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Effective asymmetric oxidation of enones and alkyl aryl sulfides

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Abstract

Asymmetric epoxidation of aliphatic enones can be achieved with good conversions and high levels of enantiomeric excess using a catalyst, formulated as **6**, derived from dibutylmagnesium and a range of dialkyl tartrates, with *tert*-butylhydroperoxide as the oxidant. This process works best with the addition of small amounts of water and 4 Å molecular sieves, and can be scaled up to good effect. Optimisation of Bolm and Bienewald's vanadium-based method for asymmetric oxidation of alkyl aryl sulfides by aqueous hydrogen peroxide using Schiff bases derived from *tert*-leucinol as ligands, confirmed that the ligand **12** derived from 3,5-diiodosalicylaldehyde is the optimum choice.

Keywords: Asymmetric; Nucleophilic epoxidation; Magnesium; Sulfur oxidation; Vanadium

1. Catalytic asymmetric epoxidation of enones

Since the pioneering studies of Julia and Colonna [1,2], who discovered the first effective method for the catalytic asymmetric epoxidation of chalcone derivatives using a combination of polyamino acid, base and aqueous hydrogen peroxide, a great deal of effort has been devoted to improving the practicality of this method [3–11], and to discovering new methods to achieve this transformation. In this latter regard, chiral phase transfer catalysts in combination with a base and a suitable oxidant have proved to be effective [12–19], as has the use of various metal-based systems. Initial results included the stoichiometric use of alkylzinc alkylperoxides [20,21], the use of chiral polybinaphthyl zinc complexes as catalysts with *tert*-butylhydroperoxide as oxidant [22], and the catalytic use of zinc/BINOL derivatives [23]. Each of these approaches generally only works well for enones in which at least one of the substituents is an aromatic residue (or another residue which prevents enolisation), and this is a limitation. Arguably the most general method for the catalytic asymmetric epoxidation of enones is that discovered by Shibasaki and co-workers, using a combination of lanthanide alkoxides and (substituted) BINOL derivatives, with *tert*-butylhydroperoxide as the oxygen source [24,25]. This reagent system not only epoxidises simple *trans*-aliphatic enones, but is also able to epoxidise *cis*-aliphatic enones [26] preserving the original stereochemistry of the alkene in the *cis*-epoxide product. Recent work has shown how the process can be adapted for the epoxidation of a range of unsaturated carboxylic acid derivatives [27,28], culminating in a process for epoxidation of unsaturated esters [29]. A comprehensive review of the whole area of asymmetric epoxidation has very recently been published [30], which updates an earlier, more specific, review on nucleophilic epoxidation [31].

2. Results and discussion

Our contributions in this field have been based on the use of main group metals. We first established that treatment of chalcone **1** with a reagent prepared from lithium *tert*-butylperoxide, prepared from *n*-butyllithium and *tert*-butylhydroperoxide (dried by azeotropic distillation using the method of Sharpless) [32], and a stoichiometric amount of diethyl tartrate **3a** gave the corresponding epoxide **2** in reasonable yield, and 62% ee (Scheme 1). It was essential that a stoichiometric amount of lithium butoxide was also present [33].

In contrast, when use of the corresponding magnesium system was explored, it was discovered that in this case only a catalytic amount of base (dibutylmagnesium) and chiral ligand

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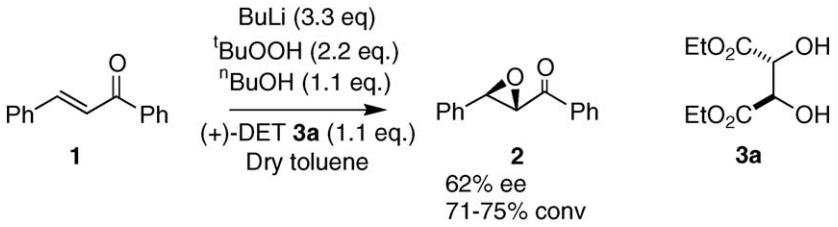
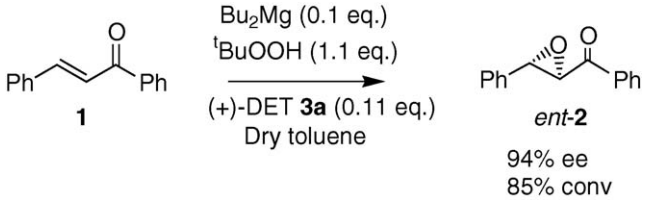
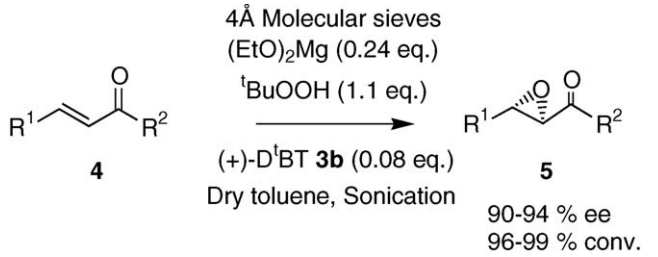


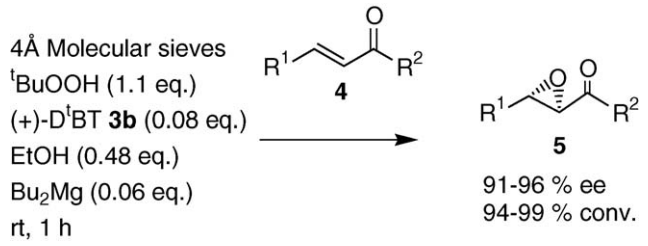
Scheme 1. Stoichiometric asymmetric epoxidation of chalcone using lithium *tert*-butylperoxide.



Scheme 2. Catalytic asymmetric epoxidation of chalcone.



Scheme 4. Catalytic asymmetric epoxidation of aliphatic enones using $Mg(OEt)_2$ as the base and ultrasonication.



Scheme 5. Addition of ethanol allows the catalytic asymmetric epoxidation of aliphatic enones using $Mg(OEt)_2$ as the base without ultrasonication.

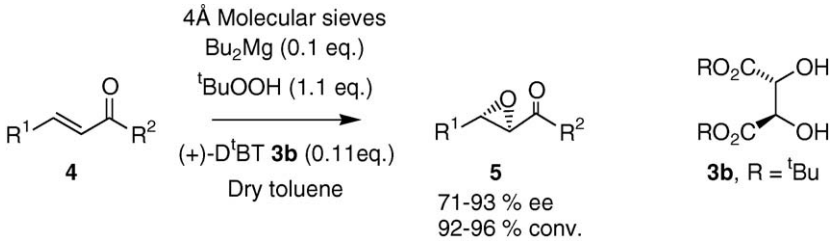
(diethyl tartrate) were required to effect epoxidation. The reaction was substantially more enantioselective, giving chalcone epoxide *ent*-**2** in 94% ee, and of the opposite absolute configuration to that obtained in the lithium system with the same enantiomer of ligand (Scheme 2) [33].

Application of the same reaction conditions to the epoxidation of simple aliphatic enones **4** gave results that were encouraging from the point of view of enantioselectivity (with the epoxy ketone products **5** being formed in up to 76% ee), but the conversions were modest (typically 33%), suggesting that catalyst inactivation was occurring. Reminiscent of the way that addition of activated 4 Å molecular sieves renders the Sharpless asymmetric epoxidation process catalytic [34,35], addition of powdered, activated 4 Å molecular sieves to our nucleophilic epoxidation system increased not only the conversion, but also the enantioselectivity. Exploration of a range of different tartrate derivatives showed that tartrate esters derived from secondary or tertiary alcohols performed the best, with di-*tert*-butyl tartrate **3b** giving high conversions (92–96%) and excellent enantioselectivity (up to 93%) of the product epoxy ketones **5** (Scheme 3) [36].

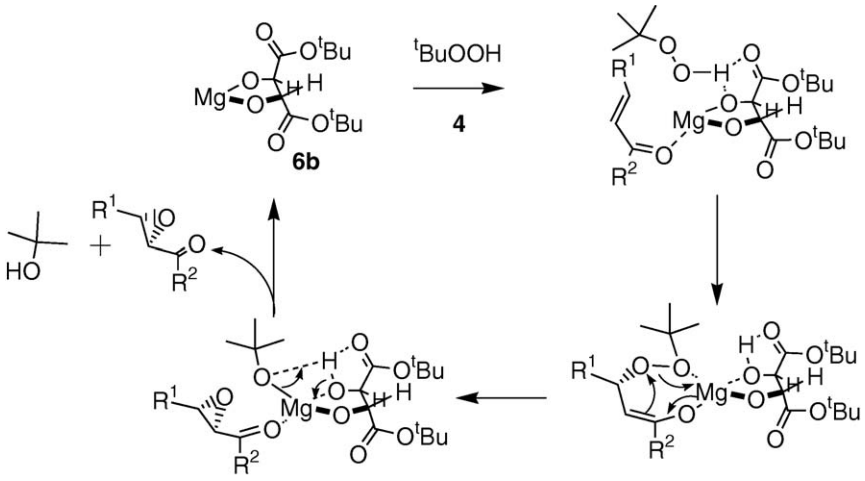
Given that the presumed catalyst was prepared by treatment of dibutylmagnesium with a dialkyl tartrate, it seemed reasonable to explore other magnesium bases. Provided ultrasonication was employed, magnesium ethoxide allowed similarly high levels of conversion and enantioselectivity to be attained (Scheme 4).

While the use of ultrasonication was effective, it was not especially convenient, and it was therefore gratifying to discover that addition of a small amount of ethanol could fulfill the same purpose. This modification also allowed a substantial reduction in the amount of base required (Scheme 5). After formation of the active catalyst (normally treatment for 1 h), epoxidation was usually complete within 18–24 h at room temperature.

The nature of the active catalytic species remains an open question, but it appears reasonable to speculate that it is the magnesium alkoxide **6b**, derived from the di-*tert*-butyl tartrate ligand. Such a species would be able to activate both the substrate enone **4** (by magnesium complexation to the carbonyl group), and the *tert*-butylhydroperoxide, by deprotonation. It seems likely that both of these steps take place within the chiral environment of the tartrate ligand, thus allowing facial discrimination in the attack of the nucleophilic *tert*-butylhydroperoxide



Scheme 3. Catalytic asymmetric epoxidation of aliphatic enones using Bu_2Mg as the base.



Scheme 6. Proposed catalytic cycle for the asymmetric epoxidation of enones.

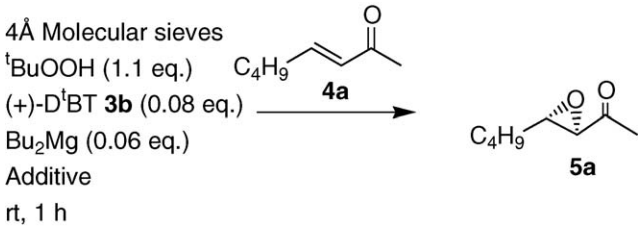
anion onto the enone. The normal Weitz–Scheffer mechanism can then take place, leading to formation of the epoxyketone, and regeneration of the catalyst (Scheme 6).

It is worthwhile noting that the pK_a of a dialkyl tartrate is likely to be intermediate between that of *tert*-butylhydroperoxide (pK_a 12.8, in water) [37] and the by-product *tert*-butanol (pK_a 16.6, in water) [38]. This is an ideal situation for catalysis, since both the initial deprotonation of *tert*-butylhydroperoxide and the regeneration of the catalyst are favourable processes. The presence of the carbonyl ester group does appear to be necessary for the catalyst to be effective, and one possible role is the formation of a hydrogen bond to the *tert*-butylhydroperoxide during the deprotonation process. The absolute stereochemical outcome of the process can be rationalized by this overall scheme.

The observation that addition of ethanol to the reaction mixture was beneficial suggested that it would be worthwhile to study the effect of other additives when using dibutylmagnesium as base in the epoxidation of 3-octen-2-one **4a** to give the corresponding epoxy ketone **5a** (Scheme 7). Addition of water (0.48 equiv., but 8 equiv. relative to dibutylmagnesium) (Table 1, entry 2) gave a similar result to that obtained using magnesium ethoxide and ethanol. Addition of more water (1.0 equiv., entry 3) showed an improved result, but omission of the molecular sieves completely inhibited the reaction (entry 4). Of most interest from a practical point of view, was that the use of "wet" *tert*-butylhydroperoxide (simply prepared by extraction of commercial 70% aqueous *tert*-butylhydroperoxide into toluene, without azeotropic distillation) gave a similar excellent result (entry 5). This observation has substantial implications when considering larger scale operations, since although the azeotropic distillation has been conducted on many occasions without incident it is still a potentially hazardous operation.

The discovery that a combination of water and 4 Å molecular sieves was optimal for the process raises questions concerning the role of each component. Similar observations have been made during studies on the optimization of the Shibasaki epoxidation system [39]. The fact that the intrinsic enantioselectivity of the process does not depend on the presence of 4 Å molecular sieves suggests that the sieves are not modifying the catalyst substantially (for example by cation exchange). A linear dependence of ee of the product on ee of the tartrate ester was observed, consistent with the active species being monomeric. In earlier work, we had established that treatment of diethyl tartrate with dibutylmagnesium under anhydrous conditions gave an amorphous white precipitate which did act as a catalyst for the nucleophilic epoxidation reaction [36]. This material appeared to be oligomeric, and we can therefore speculate that the main role of water is to solubilise the catalyst by disrupting the aggregates, perhaps to the extent of forming a monomeric species. It appears that an excess of water is detrimental, presumably because it causes hydrolysis of the magnesium alkoxide.

In our studies using "wet" *tert*-butylhydroperoxide, it became apparent that better, more consistent results were obtained by the use of di-*iso*-propyl tartrate **3c**, rather than di-*tert*-butyl tartrate **3b**, as the chiral ligand. This had the added benefit that the former

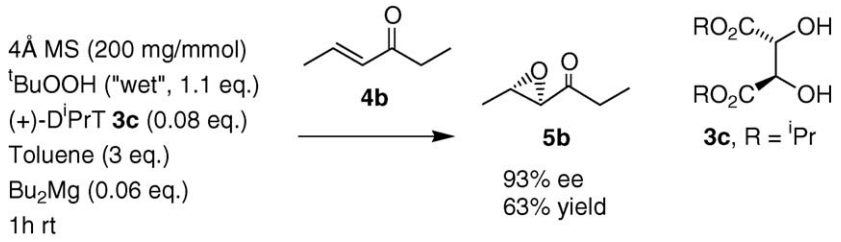


Scheme 7. Catalytic asymmetric epoxidation of 3-octen-2-one in the presence of additives.

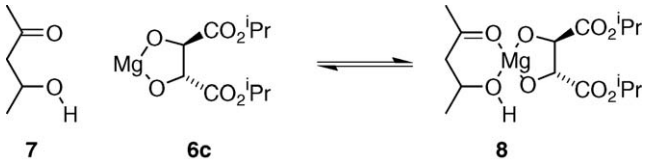
Table 1
Epoxidation of 3-octen-2-one **4a** in the presence of different additives

Entry	Additive	Ee (%)/conv. (%)[a]
1	Control (ethanol 0.48 equiv.)	94/99
2	Water (0.48 equiv.)	92/92
3	Water (1.0 equiv.)	97/99
4	Water (1.0 equiv.), no MS	Sm
5	None, but 'wet' tBuOOH used	97/100

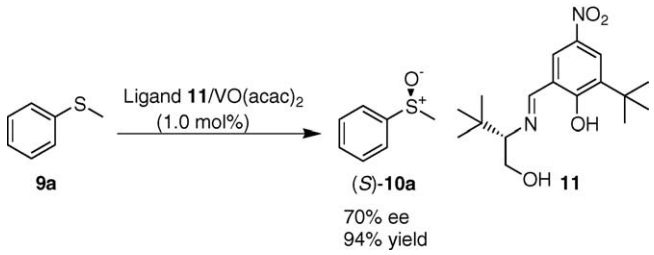
[a] Determined by chiral phase GC analysis using a heptakis(2,6-di-*O*-methyl-3-*O*-pentyl)-β-cyclodextrin column.



Scheme 8. Large scale asymmetric epoxidation of 4-hexen-3-one.



Scheme 9. Proposed mechanism for inhibition of catalysis by 4-hydroxypentan-2-one.



Scheme 10. Bolm and Bienewald's asymmetric oxidation of methyl phenyl sulfide.

is substantially less expensive than the latter, which we routinely prepared by the method of Evans et al. [40]. A larger scale epoxidation of the low molecular weight substrate 4-hexen-3-one **4b** was therefore conducted (using 10 g of substrate) using these conditions, and a satisfactory yield (63%) of the corresponding epoxyketone **5b** (ee 93%) was obtained, simply by distillation of the product (Scheme 8). In this case, addition of a small amount of toluene ensured that stirring was much more efficient.

When these optimized conditions were applied to a series of other substrates, specifically a set of separate batches of undistilled 3-penten-2-one, no conversion was observed in one case. Careful analysis by GC/MS established that this particular batch contained a significant amount (4.2%) of 4-hydroxypentan-2-one **7**. When this same batch was purified by distillation (reducing the amount of 4-hydroxypentan-2-one to 0.05%), and subjected to the same epoxidation reaction conditions, the expected epoxyketone was obtained (92% ee, 96% conversion, determined by GC). The most obvious interpretation of this result is that 4-hydroxypentan-2-one **7** is a ligand for the presumed catalyst **6c**, and acts as a competitive inhibitor forming adduct **8** (Scheme 9). This seems entirely consistent with a catalytic intermediate in which binding of both *tert*-butylhydroperoxide and enone to magnesium is required.

3. Conclusions

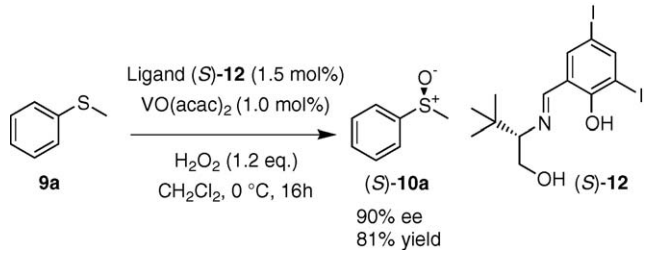
We have developed a simple method for the catalytic asymmetric nucleophilic epoxidation of simple aliphatic enones (giving enantiomeric excesses in the range 92–97%), using inexpensive reagents that are commercially available. The only significant drawback of this process is the need for (relatively) large amounts of activated 4 Å molecular sieves.

4. Asymmetric oxidation of alkyl aryl sulfides

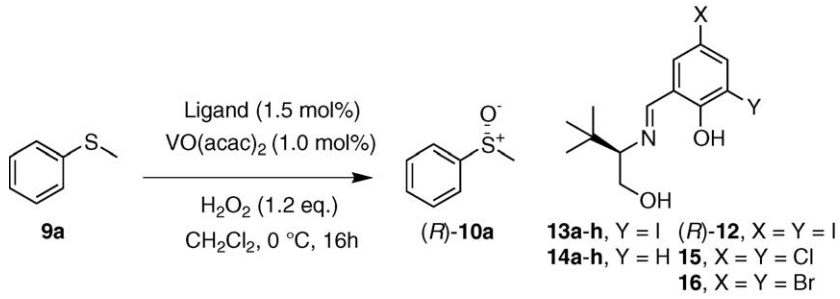
Chiral sulfoxides are an important class of compounds that find increasing use as chiral auxiliaries in asymmetric synthesis [41,42], and are a key structural unit in compounds with useful biological properties [43]. Many methods for the asymmetric oxidation of prochiral sulfides have been reported, and this work has been extensively reviewed [41,44–46], following the initial reports by Kagan [47,48] and Modena [49] on the use of variously modified Sharpless reagents for this reaction.

One of the most widely studied metal-based systems has been that discovered by Bolm and Bienewald [50–53], who employed a combination of *tert*-leucinol-derived Schiff bases **11** and $VO(acac)_2$ (1.0 mol%), with aqueous hydrogen peroxide as oxidant, in a two-phase system using dichloromethane as solvent at room temperature. This allows the oxidation of methyl phenyl sulfide **9a** to the corresponding sulfoxide (*S*)-**10a** (70% ee, 94% yield) (Scheme 10). Other groups sought to optimize the system, by variation of the aromatic aldehyde [54–56], and the amino alcohol [57,58], and to extend it to other substrates [59,60].

Anson et al. screened a variety of chiral Schiff base ligands, and found that the 3,5-diiodo ligand (*S*)-**12**, in combination with $VO(acac)_2$ gave excellent results in the catalytic asymmetric sulfoxidation of alkyl aryl sulfides using hydrogen peroxide, again in dichloromethane as solvent, but at 0 °C [61]. For example, methyl phenyl sulfide **9a** was oxidized to (*S*)-methyl phenyl sulfoxide **10a** (81%, 90% ee) (Scheme 11). Recently, Legros and Bolm reported that a combination of this ligand with iron is also



Scheme 11. Anson and co-workers's improved asymmetric oxidation of methyl phenyl sulfide.



Scheme 12. Use of new Schiff-base ligands for the asymmetric oxidation of methyl phenyl sulfide.

very effective for the asymmetric oxidation of prochiral sulfides [62,63], especially in the presence of substituted benzoic acids and the corresponding lithium salts as additives [64,65].

The success of the combination of ligand **12** with vanadium in the catalytic asymmetric oxidation of alkyl aryl sulfides is intriguing, and in an effort to understand the impact of variation of the aromatic substituents, the performance of a series of previously unreported 3-iodo-5-substituted derivatives **13** was compared with the corresponding ligands unsubstituted at C-3 **14** (Scheme 12, Table 2), together with the chloro and bromo analogues of (*R*)-**12**, namely **15** and **16**. In this screening, all the ligands were prepared from (*R*)-*tert*-leucinol, which has recently become commercially available. The results clearly indicated that, in all cases, the 3-iodo-derivatives performed better than those lacking the 3-iodo substituent. Two new ligands performed well, namely the 3-iodo-5-chloro ligand **13b** (entry 3) and the 3,5-dichloro ligand **15** (entry 17), but the 3,5-diiodo ligand (*R*)-**12**, which gave the (*R*)-sulfoxide **10a**, proved to be optimal. The good results from the 3,5-dichloro ligand **15** establish that the presence of a 3-iodo substituent is not essential for high ee.

The overall conclusion from these studies is that the diiodo ligand **12** remains the best, and the only drawback is that the

Table 2
Ligand screening: asymmetric oxidation of methyl phenyl sulfide with $VO(acac)_2$, under reaction conditions shown in Scheme 12

Entry	Ligand	X	Y	Yield (%)[a]	ee (R)[a]
1	**13a**	F	I	81	83.6
2	**14a**	F	H	81	42.6
3	**13b**	Cl	I	83	88.5
4	**14b**	Cl	H	83	66.7
5	**13c**	Br	I	75	81.0
6	**14c**	Br	H	70	73.2
7	**13d**	H	I	88	75.5
8	**14d**	I	H	85	50.6
9	**13e**	^{t}Bu	I	81	75.3
10	**14e**	^{t}Bu	H	83	58.4
11	**13f**	Me	I	81	80.0
12	**14f**	Me	H	80	33.8
13	**13g**	MeO	I	81	79.2
14	**14g**	MeO	H	76	50.5
15	**13h**	NO_2	I	83	77.5
16	**14h**	NO_2	H	76	61.6
17	**15**	Cl	Cl	79	88.0
18	**16**	Br	Br	79	73.5
19	(*R*)-**12**	I	I	75	92.1

[a] Determined by chiral phase h.p.l.c. using a Chiralpak AS column.

Scheme 13. Asymmetric oxidation of alkyl aryl sulfides using ligand (*R*)-**12** in chloroform.

enantiomeric excess is typically around 90%, with that obtained with 2-naphthyl methyl sulfide (97% ee) being exceptional [61]. After a substantial amount of screening, we eventually established that the use of the diiodo ligand in chloroform, rather than dichloromethane, as solvent resulted in excellent levels of enantiomeric excess (97–99.5% ee) for a range of alkyl aryl sulfides, which were isolated in good yields (71–88%) (Scheme 13). This solvent effect appears, at least partially, to result from a highly efficient kinetic resolution of the product sulfoxides **10**, in which the minor enantiomer of the sulfoxide is converted selectively into the corresponding sulfone **17**. Further details of this work have appeared elsewhere [66].

5. Conclusions

We have confirmed that the diiodo ligand **12** is amongst the best ligands in the vanadium-catalysed asymmetric oxidation of alkyl aryl sulfides using hydrogen peroxide as oxidant. Minor variations in the structure of the ligand result in a reduction in the enantioselectivity of the oxidation process. However, use of chloroform as solvent, allows very high levels of enantioselectivity to be obtained for a range of alkyl aryl sulfides. The cause of this solvent effect is a subject for further study.

Acknowledgements

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References

[1] S. Julia, J. Masana, J.C. Vega, Angew. Chem. Int. Ed. 19 (1980) 929.
[2] S. Julia, J. Guixer, J. Masana, J. Rocas, S. Colonna, R. Annunziata, H. Molinari, J. Chem. Soc., Perkin Trans. 1 (1982) 1317.

[3] B.M. Adger, J.V. Barkley, S. Bergeron, M.W. Cappi, B.E. Flowerdew, M.P. Jackson, R. McCague, T.C. Nugent, S.M. Roberts, J. Chem. Soc., Perkin Trans. 1 (1997) 3501.
[4] M.W. Cappi, W.P. Chen, R.W. Flood, Y.W. Liao, S.M. Roberts, J. Skidmore, J.A. Smith, N.M. Williamson, Chem. Commun. (1998) 1159.
[5] L. Carde, H. Davies, T.P. Geller, S.M. Roberts, Tetrahedron Lett. 40 (1999) 5421.
[6] T. Geller, S.M. Roberts, J. Chem. Soc., Perkin Trans. 1 (1999) 1397.
[7] R.W. Flood, T.P. Geller, S.A. Petty, S.M. Roberts, J. Skidmore, M. Volk, Org. Lett. 3 (2001) 683.
[8] A. Berkessel, N. Gasch, K. Glaubitz, C. Koch, Org. Lett. 3 (2001) 3839.
[9] T. Geller, A. Gerlach, C.M. Kruger, H.C. Militzer, Tetrahedron Lett. 45 (2004) 5065.
[10] T. Geller, C.M. Kruger, H.C. Militzer, Tetrahedron Lett. 45 (2004) 5069.
[11] A. Gerlach, T. Geller, Adv. Synth. Catal. 346 (2004) 1247.
[12] S. Arai, H. Tsuge, T. Shioiri, Tetrahedron Lett. 39 (1998) 7563.
[13] B. Lygo, P.G. Wainwright, Tetrahedron Lett. 39 (1998) 1599.
[14] E.J. Corey, F.Y. Zhang, Org. Lett. 1 (1999) 1287.
[15] B. Lygo, P.G. Wainwright, Tetrahedron 55 (1999) 6289.
[16] W. Adam, P.B. Rao, H.G. Degen, C.R. Saha-Moller, Tetrahedron: Asymmetry 12 (2001) 121.
[17] B. Lygo, D.C.M. To, Tetrahedron Lett. 42 (2001) 1343.
[18] S. Arai, H. Tsuge, M. Oku, M. Miura, T. Shioiri, Tetrahedron 58 (2002) 1623.
[19] B. Lygo, D.C.M. To, Chem. Commun. (2002) 2360.
[20] D. Enders, J. Zhu, G. Raabe, Angew. Chem. Int. Ed. 35 (1996) 1725.
[21] D. Enders, J.Q. Zhu, L. Kramps, Liebigs Ann. Recl. (1997) 1101.
[22] H.B. Yu, X.F. Zheng, Z.M. Lin, Q.S. Hu, W.S. Huang, L. Pu, J. Org. Chem. 64 (1999) 8149.
[23] A. Minatti, K.H. Dotz, Synlett (2004) 1634.
[24] M. Bougauchi, S. Watanabe, T. Arai, H. Sasai, M. Shibasaki, J. Am. Chem. Soc. 119 (1997) 2329.
[25] T. Nemoto, T. Ohshima, K. Yamaguchi, M. Shibasaki, J. Am. Chem. Soc. 123 (2001) 2725.
[26] S. Watanabe, T. Arai, H. Sasai, M. Bougauchi, M. Shibasaki, J. Org. Chem. 63 (1998) 8090.
[27] T. Nemoto, T. Ohshima, M. Shibasaki, J. Am. Chem. Soc. 123 (2001) 9474.
[28] T. Ohshima, T. Nemoto, S. Tosaki, H. Kakei, V. Gnanadesikan, M. Shibasaki, Tetrahedron 59 (2003) 10485.
[29] H. Kakei, R. Tsuji, T. Ohshima, M. Shibasaki, J. Am. Chem. Soc. 127 (2005) 8962.
[30] Q.H. Xia, H.Q. Ge, C.P. Ye, Z.M. Liu, K.X. Su, Chem. Rev. 105 (2005) 1603.
[31] M.J. Porter, J. Skidmore, Chem. Commun. (2000) 1215.
[32] J.G. Hill, B.E. Rossiter, K.B. Sharpless, J. Org. Chem. 48 (1983) 3607.
[33] C.L. Elston, R.F.W. Jackson, S.J.F. MacDonald, P.J. Murray, Angew. Chem. Int. Ed. 36 (1997) 410.
[34] R.A. Johnson, K.B. Sharpless, in: I. Ojima (Ed.), Catalytic Asymmetric Synthesis, VCH, New York, 1993, p. 103.
[35] T. Katsuki, V.S. Martin, Org. React. (NY) 48 (1996) 1.
[36] O. Jacques, S.J. Richards, R.F.W. Jackson, Chem. Commun. (2001) 2712.
[37] W.H. Richards, V.F. Hodge, J. Org. Chem. 35 (1970) 4012.
[38] W. Reeve, C.M. Erikson, P.F. Aluotto, Can. J. Chem., Rev. Can. Chim. 57 (1979) 2747.
[39] S. Watanabe, Y. Kobayashi, T. Arai, H. Sasai, M. Bougauchi, M. Shibasaki, Tetrahedron Lett. 39 (1998) 7353.
[40] D.A. Evans, B.W. Trotter, J.C. Barrow, Tetrahedron 53 (1997) 8779.
[41] I. Fernandez, N. Khiar, Chem. Rev. 103 (2003) 3651.
[42] M.C. Carreno, Chem. Rev. 95 (1995) 1717.
[43] J. Legros, J.R. Dehli, C. Bolm, Adv. Synth. Catal. 347 (2005) 19.
[44] C. Bolm, K. Muniz, J.P. Hildebrand, in: E.N. Jacobsen, A. Pfaltz, H. Yamamoto (Eds.), Comprehensive Asymmetric Catalysis I–III, vol. 2, Springer-Verlag, Berlin, Germany, 1999, p. 697.
[45] K.P. Volcho, N.F. Salakhutdinov, A.G. Tolstikov, Russ. J. Org. Chem. 39 (2003) 1537.
[46] H.B. Kagan, T.O. Luukas, in: M. Beller, C. Bolm (Eds.), Transition Metals for Organic Synthesis, vol. 2, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2004, p. 479.
[47] P. Pitchen, H.B. Kagan, Tetrahedron Lett. 25 (1984) 1049.
[48] P. Pitchen, E. Dunach, M.N. Deshmukh, H.B. Kagan, J. Am. Chem. Soc. 106 (1984) 8188.
[49] F. Di Furia, G. Modena, R. Seraglia, Synthesis (1984) 325.
[50] C. Bolm, F. Bienewald, Angew. Chem. Int. Ed. 34 (1996) 2640.
[51] C. Bolm, G. Schlingloff, F. Bienewald, J. Mol. Catal. A-Chem. 117 (1997) 347.
[52] C. Bolm, F. Bienewald, Synlett (1998) 1327.
[53] C. Bolm, Coord. Chem. Rev. 237 (2003) 245.
[54] A.H. Vetter, A. Berkessel, Tetrahedron Lett. 39 (1998) 1741.
[55] J. Skarzewski, E. Ostrycharz, R. Siedlecka, Tetrahedron-Asymmetry 10 (1999) 3457.
[56] Y.C. Jeong, S. Choi, Y.D. Hwang, K.H. Ahn, Tetrahedron Lett. 45 (2004) 9249.
[57] C. Ohta, H. Shimizu, A. Kondo, T. Katsuki, Synlett (2002) 161.
[58] M.E. Cucciolito, R. Del Litto, G. Roviello, F. Ruffo, J. Mol. Catal. A-Chem. 236 (2005) 176.
[59] D.A. Cogan, G.C. Liu, K.J. Kim, B.J. Backes, J.A. Ellman, J. Am. Chem. Soc. 120 (1998) 8011.
[60] S.A. Blum, R.G. Bergman, J.A. Ellman, J. Org. Chem. 68 (2003) 150.
[61] B. Pelotier, M.S. Anson, I.B. Campbell, S.J.F. Macdonald, G. Priem, R.F.W. Jackson, Synlett (2002) 1055.
[62] J. Legros, C. Bolm, Angew. Chem. Int. Ed. 42 (2003) 5487.
[63] A. Korte, J. Legros, C. Bolm, Synlett (2004) 2397.
[64] J. Legros, C. Bolm, Angew. Chem. Int. Ed. 43 (2004) 4225.
[65] J. Legros, C. Bolm, Chem.-Eur. J. 11 (2005) 1086.
[66] C. Drago, L. Caggiano, R.F.W. Jackson, Angew. Chem. Int. Ed. 44 (2005) 7221.