Heteroatom Chemistry
Volume 20, Number 3, 2009

Convenient Synthesis of Symmetrical Diketosulfides from Enolizable Ketones Using [Hydroxy(tosyloxy)iodo]benzene and $Na_2S \cdot 9H_2O$

Nandkishor N. Karade, Girdharilal B. Tiwari, Sumit V. Gampawar, and Sandeep V. Shinde

School of Chemical Sciences, Swami Ramanand Teerth Marathwada University, Nanded 431 606, Maharashtra, India

Received 8 July 2008; revised 11 September 2008

ABSTRACT: *An efficient method for the preparation of symmetrical diketosulfides of the type $ArCOCH_2SCH_2COAr$ has been developed from the reaction of [hydroxy(tosyloxy)iodo]benzene with various acetophenones, followed by treatment with $Na_2S \cdot 9H_2O$.* © 2009 Wiley Periodicals, Inc. Heteroatom Chem 20:172–176, 2009; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20524

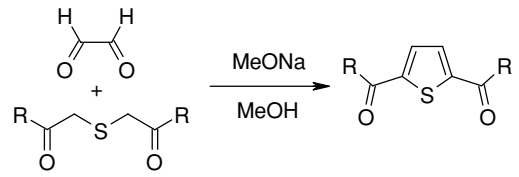
INTRODUCTION

[Hydroxy(tosyloxy)iodo]benzene (HTIB or Koser's reagent) is a valuable trivalent iodine reagent used for inducing α-tosyloxylation of enolizable ketones [1]. Since it is generally not necessary to isolate α-tosyloxy ketone, they can be utilized in situ as a strategic precursor for the one-pot synthesis of a wide range of heterocycles such as thiazoles, selenazoles, oxazoles, imidazoles, pyrazoles, and benzofurans [2]. The α-functionalization of ketones can also be accomplished by the reaction of enolizable ketone with HTIB, followed by nucleophilic substitution reactions with KSCN [3], NaN_3 [4], and $ArNH_2$ [5].

Thiophenes have been synthesized by the well-known Paal–Knorr reaction, involving the cyclization reaction of 1,4-diketones with hydrogen sulfides or P_2S_5 [6]. However, the application of Paal–Knorr reaction for the synthesis of thiophene derivatives is limited due to less commercial availability of wide range of 1,4-dicarbonyl compounds. Another alternative noteworthy route of the synthesis of 2,5-disubstituted thiophene is demonstrated from diketosulfides of the type $RCOCH_2SCH_2COR$ via the base-catalyzed condensation reaction with 1,2-dicarbonyl compounds (Scheme 1) [7].

This reaction involves an important building block, diketosulfide of the type $RCOCH_2SCH_2COR$ that contains two active methylene groups flanked by carbonyl and sulfide groups. There is only one literature report for the synthesis of diketosulfide, $RCOCH_2SCH_2COR$ from α-haloketones and $Na_2S \cdot 9H_2O$ in refluxing ethanol or acetone [7]. In this case, the required α-haloketones ($RCOCH_2X$, where X is Br or Cl) were in turn obtained from the side chain bromination reaction of methyl ketone using molecular bromine as well as the

Correspondence to: Nandkishor N. Karade; e-mail: nnkarade@gmail.com.
Contract grant sponsor: Department of Science and Technology, New Delhi, India.
Contract grant number: SR/FTP/CS-77/2005.
Contract grant sponsor: University Grants Commission, New Delhi, India.
Contract grant number: MRP 32-245/2006 SR.



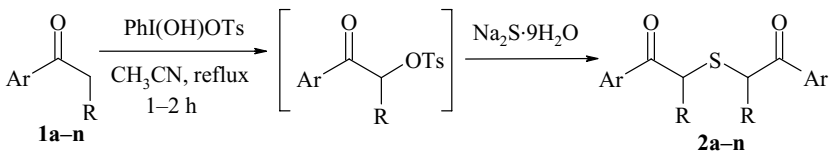
SCHEME 1

nuclear chloroacetylation reaction of appropriate substituted acetophenones using $ClCH_2COCl/AlCl_3$. α-Haloketones are potentially unstable, relatively toxic, and lachrymatory in nature. Owing to the hazards associated with the α-halogenation of methyl ketones and the limited commercial availability of a wide range of α-haloketones, the alternative to the use of α-haloketones is desired. The α-tosyloxy ketone, which is obtained easily from enolizable ketone by the reaction with HTIB is, therefore, considered as environmentally benign alternative to the toxic and lachrymatory α-haloketones. In continuation of our interest in hypervalent iodine reagents [8], herein we report the novel synthesis of diketosulfide by the reaction of enolizable ketones with HTIB, followed by treatment with $Na_2S \cdot 9H_2O$ (Scheme 2).

RESULTS AND DISCUSSION

The optimum reaction conditions were investigated by using the model reaction of acetophenone with HTIB to furnish α-tosyloxyacetophenone, followed by the treatment with $Na_2S \cdot 9H_2O$. The problems associated with the insolubility of $Na_2S \cdot 9H_2O$ in different solvents such as CH_3CN, DMSO, DMF, and THF were the major concern while selecting the appropriate solvent for the reaction. However, the choice of CH_3CN was relatively unambiguous as the α-tosyloxylation of enolizable ketones is usually carried out in CH_3CN. A homogeneous mixture of acetophenone (2 mmol) and HTIB (2.2 mmol) in CH_3CN (15 mL) was refluxed for 1 h, and the formation of α-tosyloxyacetophenone was ascertained as monitored by TLC. Then, $Na_2S \cdot 9H_2O$ (4 mmol) was subsequently added to the above reaction mixture and continued the reflux for another 7–8 h. The insolubility of $Na_2S \cdot 9H_2O$ in CH_3CN prompted us to utilize excess quantity. In spite of these quantitative variations in the stoichiometry of $Na_2S \cdot 9H_2O$, we noticed the formation of several side products and the desired product, that is $PhCOCH_2SCH_2COPh$ **2a** was obtained in poor (17%) yield. To circumvent this solubility problem of $Na_2S \cdot 9H_2O$, we decided to carry the reaction of $Na_2S \cdot 9H_2O$ with in situ generated α-tosyloxyacetophenone using the grinding technique, developed by Toda and coworkers in which many reactions can be conducted in high yields under solvent-free conditions just by grinding the reactants together [9]. Usually these reactions were carried out on a very small scale in an agate pestle and mortar. After the formation of α-tosyloxyacetophenone from the reaction between acetophenone (2 mmol) and HTIB (2.2 mmol) in CH_3CN solvent, the reaction mixture was subjected under vacuum and the crude solid α-tosyloxyacetophenone was transferred to mortar and it was subsequently mechanically ground with $Na_2S \cdot 9H_2O$ (3 mmol, 0.720 g) using pestle for 20 min. After the usual workup procedure, the formation of **2a** with 73% yield was realized (see the section Experimental Procedure for the Preparation of Symmetrical Diketosulfides).

To demonstrate the efficiency and the applicability of the present method, we performed the reactions of a variety of substituted acetophenones with HTIB, followed by treatment with $Na_2S \cdot 9H_2O$ and the results are summarized in Table 1. This method is as such general as it permits the synthesis of a wide range of diketosulfides from easily accessible substituted acetophenones. It follows from Table 1 that acetophenones containing both electron-donating groups (such as methoxy and methyl) and electron-withdrawing groups (such as halogens and nitro) were employed and reacted well to give the corresponding diketosulfides in good to excellent yields. The methodology was extended to the other ketones such as propiophenone, butyrophenone, pentanophenone, and phenyl benzyl ketone (Table 1, entries 11–14). All the isolated products, $ArCOCH_2SCH_2COAr$ were completely characterized by IR, NMR, and mass spectral analysis. The ^1H NMR spectra of the symmetrical diketosulfides show a sharp singlet around δ 3.91–3.94 ppm, which is reminiscent of the methylene protons flanked by carbonyl and sulfide groups (see the section Spectral Data of Selected Molecules).



SCHEME 2

TABLE 1 Synthesis of Symmetrical Diketosulfide from Enolizable Ketones Using HTIB and $Na_2S \cdot 9H_2O$

Entry	*Ar*	*R*	*Product*	*Yield (%)*[a]
1	C_6H_5	H	**2a**	73
2	2-$MeOC_6H_4$	H	**2b**	56
3	4-$MeOC_6H_4$	H	**2c**	77
4	4-MeC_6H_4	H	**2d**	72
5	2-ClC_6H_4	H	**2e**	61
6	3-ClC_6H_4	H	**2f**	67
7	4-ClC_6H_4	H	**2g**	71
8	2-BrC_6H_4	H	**2h**	59
9	4-BrC_6H_4	H	**2i**	73
10	3-$NO_2C_6H_5$	H	**2j**	64
11	C_6H_5	CH_3	**2k**	69
12	C_6H_5	CH_2CH_3	**2l**	67
13	C_6H_5	$(CH_2)_2CH_3$	**2m**	64
14	C_6H_5	C_6H_5	**2n**	63

[a]Isolated yield.

In summary, a novel and highly efficient methodology for the synthesis of symmetrical diketosulfides from the reaction between enolizable ketones with HTIB, followed by the reaction with $Na_2S \cdot 9H_2O$ is reported. In view of the synthetic possibilities of diketosulfides, this method no doubt will find wide application.

Experimental Procedure for the Preparation of Symmetrical Diketosulfides

A mixture of appropriate acetophenone (2 mmol) and HTIB (2.2 mmol) in CH_3CN (15 mL) was refluxed for 1–2 h. After the disappearance of ketone, as indicated by TLC, the reaction mixture was subjected to vacuum under reduced pressure to obtain the intermediate α-tosyloxy ketone as crude solid product. The resulting solid α-tosyloxy ketone and $Na_2S \cdot 9H_2O$ (3 mmol, 0.720 gm) were then transferred to mortar and ground mechanically using pestle for 15 min. The progress of reaction was again monitored by TLC by taking a small amount of the mixture and dissolving it in chloroform. After completion of reaction, the solid reaction mixture was washed with water and extracted with CH_2Cl_2 (3×15 mL). The combined organic extract was dried over anhydrous sodium sulfate, concentrated in vacuum and subjected to column chromatography (silica gel mesh size 100–200) to obtain the symmetrical diketosulfide in pure form.

Spectral Data of Selected Molecules

*2-(2-Oxo-2-phenyl-ethylsulfanyl)-1-phenyl-ethanone (**2a**).* mp 77–79°C (lit. [7a] 76–77°C); IR (KBr) ν: 2913, 1676, 1599, 1275, 1213, 755, 672 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, δ): 3.94 (s, 4H, CH_2), 7.45–7.49 (m, 4H, ArH), 7.59 (t, 2H, $J = 7.36$ Hz, ArH), 7.96–7.99 (m, 4H, ArH); ^{13}C NMR (400 MHz, $CDCl_3$, δ): 37.67, 128.69, 128.80, 133.65, 135.38, 194.24; LCMS *m/z*: 271 (M + 1), 293 (M + 23).

*1-(2-Methoxyphenyl)-2-[2-(2-methoxyphenyl)-2-oxo-ethylsulfanyl]-ethanone (**2b**).* mp 123–125°C; IR (KBr) ν: 2907, 1674, 1598, 1432, 1302, 1212, 1032, 752, 670 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, δ): 3.89 (s, 4H, OCH_3), 3.94 (s, 4H, CH_2), 6.95 (d, 2H, $J = 8.4$ Hz, ArH), 7.01 (t, 2H, $J = 8.36$ Hz, ArH), 7.48 (t, 2H, $J = 8.4$ Hz, ArH), 7.80 (d, 2H, $J = 7.76$ Hz, ArH); ^{13}C NMR (400 MHz, $CDCl_3$, δ): 42.61, 55.67, 111.64, 120.90, 126.28, 131.28, 134.20, 158.80, 195.96; LCMS *m/z*: 331 (M + 1), 353 (M + 23).

*1-(4-Methoxyphenyl)-2-[2-(4-methoxyphenyl)-2-oxo-ethylsulfanyl]-ethanone (**2c**).* mp 86–88°C (lit. [7a] 88–89°C); IR (KBr) ν: 3028, 2908, 1687, 1593, 1508, 1458, 1377, 1323, 1267, 1166, 114, 1022, 829, 740 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, δ): 3.87 (s, 6H, OCH_3), 3.93 (s, 4H, CH_2), 6.93 (d, 4H, $J = 8.88$ Hz, ArH), 7.96 (d, 4H, $J = 8.92$ Hz, ArH); ^{13}C NMR (400 MHz, $CDCl_3$, δ): 37.53, 55.60, 113.97, 128.44, 131.10, 163.91, 193.06; LCMS *m/z*: 331 (M + 1), 353 (M + 23).

*2-(2-Oxo-2-p-tolyl-ethylsulfanyl)-1-p-tolyl-ethanone (**2d**).* mp 91–92°C; (lit. [7a] 89–90°C); IR (KBr) ν: 2912, 1678, 1603, 1572, 1411, 1278, 1187, 1011, 807, 755, 670 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, δ): 2.41 (s, 6H, $ArCH_3$), 3.96 (s, 4H, CH_2), 7.26 (d, 4H, $J = 7.96$ Hz, ArH), 7.87 (d, 4H, $J = 8.24$ Hz, ArH); ^{13}C NMR (400 MHz, $CDCl_3$, δ): 21.80, 37.68, 128.85, 129.50, 132.94, 144.59, 194.04; LCMS *m/z*: 299 (M + 1), 321 (M + 23).

*1-(2-Chlorophenyl)-2-[2-(2-chlorophenyl)-2-oxo-ethylsulfanyl]-ethanone (**2e**).* mp 109–111°C; IR (KBr) ν: 2869, 1697, 1591, 1432, 1283, 1037, 821, 756, 671 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, δ): 3.95 (s, 4H, CH_2), 7.32–7.36 (m, 2H, ArH), 7.40–7.42 (m, 4H, ArH), 7.58 (d, 2H, $J = 7.32$ Hz, ArH); ^{13}C NMR (400 MHz, $CDCl_3$, δ): 40.94, 127.06, 129.86, 130.57, 131.31, 132.34, 137.50, 196.74; LCMS (M + 1) *m/z*: 339 (M + 1), 341 (M + 3).

*1-(3-Chlorophenyl)-2-[2-(3-chlorophenyl)-2-oxo-ethylsulfanyl]-ethanone (**2f**).* mp 162–165°C; IR (KBr) ν: 2926, 2912, 1679, 1569, 1422, 1287, 1270, 1212, 1031, 880, 759, 672 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, δ): 3.87 (s, 4H, CH_2), 7.35 (t, 2H, $J = 7.88$ Hz, ArH), 7.49 (d, 2H, $J = 7.96$ Hz, ArH), 7.76 (d, 2H, $J = 7.72$ Hz, ArH), 7.86 (s, 2H, ArH); ^{13}C

NMR (400 MHz, $CDCl_3$, δ): 37.58, 126.80, 128.75, 130.16, 133.64, 135.20, 136.84, 192.78; LCMS *m/z*: 339 (M + 1), 341 (M + 3).

*1-(4-Chlorophenyl)-2-[2-(4-chlorophenyl)-2-oxo-ethylsulfanyl]-ethanone (***2g***)*. mp 123–125°C (lit. [7a] 122–123°C); IR (KBr) ν: 2918, 1701, 1671, 1591, 1400, 1361, 1288, 1174, 1093, 968, 819, 777 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, δ): 3.93 (s, 4H, CH_2), 7.45 (d, 4H, $J = 8.6$ Hz, ArH), 7.91 (d, 4H, $J = 8.6$ Hz, ArH); ^{13}C NMR (400 MHz, $CDCl_3$, δ): 37.52, 129.16, 130.11, 133.61, 140.84, 192.94; LCMS *m/z*: 339 (M + 1), 341 (M + 3).

*1-(2-Bromophenyl)-2-[2-(2-bromophenyl)-2-oxo-ethylsulfanyl]-ethanone (***2h***)*. mp 94–96°C; ^1H NMR (400 MHz, $CDCl_3$, δ): 3.94 (s, 4H, CH_2), 7.34 (t, 2H, $J = 7.84$ Hz, ArH), 7.40 (t, 2H, $J = 7.56$ Hz, ArH), 7.51 (d, 2H, $J = 7.64$ Hz, ArH), 7.63 (d, 2H, $J = 7.92$ Hz, ArH); ^{13}C NMR (400 MHz, $CDCl_3$, δ): 40.58, 127.56, 129.50, 132.19, 133.75, 139.90, 197.54; LCMS (M + 1) *m/z*: 339 (M + 1), 341 (M + 3).

*1-(4-Bromophenyl)-2-[2-(4-bromophenyl)-2-oxo-ethylsulfanyl]-ethanone (***2i***)*. mp 141–143°C (lit. [7a] 142–143°C); IR (KBr) ν: 2922, 1671, 1583, 1402, 1204, 1071, 814, 769 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, δ): 3.92 (s, 4H, CH_2), 7.62 (d, 4H, $J = 8.56$ Hz, ArH), 7.82 (d, 4H, $J = 8.64$ Hz, ArH); ^{13}C NMR (400 MHz, $CDCl_3$, δ): 37.51, 129.04, 130.22, 132.19, 134.05, 193.16; LCMS *m/z*: 427 (M + 1), 429 (M + 3), 449 (M + 23).

*1-(3-Nitrophenyl)-2-[2-(3-nitrophenyl)-2-oxo-ethylsulfanyl]-ethanone (***2j***)*. mp 129–131°C; IR (KBr) ν: 2924, 1678, 1526, 1405, 1348, 1262, 1022, 810, 764, 679 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, δ): 4.03 (s, 4H, CH_2), 7.72 (t, 2H, $J = 8.0$ Hz, ArH), 8.30 (d, 2H, $J = 7.8$ Hz, ArH), 8.46 (d, 2H, $J = 8.24$ Hz, ArH), 8.78 (s, 2H, ArH); ^{13}C NMR (400 MHz, $CDCl_3$, δ): 37.58, 123.59, 127.99, 130.22, 134.22, 136.53, 148.57, 191.69; LCMS *m/z*: 361 (M + 1).

*2-(1-Methyl-2-oxo-2-phenylethylsulfanyl)-1-phenyl-propan-1-one (***2k***)*. mp 146–148°C; IR (KBr) ν: 3061, 2974, 2928, 2866, 1994, 1682, 1595, 1578, 1512, 1442, 1374, 1340, 1234, 1204, 1078, 1001, 951, 797, 716, 687 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, δ): 1.44 (d, 6H, $J = 5.12$ Hz, $2CH_3$), 4.45 (q, 2H, $J = 5.36$ Hz, 2CH), 7.37 (t, 2H, $J = 8.2$ Hz, ArH), 7.48 (t, 3H, $J = 7.64$ Hz, ArH), 7.56 (t, 1H, $J = 8.08$ Hz, ArH), 7.81 (d, 2H, $J = 7.04$ Hz, ArH), 7.99 (d, 2H, $J = 7.04$ Hz, ArH); ^{13}C NMR (400 MHz, $CDCl_3$, δ): 18.60, 41.95, 128.67, 128.88, 133.56, 135.20, 196.97; LCMS *m/z*: 299 (M + 1).

*2-(1-Benzoyl-propylsulfanyl)-1-phenyl-butan-1-one (***2l***)*. mp 133–135°C; IR (KBr) ν: 3061, 2960, 2926, 2008, 1682, 1597, 1579, 1449, 1340, 1221, 1076, 1030, 905, 685 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, δ): 0.89 (t, 6H, $J = 7.32$ Hz, $2CH_3$), 1.73–1.82 (m, 4H, $2CH_2$), 4.09 (t, 2H, $J = 8.2$ Hz, 2SCH), 7.26 (t, 2H, $J = 8.0$ Hz, ArH), 7.39 (t, 3H, $J = 7.84$ Hz, ArH), 7.48 (t, 1H, $J = 7.4$ Hz, ArH), 7.71 (d, 2H, $J = 7.2$ Hz, ArH), 7.92 (d, 2H, $J = 7.08$ Hz, ArH); ^{13}C NMR (400 MHz, $CDCl_3$, δ): 12.09, 25.94, 48.69, 128.45, 128.75, 133.06, 135.97, 197.12; LCMS *m/z*: 327 (M + 1).

*2-(1-Benzoyl-butylsulfanyl)-1-phenyl-pentan-1-one (***2m***)*. mp 154–157°C; IR (KBr) ν: 3061, 2959, 2924, 2980, 2342, 1813, 1682, 1598, 1580, 1447, 1368, 1339, 1202, 1105, 1001, 899, 812, 746, 689 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, δ): 0.91 (t, 6H, $J = 2.72$ Hz, $2CH_3$), 1.24–1.28 (m, 4H, $2CH_2$), 1.82–1.85 (m, 2H, $2CH_2$), 4.25–4.29 (m, 2H, 2SCH), 7.35 (t, 2H, $J = 8.0$ Hz, ArH), 7.48 (t, 3H, $J = 7.88$ Hz, ArH), 7.57 (t, 1H, $J = 7.4$ Hz, ArH), 7.79 (d, 2H, $J = 8.2$ Hz, ArH), 8.0 (d, 2H, $J = 7.2$ Hz, ArH); ^{13}C NMR (400 MHz, $CDCl_3$, δ): 13.65, 20.50, 34.17, 46.57, 128.44, 128.74, 133.05, 135.94, 197.19; LCMS *m/z*: 355 (M + 1).

*2-(2-Oxo-1,2-diphenyl-ethylsulfanyl)-1,2-diphenyl-ethanone (***2n***)*. mp 69–71°C; IR (KBr) ν: 3061, 2928, 1804, 1676, 1595, 1571, 1493, 1449, 1273, 1207, 1001, 841, 760, 694 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, δ): 5.28 (3, 2H, 2ArCH), 7.18–7.45 (m, 12H, ArH), 7.48–7.51 (m, 3H, ArH), 7.76–7.79 (m, 5H, ArH); ^{13}C NMR (400 MHz, $CDCl_3$, δ): 62.31, 127.87, 128.07, 128.42, 128.43, 133.46, 133.56, 135.61, 136.32, 195.57; LCMS *m/z*: 377 (M + 1).

SUPPORTING INFORMATION

Supporting Information related to the structure and spectral data of different compounds is available from the corresponding author (e-mail: nnkarade@gmail.com).

REFERENCES

[1] (a) Koser, G. F.; Wettach, R. H. J Org Chem 1976, 41, 3609; (b) Koser, G. F.; Wettach, R. H. J Org Chem 1976, 42, 176; (c) Koser, G. F.; Wettach, R. H. J.; Smith, C. S. J Org Chem 1980, 45, 1542; (d) Koser, G. F.; Relenyi, A. G.; Kalos, A. N.; Rebrovic, L.; Wettach, R. H. J Org Chem 1982, 47, 2487; (e) Moriarty, R. M.; Vaid, R. K.; Koser, G. F. Synlett 1990, 365; (f) Varvoglis, A. Hypervalent Iodine in Organic Synthesis; Academic Press: London, 1997; Chap. 7, p. 115.

[2] (a) Koser, G. F.; Wettach, R. H. J Org Chem 1977, 42, 1476; (b) Moriarty, R. M.; Vaid, R. K.; Hopkins, T. E.; Vaid, B. K.; Prakash, O. Tetrahedron Lett 1990, 31, 201; (c) Moriarty, R. M.; Vaid, B. K.; Duncan, M. P.; Levy, S. G.; Prakash, O.; Goyal, S. Synthesis 1992, 845; (d) Prakash, O.; Goyal, S. Synthesis 1992, 629; (e) Prakash, O.; Rani, N.; Goyal, S. J Chem Soc, Perkin Trans 1 1992, 707; (f) Prakash, O.; Saini, N.; Sharma, P. K. Synlett 1994, 221. (g) Prakash, O.; Saini, N.; Sharma, P. K. Heterocycles 1994, 38, 409; (h) Uneno, M.; Togo, H. Synthesis 2004, 16, 2673.
[3] Prakash, O.; Saini, N. Synth Commun 1993, 23, 1455.
[4] Prakash, O.; Pannu, K.; Prakash, R.; Batra, A. Molecules 2006, 11, 523.
[5] Prakash, O.; Rani, N.; Goyal, S. Ind J Chem Sect B 1992, 31, 349.
[6] (a) Wynberg, H.; Wiersum, U. J Org Chem 1965, 30, 1058; (b) Smith, A. J Chem Soc 1890, 57, 643; (c) Scheeren, J. W.; Oomes, P. H. J.; Nivard, R. J. F. Synthesis 1973, 149.
[7] (a) Miyahara, Y. J Heterocycl Chem 1979, 16, 1147; (b) Miyahara, Y. J Org Chem 2006, 71, 6516.
[8] (a) Karade, N. N.; Tiwari, G. B.; Shinde, S. V.; Gampawar, S. V.; Kondre, J. M. Tetrahedron Lett 2008, 49, 3441; (b) Karade, N. N.; Gampawar, S. V.; Kondre, J. M.; Shinde, S. V.; Tetrahedron Lett 2008, 49, 4402; (c) Karade, N. N.; Tiwari, G. B.; Huple, D. B. Synlett 2005, 2039; (d) Karade, N. N.; Tiwari, G. B.; Gampawar, S. V. Synlett 2007, 1921; (e) Karade, N. N.; Gampawar, S. V.; Kondre, J. M.; Shinde, S. V. ARKIVOC 2008, xii, 9.
[9] (a) Toda, F.; Tanaka, K.; Sekikawa, A. J Chem Soc, Chem Commun 1987, 279; (b) Toda, F.; Suzuki, T.; Higa, S. J Chem Soc, Perkin Trans 1 1998, 3521; (c) Scott, J. L.; Raston, C. L. Green Chem 2000, 2, 245.