv (2.2 mmol) of mercaptan **2** in the presence of 2 mol % of Fe(III)Cl$_3$ under solvent free condition and air atmosphere.

[b] Isolated yields.

[c] Reaction was carried out in 1 mL of EtOAc.

[d] 3 mol % of FeCl$_3$ was used.

[e] The distereomeric ratio was determined by GC.

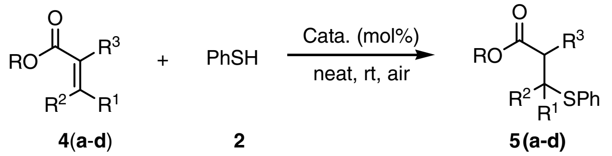


Scheme 1. Plausible cyclization mechanism of Fe(III)Cl$_3$ as a catalyst for Michael addition of thiols to α,β-unsaturated ketones.

the 2-phenyl group of **4d**, which sterically hinders the approaching thiol **2a**. Furthermore, the inferior results are probably due to the specific affinity and the electronic effect of the methoxyl group in the ester, which interferes with the formation of a coordinate bond between the carbonyl oxygen atom and the Fe^{3+} ion. However, a double electronic effect of a α-carbonyl ester substituent proceeded efficiently, giving excellent yields within 30 min at room temperature (Table 4, entry 4).

In summary, we describe a simple, convenient and efficient protocol for the 1,4-conjugate addition of thiols to α,β-unsaturated ketones and esters using anhydrous iron chloride as catalyst under mild and neutral conditions. Anhydrous iron chloride plays the role of a promoter. The enones exhibit an enhanced reactivity in anhydrous iron chloride thereby reducing the reaction times and significantly improving the yields. The simple experimental procedure, which is environmentally friendly, is expected to contribute to the development

Table 4. $FeCl_3$-Catalyzed conjugate addition of thiophenol to α,β-unsaturated esters[a]



Entry	R	R^1	R^2	R^3	Catalyst (mol %)	Time	5^b (%)
1	Me	H	H	H	$FeCl_3$ (15)	2 h	**5a** (88)
2	Me	H	H	Me	$FeCl_3$ (15)	2 h	**5b** (76)
3	Et	Ph	H	H	$FeCl_3$ (15)	4.5 h	**5c** (15)
4	Me	Ph	H	CO_2Me	$FeCl_3$ (5)	30 min	**5d** (95)

[a] All reactions were performed by using 1 equiv (2 mmol) of esters **4** and 1.1 equiv (2.2 mmol) of thiophenol **2a** in the presence of $Fe(III)Cl_3$ under solvent free condition and air atmosphere.

[b] Isolated yields.

of a green strategy for the conjugate addition of thiols to enones. Further exploration of the scope of such addition reactions with complex structures of biological significance is currently underway.

3. Experimental

3.1. General procedure for the 1,4-addition of thiophenol 2a to *trans*-4-phenyl-3-butene-2-one 1d in the presence of anhydrous Fe(III)Cl$_3$ to generate 4-phenyl-4-phenylsulfanyl-butan-2-one (3da)[14] (entry 12 of Table 3)

Typical experimental procedures: In a typical experiment, *trans*-4-phenyl-3-butene-2-one **1d** (0.292 g, 2.0 mmol) and thiophenol **2a** (0.249 g, 2.2 mmol) were mixed together and then anhydrous $Fe(III)Cl_3$ (0.0065 g, 0.02 mmol) was added and the solution stirred at room temperature under an air atmosphere for 10 min. After the completion of the reaction (monitored by TLC and GC), the crude mixture was worked up in ice cold brine solution and then extracted with diethyl ether solution (3 × 10 mL). The combined ether extract was dried over anhydrous $MgSO_4$, filtered and then concentrated in vacuo, and the resulting product was directly charged on a small silica gel column and eluted with a mixture of ethyl acetate/*n*-hexane (1:25) to afford the pure 1,4-adduct **3da** as a colourless oil (0.481 g, 94% yield) ^1H NMR (400 MHz, $CDCl_3$) δ 7.31–7.24 (m, 6H), 7.24–7.16 (m, 4H), 4.70 (dd, $J = 7.8$, 6.8 Hz, 1H), 3.08 (dd, $J = 14.0$, 7.8 Hz, 1H), 3.02 (dd, $J = 14.0$, 6.8 Hz, 1H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.64, 141.24, 134.25, 133.08, 129.02, 128.67, 127.89, 127.80, 127.61, 49.71, 48.26, 30.87. *m/z* (relative intensity) 256 (M^+, 71), 148 (11), 147 (99), 135 (9), 111 (11), 109 (100), 105 (14), 104 (41), 103 (41), 91 (18), 77 (44), 65 (37), 51 (23). HRMS calcd for $C_{16}H_{16}OS$ 256.0922, found 256.0915.

Acknowledgement

Financial support provided by the National Science Council of the Republic of China is gratefully acknowledged.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.07.151.

References and notes

1. (a) Fluharty, A. L. In *The Chemistry of the Thiol Group*; Patai, S., Ed.; Wiley: New York, 1974; p 589, Part 2; (b) Fujita, E.; Nagao, Y. J. *Bioorg. Chem.* **1977**, *6*, 287.
2. (a) Julia, M.; Badet, B. *Bull. Soc. Chim. Fr.* **1975**, 1363; (b) Trost, B. M.; Keeley, D. E. *J. Org. Chem.* **1975**, *40*, 2013; (c) Shono, T.; Matsumura, Y.; Kashimura, S.; Hatanaka, K. *J. Am. Chem. Soc.* **1979**, *101*, 4752; (d) Chang, Y.-H.; Pinnick, H. W. *J. Org. Chem.* **1978**, *43*, 373; (e) Shono, T.; Matsumura, Y.; Kashimura, S.; Hatanaka, K. *J. Am. Chem. Soc.* **1979**, *101*, 4752.
3. (a) Bergman, E. D.; Ginsberg, D.; Rappo, R. *Org. React.* **1959**, *10*, 179; (b) Oare, D. A.; Heathcock, C. A. In *Topics in Stereochemistry*; Eliel, E. L., Wilen, S. H., Eds.; Wiley: New York, 1989; Vol. 9, p 277.
4. Zhu, S.; Cohen, T. *Tetrahedron* **1997**, *53*, 17607.
5. (a) Hiemstra, H.; Wiberg, H. *J. Am. Chem. Soc.* **1981**, *103*, 417; (b) Suzuki, K.; Ikekawa, A.; Mukaiyama, T. *Bull. Soc. Chem. Jpn.* **1982**, *55*, 3277; (c) Yamashita, H.; Mukaiyama, T. *Chem. Lett.* **1985**, 363; (d) Emori, E.; Arai, T.; Sasai, H.; Shibasaki, M. *J. Am. Chem. Soc.* **1998**, *120*, 4043.
6. (a) Kobyashi, S.; Ogawa, C.; Kawamura, M.; Sugiura, M. *Synlett* **2001**, 983; (b) Bandini, M.; Cozzi, P. G.; Giacomini, M.; Melchiorre, P.; Selva, S.; Umani-Ronchi, A. *J. Org. Chem.* **2002**, *67*, 3700; (c) Srivastava, N.; Banik, B. K. *J. Org. Chem.* **2003**, *68*, 2109; (d) Alam, M. M.; Varala, R.; Adapa, S. R. *Tetrahedron Lett.* **2003**, *44*, 5115; (e) Ranu, B. C.; Dey, S. S.; Samanta, S. *ARKIVOC* **2005**, 44; (f) Garg, S. K.; Kumar, R.; Chakraborti, A. K. *Tetrahedron Lett.* **2005**, *46*, 1721; (g) Garg, S. K.; Kumar, R.; Chakraborti, A. K. *Synlett* **2005**, 1370.
7. Novak, L.; Kolontis, P.; Szantay, C.; Aszodi, D.; Kajtar, M. *Tetrahedron* **1982**, *38*, 153.
8. In our studies, a solution of deionized water was treated with a mixture of 2-cyclohexen-1-one and thiophenol precisely under the conditions given in Tale's paper as follows. Only 15% of the expected product was observed by NMR analysis. As expected, similar results were observed and only 35% and 20% of product, for a 24 h reaction were found when chalcone and *trans*-4-phenyl-3-

butene-2-one were used, respectively: Khatik, G. L.; Kumar, R.; Chakraborti, A. K. *Org. Lett.* **2006**, *8*, 2433.

9. (a) Shinde, P. D.; Mahajan, V. A.; Borate, H. B.; Tillu, V. H.; Bal, R.; Chandwadkar, A.; Wakharkar, R. D. *J. Mol. Catal. A Chem.* **2004**, *216*, 115; (b) Sreekumar, R.; Rugmini, P.; Padmakumar, R. *Tetrahedron Lett.* **1997**, *38*, 6557.
10. Sheldon, R. A. *Chirotechnology: Industrial Synthesis of Optically Active Compounds*; Dekker: New York, 1993.
11. (a) Laszlo, P.; Montaufier, M.-T.; Randriamahefa, S. L. *Tetrahedron Lett.* **1990**, *31*, 4867; (b) Christoffers, J. *Synlett* **2001**, 763.
12. (a) Nakamura, M.; Matsuo, K.; Ito, S.; Nakamura, E. *J. Am. Chem. Soc.* **2004**, *126*, 3686; (b) Nakamura, M.; Hirai, A.; Nakamura, E. *J. Am. Chem. Soc.* **2000**, *122*, 978; (c) Nakamura, M.; Matsuo, K.; Inoue, T.; Nakamura, E. *Org. Lett.* **2003**, *5*, 1373.
13. (a) Martin, R.; Fürstner, A. *Angew. Chem., Int. Ed.* **2004**, *43*, 3955; (b) Nagano, T.; Hayashi, T. *Org. Lett.* **2004**, *6*, 1297; (c) Bedford, R. B.; Bruce, D. W.; Frost, R. M.; Goodby, J. W.; Hird, M. *Chem. Commun.* **2004**, 2822.
14. (a) Bodwell, J. R.; Patwardhan, B. H.; Dittmer, D. C. *J. Org. Chem.* **1984**, *49*, 4192; (b) Firouzabadi, H.; Iranpoor, N.; Jafari, A. A. *Synlett* **2005**, 299.