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Micellar media for the efficient ring opening of epoxides with CN^-, N_3^-, NO_3^-, NO_2^-, SCN^-, Cl^- and Br^- catalyzed with $Ce(OTf)_4$

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Micellar media are introduced for the efficient ring opening of epoxides with sodium salts of nucleophiles such as CN^-, N_3^-, NO_3^-, NO_2^-, SCN^-, Br^- and Cl^-, catalyzed with $Ce(OTf)_4$. This method is an efficient procedure for the synthesis of different β-substituted alcohols under mild reaction conditions. The reaction with SCN^- is an easy procedure for the high yielding preparation of epoxy sulfides.

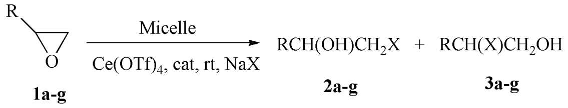
Introduction

It is well established that, in many cases, performing the reactions in micellar media instead of organic solvents can alter rates and the pathways of the reactions. Micelles can concentrate the reactants within their small volumes;[1–3] stabilize substrates, intermediates or products;[4–7] and orient substrates;[8–10] so that ionization potentials and oxidation–reduction properties,[11,12] dissociation constants,[13,14] physical properties, quantum efficiencies and reactivities[15,16] are changed. Therefore, we may control the reaction rates, mechanism, regio- and stereochemistry in the presence of micellar media.[17–20] Although, application of micelles in analytical chemistry is widely studied,[21,22] their synthetic applications as media in organic reactions, especially in Lewis acid mediated reactions are not well investigated.[23]

Recently, great attention has been paid to the development of organic reactions in water to achieve green chemistry.[23a,24] Ceric triflate,[25] $Ce(OTf)_4$, is stable in water and could be considered as a suitable catalyst for performing the organic reactions in aqueous media.[24] In continuation of our recent work,[23b] we decided to study the ring opening reaction of epoxides with the sodium salt of different anions such as CN^-, N_3^-, NO_3^-, NO_2^-, SCN^-, Br^- and Cl^- in micellar media with the aid of $Ce(OTf)_4$ as catalyst. Due to the insolubility of metal salts of inorganic nucleophiles in organic solvents, nucleophilic ring opening reactions of epoxides is usually carried out in the presence of their quaternary ammonium salts and mostly in aqueous organic solvents and at high temperatures.[26] The use of metal salts of nucleophiles for ring opening of epoxides usually suffers from some disadvantages. For example, Na, K, Cs and Cu salts of bromide supported on silica-gel have been reported to react with epoxides very sluggishly (48–720 h). These reactions produce a mixture of β-bromohydrins and diols. The ring opening reaction of epoxides with LiCl and LiBr supported on silica-gel has also been performed, but again the regioselectivity is not good.[27] However, the reactions of LiCl/silica-gel with epoxides suffer from very long reaction times (13 and 22 days) and give a mixture of regio-isomers together with the corresponding diols.[27]

Results and discussion

Considering the problems encountered in cyanolysis of epoxides, such as the use of crown ethers to activate the cyanide anion in metal–CN, the low yields of the products, long reaction times or unavailability of the reagent,[28–32] we first studied the effect of different micellar media for this important transformation. The ring opening reaction of styrene oxide with NaCN was studied in the micellar solution of sodium dodecyl sulfate (SDS) as an anionic micelle, cetyl trimethylammonium bromide (CTAB) as a cationic micelle, and Triton X-100 as a neutral micelle at different concentrations in the presence of catalytic amounts of $Ce(OTf)_4$. This reaction with 1.5 molar equivalents of NaCN in the presence of 10 mol% $Ce(OTf)_4$ was optimized in the above mentioned micellar media at room temperature (Scheme 1).



a: Ph, **b**: epoxide = cyclohexene oxide, **c**: n-C_4H_9, **d**: $(CH_3)_2CHOCH_2$,
e: CH_2=$CHCH_2OCH_2$, **f**: $ClCH_2$, **g**: $PhOCH_2$
X: CN^-, Cl^-, Br^-, N_3^-, NO_3^-, NO_2^-
Micelle: SDS, CTAB, Triton X-100

Scheme 1

When styrene oxide reacted with sodium cyanide in water alone and in the presence of $Ce(OTf)_4$ as catalyst (Table 1, entry 1), a mixture of 1,2-cyanohydrines (**2a** + **3a**, R = Ph) was obtained in 70% yield after 30 h with low regeioselectivity of 35 and 65% respectively. We then tried this reaction in micellar solutions of SDS, CTAB and Triton X-100. The best result was obtained in 0.1 M SDS solution. This concentration is slightly more than the c.m.c. concentration (8.1×10^{-2} M) of SDS micellar solution. Under these conditions (Table 1, entry 2), the same mixture of regio-isomers was obtained in 92% yield after 4.5 h, but the regioselectivity was found to be much improved (8% of **2a** + 92% of **3a**). In CTAB solutions, the major product was found to be the corresponding diol instead of 1,2-cyanohydrine. The use of 2% and 4% micellar solutions of Triton X-100 as reaction media, in comparison with using water alone, did not show any advantage. We therefore concluded the Triton X-100 does not have any pronounced effect on the rate of the reaction. The results of the reaction of styrene oxide with cyanide ion in different micellar solutions are summarized in Table 1.

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Table 1 Reaction of styrene oxide (**1a**) with 1.5 molar equivalents of NaCN in the presence of 10 mol% $Ce(OTf)_4$ in different micellar solutions[a] at room temperature

	Media	Conc.	Time/h	Yield (%)[b]	Ratio of **2a**/**3a**[a]
1	Water[c]	–	30	70	35/65
2	SDS	0.1 M	4.5	92	8/92
3	SDS	0.05 M	10	87	15/85
4	SDS	0.01 M	15	85	20/80
5	SDS	0.1 M	10	19[d]	25/75
6	CTAB	1.3×10^{-3} M	3	–[e]	–
7	CTAB	1.3×10^{-2} M	1	–[e]	–
8	Triton X-100	2%	30	80	30/70
9	Triton X-100	4%	25	75	30/70

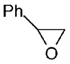
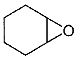
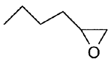
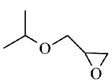
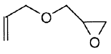
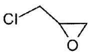
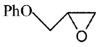
[a] The c.m.c. of SDS = 8.1×10^{-3} M,[33a] CTAB = 1.3×10^{-3} M,[33a] Triton X-100 = 3.0×10^{-4} M;[33b] **2a** = 1-phenyl-2-cyanoethanol; **3a** = 2-phenyl-2-cyanoethanol. [b] Isolated yield. [c] The reaction was performed in the absence of micelles. [d] The reaction was performed in micellar solution of SDS in the absence of $Ce(OTf)_4$. [e] A mixture of 1,2- cyanohydrins was obtained in 10–15% yields together with 45% and 60% of 1,2-dihydroxy-1-phenylethane for entries 5 and 6 respectively.

The higher rate and regioselectivity of the reaction in anionic micelle (SDS) could well be due to the different micellar environmental factors. We suggest that in this medium, the partial cationic character which is induced on the epoxide ring due to the interaction of oxygen of the ring with Ce(IV) could be stabilized through the interaction with the anionic part of the micelle on the surface. Triton X-100 as a neutral micelle can just increases the solubility of the organic reactants and causes a slight increase in the reaction rate. In the cationic micellar media of CTAB, the cyanide anion interacts strongly with the bromide anion of CTAB which results in deactivation of CN^- anion. This deactivation results in hydrolysis of the epoxide as the major pathway rather than cyanolysis. We therefore, applied the resulting optimized conditions for the cyanolysis of structurally different epoxides with success. Different classes of epoxides were converted to their corresponding β-hydroxy nitriles in high yield and regioselectivity in 0.1 M aqueous SDS solution (Table 2). Under these conditions, epoxides carrying either electron-donating or withdrawing substituents produced the desired β-hydroxy nitriles with high regioselectivity. We continued this study to investigate the applicability of this method to the ring opening of epoxides with other nucleophiles such as halides, azide, nitrate, and nitrite anions.

Quaternary ammonium salts ($R_4N^+X^-$) are frequently used as sources of halide ions for the preparation of vicinal halohydrins from epoxides.[26,34,35] To show the applicability and advantages of this protocol, we successfully used the cheap and readily available NaBr and NaCl in 0.1 M SDS solution for the ring opening of structurally different epoxides in the presence of $Ce(OTf)_4$ as catalyst at room temperature (Table 3).

β-Azido alcohols as important intermediates in organic synthesis are prepared from the reaction of epoxides and azide anions using different protocols.[24c,36–38] Thus, we applied this method to the synthesis of β-azido alcohols using azide anions in 0.1 M SDS solution in the presence of catalytic amounts of $Ce(OTf)_4$. We, thereby, converted styrene oxide, cyclohexene oxide and allyl 2,3-epoxypropyl ether as examples of aryl, alkyl and electron-withdrawing substituted epoxides to their corresponding β-azido alcohols within 5–10 min with high yields (Table 3). In comparison with the recent report on azidolysis of epoxides which takes 30–120 min using sodium azide and 0.5 molar equivalents of Oxone®,[36] our presented method is more efficient for this purpose.

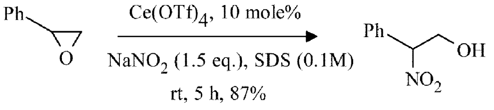
Table 2 Reaction of epoxides with 1.5 equimolar amounts of NaCN catalyzed with 0.1 equimolar of $Ce(OTf)_4$ in SDS (0.1M)at room temperature

Epoxide	Product[a]	(Time/h)/(Yield (%))[b]
	$PhCH(CN)CH_2OH$[c]	4.5 (85)
	*trans*-2-Cyanocyclohexanol	5 (85)
	$C_4H_9CH(CN)CH_2OH$[d]	5 (70)
	${}^iPrOCH_2CH(OH)CH_2CN$[d]	8 (90)
	$RCH(OH)CH_2CN$[e] (R: $CH_2{=}CHCH_2O{-}$)	8 (85)
	$ClCH_2CH(OH)CH_2CN$[e]	7 (85)
	$PhOCH_2CH(OH)CH_2CN$[e]	10 (88)

[a] The products were isolated and identified by comparison with known samples. [b] Isolated yield. [c] 2-Cyano-1-phenylethanol was formed in 7% yield. [d] GC yield. [e] In the case of epoxides carrying electron-withdrawing groups, trace amounts (2–5%) of the other regio-isomer was also observed.

We next studied the reaction of epoxides with nitrate and nitrite anions using $NaNO_3$ and $NaNO_2$ as the source of nucleophiles in 0.1 M SDS in the presence of $Ce(OTf)_4$ as catalyst. The reaction rates for the formation of β-nitrato alcohols obtained from the reaction of epoxides in SDS micellar solution with sodium nitrate were found to be much better than the same reactions using tetra-*n*-butyl ammonium nitrate in acetonitrile at 80 °C catalysed with ceric ammonium nitrate.[40] Table 3, entries 10–12 show the results of this transformation with different epoxides.

In the case of using $NaNO_2$ as the source of the NO_2 nucleophile, β-nitro alcohols were obtained with good regioselectivity in high yields (Scheme 2, Table 3, entries 13–15). Except in the case of styrene oxide, for which the β-nitro alcohol was formed as the only product, the reaction of the other epoxides produced some β-nitrito alcohols (10–15%) as side products. Sodium nitrite is an ambident nucleophile and it seems that in SDS micellar solution, N-attack is more favored due to the solvation of the O site.



Scheme 2

In the course of these studies, we also decided to investigate

Table 3 Reaction of epoxides with 1.5 equimolar amounts of NaX (X = Cl, Br, N_3, NO_3, NO_2) catalyzed with 0.1 molar equivalents of Ce(OTf) in SDS (0.1M) at room temperature

Entry	Epoxide	Nucleophile	Time (min)	Product[a]	Yield (%)[b]
1	**1a**	NaBr	20	$PhCH_2(Br)CH_2OH$	85
2	**1b**	NaBr	10	*trans*-2-bromo-cyclohexanol	88
3	**1e**	NaBr	10	$CH_2{=}CHCH_2OCH_2CH(OH)CH_2Br$	87
4	**1a**	NaCl	20	$PhCH_2(Cl)CH_2OH$	83
5	**1b**	NaCl	10	*trans*-2-chloro-cyclohexanol	85
6	**1e**	NaCl	10	$CH_2{=}CHCH_2OCH_2CH(OH)CH_2Br$	87
7	**1a**	NaN_3	5	$PhCH_2(N_3)CH_2OH$	90
8	**1b**	NaN_3	10	*trans*-2-azido-cyclohexanol	89
9	**1e**	NaN_3	10	$CH_2{=}CHCH_2OCH_2CH(OH)CH_2N_3$	95
10	**1a**	$NaNO_3$	20	$PhCH_2(ONO_2)CH_2OH$	87
11	**1b**[c]	$NaNO_3$	30	*trans*-2-nitrato-cyclohexanol	85
12	**1e**[c]	$NaNO_3$	20	$CH_2{=}CHCH_2OCH_2CH(OH)CH_2ONO_2$	78
13	**1a**	$NaNO_2$	5	$PhCH_2(NO_2)CH_2OH$	90
14	**1b**	$NaNO_2$	10	***trans***-2-nitro-cyclohexanol	78
15	**1e**	$NaNO_2$	10	$CH_2{=}CHCH_2OCH_2CH(OH)CH_2NO_2$	75

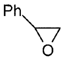
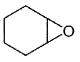
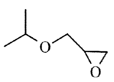
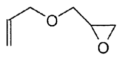
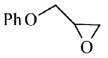
[a] Products were identified by comparison of their spectral data with those in the literature.[26,31,36,39,40] [b] Isolated yield. [c] The corresponding β-nitrito alcohols were also obtained in 10–15% yield.

Table 4 Conversion of styrene oxide to styrene sulfide with NaSCN (1.5 equimolar.) in the presence of 10 mol% of $Ce(OTf)_4$ in different micellar solutions

Micelle	Concentration	Time/h	Yield (%)[a]
–	–	7	70
SDS	0.1	0.5	100
SDS	0.01	2	77
CTAB	8×10^{-4}	5	55
Titon X-100	2%	5	70

[a] GC yield of styrene sulfide.

Table 5 Conversion of epoxides to epoxy sulfides[a] with NaSCN in the presence of Ce(OTf) as catalyst at room temperature

Epoxide	Mole ratio of Sub./Cat./SCN^-	Time/h	Yield (%)[b]
	1/0.05/1.5	0.5	92
	1/0.05/1.5	0.5	89
	1/0.05/1.5	4	91
	1/0.1/1.5	1	89
	1/0.1/1.5	3	95
	1/0.05/1.5	8	80

[a] Epoxy sulfides were identified by comparison of their physical data with those of known samples.[41] [b] Isolated yield of epoxy sulfide.

the epoxy sulfide syntheses from epoxides in the presence of $Ce(OTf)_4$ as catalyst using NaSCN as sulfurating agent in SDS micellar solution. We first studied the effect of SDS, CTAB and Triton X-100 micellar solutions for the reaction of styrene oxide and NaSCN at room temperature in the presence of the catalyst. The best results were obtained in 0.1 M SDS solution and styrene sulfide was formed in almost quantitative yield after 0.5 h (Table 4).

Different classes of epoxides were then converted to their corresponding epoxy sulfides using the above mentioned reaction conditions. Allyl, isopropyl, and phenyl glycidyl ethers, as examples of epoxides carrying electron-withdrawing groups, and styrene oxide and 1,2-epoxy hexane, as examples of epoxides carrying aryl and alkyl groups were converted efficiently to their corresponding epoxy sulfides in excellent yields (Table 5). In our previous report for the conversion of epoxides to epoxy sulfides in organic solvents, the catalytic activity of $Ce(OTf)_4$ was reported to be strongly diminished due to its complexation with SCN^-, therefore, we had to support $Ce(OTf)_4$, on poly(4-vinyl pyridine).[32] However, in SDS micellar solution, this problem has been eliminated for the synthesis of epoxy sulfides from epoxides with SCN^-. It is worthy of mention that in all the reactions we have studied in SDS micellar solution, the sodium salts of nucleophiles were found to be more reactive than their potassium, ammonium or quaternary ammonium analogs.

In conclusion, the use of SDS micellar media together with ceric triflate as a stable Lewis acid in aqueous solutions provides excellent conditions for the ring opening of epoxides with different anionic nucleophiles. The absence of organic solvent, acceleration of the reactions rates, increase of the yields of the products and high regioselectivity of the reactions are strong points of performing ionic reactions in SDS micellar media. Another useful feature of the present protocol is the use of easily available and very cheap sodium salts of nucleophiles instead of expensive and usually hygroscopic quaternary ammonium salts.

Experimental

Chemicals were either prepared in our laboratories or purchased from Merck, Fluka and Aldrich Chemical Companies. All yields refer to isolated products after column chromatography unless otherwise stated. The products were characterized by comparison of their physical data with those of known samples or by their spectral data. IR spectra were run on a Perkin Elmer 781 spectrophotometer. NMR spectra were recorded on a Bruker Avance DPX-250. Mass spectra were recorded on a Shimadzu GCMS-QP 1000 EX.

The purity of the substances and the progress of the reactions were accomplished by TLC on silica-gel polygram $SILG/UV_{254}$ plates or by a Shimadzu Gas Chromatograph GC-10A instrument with a flame-ionization detector using a column of 15% carbowax 20 M chromosorb-w acid washed 60–80 mesh.

Typical procedures

Reaction of styrene oxide (1a) with $NaNO_2$. In a round-bottom flask, a solution of cyclohexene oxide (98 mg, 1 mmol) in SDS (0.1 M, 3 cm^3) and $NaNO_2$ (104 mg, 1.5 mmol) was prepared. $Ce(OTf)_4$ (73.6 mg, 0.1 mmol) was added to this solution and the reaction mixture was stirred at room temperature for 10 h. The reaction was monitored by TLC. After completion of the reaction, the mixture was extracted with chloroform (4 × 10 cm^3). The emulsion was broken by adding small portions of NaCl. The organic layer was dried with anhydrous Na_2SO_4. The solvent was evaporated and the crude product was chromatographed on a short column of silica gel eluted with petroleum ether (60–80) to give *trans*-2-nitrocyclohexanol in 78% yields, b.p. 82–83 °C (lit.[39] 81 °C).

Reaction of allyl 2,3-epoxypropyl ether (1e) with $NaNO_3$. To a solution of allyl 2,3-epoxypropyl ether (114 mg, 1 mmol) and $NaNO_3$ (127.5 mg, 1.5 mmol) in SDS (0.1 M, 3 cm^3), $Ce(OTf)_4$ (73.6 mg, 0.1 mmol) was added and the reaction was monitored by TLC. After completion of the reaction, the mixture was extracted with chloroform (4 × 10 cm^3) and the emulsion was broken by adding small portions of NaCl. The organic layer was dried with anhydrous Na_2SO_4. The solvent was evaporated and the crude product was chromatographed on silica gel to give the corresponding β-nitrato alcohol in 78% yield (b.p. 82–84 °C/2 Torr, lit.[40] 85 °C/2 Torr).

Reaction of styrene oxide (1a) with sodium chloride. To a solution of styrene oxide (120 mg, 1 mmol) in SDS (0.1 M, 3 cm^3) and NaCl (91 mg, 1.5 mmol), $Ce(OTf)_4$ (73.6 mg, 0.1 mmol) was added. The reaction mixture was stirred for 20 min at room temperature. After completion of the reaction, water (10 cm^3) was added and extracted with chloroform (4 × 10 cm^3). NaCl was added in portions to break the emulsion. The organic layer was dried with anhydrous Na_2SO_4. Evaporation of the solvent followed by column chromatography on silica gel gave 2-chloro-2-phenylethanol in 83% yield (b.p. 115–116 °C/6 Torr, lit.[26a] 106–120 °C/5 Torr).

Conversion of styrene oxide (1a) to styrene epoxy sulfide. To a solution of styrene oxide (120 mg, 1 mmol) in SDS (0.1 M, 3 cm^3) and NaSCN (123 mg, 1.5 mmol), $Ce(OTf)_4$ (73.6 mg, 0.1 mmol) was added. The reaction mixture was stirred for 30 min at room temperature. After completion of the reaction, water (10 cm^3) was added and extracted with chloroform (4 × 10 cm^3). NaCl was added in small portions to break the emulsion of SDS solution and $CHCl_3$. The organic layer was dried with anhydrous Na_2SO_4. The solvent was evaporated. After chromatography on a short column of silica gel using CCl_4 as eluent, the pure styrene sulfide was obtained in 92% yield (b.p. 89–91 °C/5 Torr, lit.[41] 85–88 °C/5 torr).

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References

1 F. H. Quina and H. Chaimovich, *J. Phys. Chem.*, 1979, **83**, 1844.
2 K. Yamashita, M. Chiba, H. Ishida and K. Ohkubo, *J. Chem. Soc., Perkin Trans. 2*, 1991, 367.
3 (*a*) K. Yamashita, M. Chiba, H. Ishida and K. Ohkubo, *Bull. Chem. Soc. Jpn.*, 1991, **64**, 410; (*b*) S. Biggs, A. Hill, J. Selb and F. Candau, *J. Phys. Chem.*, 1992, **96**, 1505; (*c*) C. Tondre, B. Claude-Montigny, M. Ismael, P. Scrimin and P. Tecilla, *Polyhedron*, 1991, **10**, 1791; (*d*) J. A. Zoltwicz and L. B. Bloom, *J. Phys. Chem.*, 1993, **97**, 2755.
4 C. A. Bunton and M. Minch, *Tetrahedron Lett.*, 1970, 3881.
5 L. H. Gan, *Can. J. Chem.*, 1985, **63**, 598.
6 C. A. Bunton, J. R. Moffatt and E. Rodenas, *J. Am. Chem. Soc.*, 1982, **104**, 2653.
7 G. Cerichelli, G. Mancini, L. Luchetti, G. Savelli and C. A. Bunton, *J. Phys. Org. Chem.*, 1991, **4**, 71.
8 (*a*) T. J. Broxton and V. Marcou, *J. Org. Chem.*, 1991, **56**, 1041; (*b*) D. Ranganathan, S. Ranganathan, G. P. Singh and B. K. Patel, *Tetrahedron Lett.*, 1993, **34**, 525.
9 T. J. Broxton, *Aust. J. Chem.*, 1991, **44**, 667.
10 Y. S. Kang, H. J. D. McManus and L. Kevan, *J. Phys. Chem.*, 1992, **96**, 7473.
11 (*a*) A. B. Mandal and B. U. Nair, *J. Phys. Chem.*, 1991, **95**, 9008; (*b*) A. P. Abbott, C. L. Miaw and J. F. Rusling, *J. Electroanal. Chem.*, 1992, **327**, 31.
12 J. F. Rusling, *Acc. Chem. Res*, 1991, **24**, 75.
13 I. Ascone, P. D'Angelo and N. V. Pavel, *J. Phys. Chem.*, 1994, **98**, 2982.
14 T. Isoda, M. Yamasaki, H. Yano, T. Sano and S. Harada, *J. Chem. Soc., Faraday Trans.*, 1994, **90**, 869.
15 J. C. Scaiano and J. L. Shi, *Chem. Phys. Lett.*, 1990, **173**, 271.
16 P. K. Freeman and Y. S. Lee, *J. Org. Chem.*, 1992, **57**, 2846.
17 C. A. Bunton, L. Robinson and M. Stam, *Tetrahedron Lett.*, 1971, 121.
18 S. Ono, H. Shosenji and K. Yamada, *Tetrahedron Lett.*, 1981, 2391.
19 Y. M. Zhang, C. L. Fu and W. Q. Fan, *Chin. J. Chem.*, 1990, **1**, 89.
20 J. G. J. Weijnen, A. Koudijs and J. F. J. Engbersen, *J. Mol. Catal.*, 1992, **73**, 15.
21 (*a*) S. Tascioglu, *Tetrahedron*, 1996, **52**, 1113; (*b*) C. A. Bunton, F. Nome, F. H. Quina and L. S. Romsted, *Acc. Chem. Res*, 1991, **24**, 357.
22 O. S. Tee and A. A. Fedortchenko, *Can. J. Chem.*, 1997, **75**, 1434.
23 (*a*) P. A. Grieco, *Organic Synthesis in Water*; Thomson Science, London, 1998; (*b*) N. Iranpoor, H. Firouzabadi, A. Safavi and M. Shekarriz, *Synth. Commun.*, 2002, **32**, 2287.
24 (*a*) F. Fringuelli, F. Pizzo and L. Vaccaro, *Synlett*, 2000, 311; (*b*) F. Fringuelli, F. Pizzo and L. Vaccaro, *Synthesis*, 2000, 646; (*c*) F. Fringuelli, F. Pizzo and L. Vaccaro, *Tetrahedron Lett.*, 2001, **42**, 1131; (*d*) H. Y. Rhyoo, H. J. Park, W. H. Suh and Y. K. Chung, *Tetrahedron Lett.*, 2002, **43**, 269 and references cited therein.
25 T. Imamoto, Y. Koide and S. Hiyama, *Chem. Lett.*, 1990, 1445.
26 (*a*) N. Iranpoor, T. Tarrian and Z. Movahedi, *Synthesis*, 1996, 1473; (*b*) N. Iranpoor and H. Adibi, *Bull. Chem. Soc. Jpn.*, 2000, **73**, 675.
27 H. Kotsuki and T. Shimanouchi, *Tetrahedron Lett.*, 1996, **37**, 1845.
28 J.-C. Yang, D. O. Shah, N. U. M. Rao, W. A. Freeman, G. Sosnovsky and D. G. Gorenstein, *Tetrahedron*, 1988, **44**, 6305.
29 J. A. Ciaccio, C. Stanescu and J. Bontemps, *Tetrahedron Lett.*, 1992, **33**, 1431.
30 (*a*) M. Chini, P. Crotti, L. Favero and F. Macchia, *Tetrahedron Lett.*, 1991, **32**, 4775; (*b*) M. Chini, P. Crotti, L. Favero, F. Macchia and M. Pineschi, *Tetrahedron Lett.*, 1994, **35**, 433.
31 N. Iranpoor and M. Shekarriz, *Synth. Commun.*, 1999, **29**, 2249.
32 N. Iranpoor, B. Tamami and M. Shekarriz, *Synth. Commun.*, 1999, **29**, 3313.
33 (*a*) S. A. Halvati, M. M. Timotheous-Potamie and A. C. Galokerinos, *Analyst*, 1990, **115**, 1229; (*b*) W. L. Hinze, E. Pramaturo and E. Drit, *Rev. Anal. Chem.*, 1993, **24**, 133.
34 (*a*) C. Bonini and G. Righi, *Synthesis*, 1994, 225; (*b*) G. S. Bajwa and R. C. Anderson, *Tetrahedron Lett.*, 1991, **32**, 3021.
35 (*a*) H. Kotsuki and T. Shimanouchi, *Tetrahedron Lett.*, 1996, **37**, 1845; (*b*) M. Chini, P. Crotti, C. Gardelli and F. Macchia, *Tetrahedron*, 1992, **48**, 3805; (*c*) H. Kotsuki and T. Shimanouchi, *Tetrahedron Lett.*, 1996, **37**, 1845.
36 G. Sabitha, R. S. Babu, M. S. Kumar Reddy and J. S. Yadav, *Synthesis*, 2002, **15**, 2254.
37 (*a*) M. Onaka, K. Sugita and Y. Izumi, *J. Org. Chem.*, 1989, **54**, 1116; (*b*) S. Saito, T. Nishikawa, Y. Yokoyama and T. Mariwake, *Tetrahedron Lett.*, 1990, **31**, 221; (*c*) E. P. Muller, *Helv. Chim. Acta.*, 1982, **65**, 1617; (*d*) D. M. Coe, P. L. Myers, D. M. Parry, S. M. Roberts and R. S. Storer, *J. Chem. Soc., Chem. Commun.*, 1990, 151.
38 (*a*) B. Tamami and H. Mahdavi, *Tetrahedron Lett.*, 2001, **42**, 8721; (*b*) E. F. V. Seriven and K. Turnbull, *Chem. Rev.*, 1988, **88**, 297; (*c*) M. M. Campbell, R. C. Craig, J. Radpath, D. S. Savage and T. Sleigh, *J. Chem. Soc., Perkin Trans. 1*, 1979, 3042; (*d*) P. Crotti, V. D. Bussolo, L. Favero, F. Maccia and M. Pineschi, *Tetrahedron Lett.*, 1995, **36**, 1675.
39 B. Kalita, N. C. Barua, M. Bezbarua and G. Bez, *Synlett*, 2001, **9**, 1411.
40 N. Iranpoor and P. Salehi, *Tetrahedron*, 1995, **51**, 909.
41 N. Iranpoor and F. Kazemi, *Synthesis*, 1996, 821.