View Online

Green photochemistry: the use of microemulsions as green media in photooxygenation reactions

Emma E. Coyle,[a] Kieran Joyce,[a] Kieran Nolan[a] and Michael Oelgemöller*[b]

Received 1st April 2010, Accepted 8th July 2010
DOI: 10.1039/c004869k

Downloaded by City College of New York on 24 November 2010
Published on 03 September 2010 on http://pubs.rsc.org | doi:10.1039/C004869K

The use of 'green' microemulsions of ethyl acetate and water, using sodium dodecyl sulfate and alcoholic co-surfactants as a reaction medium, in photooxygenation reactions was investigated. This work looked at the optimisation of the microemulsion (the optimum ratio of components), an investigation of the effect of changing co-surfactant and optimisation of the reaction work-up for the synthesis of 5-hydroxy-1,4-naphthoquinone, Juglone. Isolated yields of 36–88% were achieved in just 4 h of irradiation. Microemulsions also allowed the usage of the sensitiser tetraphenylporphyrin (TPP) in a benign environment. The optimised procedure was furthermore applied to the synthesis of 5-amido-1,4-naphthoquinones, and moderate yields were achieved.

Introduction

Over the past few years, there has been a significant growth in interest in green chemistry, and its principles in academia and industry.[1] One of these approaches is use of light as a clean reagent.[2] We have been active in this research area and have demonstrated the feasibility of photochemical syntheses for a number of commodity chemicals. Our work has looked at green photoacylation reactions,[3] as well as the synthesis of naphthoquinones through photooxygenation reactions.[4] In particular, we have examined the synthesis of 1,4-naphthoquinones, which are important natural products that serve as valuable building blocks in synthesis and are key moieties in biologically-active compounds.[5] A well established route to these compounds is through the oxidation of the corresponding 1-naphthols,[6,7] but the known thermal pathways demonstrate disadvantages regarding selectivity, sustainability and scale-up.[6] Dye-sensitised photooxygenations represent a useful alternative, and various examples have been reported in the literature.[4,8] Our research has looked at the development of an entirely green procedure for dye-sensitised photooxygenation through the use of the solvent selection criteria developed by Pfizer[9] for the photochemical key-step and subsequent purification. The original irradiation procedures require the use of the hazardous solvents dichloromethane, acetonitrile or methanol (or their mixtures).[8] After an extensive investigation of alternate media, in particular looking at the use of alcohols,[4a–c] ionic liquids,[10] solvent-free synthesis[11] and supercritical carbon dioxide,[12] we chose to use microemulsions as green reaction media.[13]

Microemulsions are thermodynamically stable mixtures of oil (organic solvents), water, surfactants and co-surfactants, in which the surfactant surrounds microdroplets of water in the organic phase.[14] The mixtures appear homogeneous but when examined microscopically are seen to consist of nano-sized aqueous droplets in the oil phase. Holmberg has reviewed organic reactions in microemulsions, and outlined the advantages and disadvantages of this reaction medium.[14a] Advantages include increased solubilising ability (to overcome incompatibility problems), increased reaction rate compared to traditional synthesis and the ability to induce regioselectivity. A down-side to these mixtures is the use of surfactant in large quantities, which may be overcome through its recovery and recycling during purification. The use of microemulsions in oxygenation reactions has been demonstrated previously by Nardello *et al.*,[15] where singlet oxygen was generated in the "dark" from hydrogen peroxide using a sodium molybdate catalyst. The procedure has been scaled-up for the synthesis of a rose oxide precursor.[15f] Photooxygenation reactions of the 'Schenck' ene-type have also been demonstrated[15b] using a series of allylic alcohols, and were found to give different chemo- and diastereoselectivity to the photochemically-generated singlet oxygen reactions. Green microemulsions have also been reported, in which ethyl acetate is used as the organic component, instead of a halogenated organic solvent.[15a] These have demonstrated good singlet oxygen lifetimes and a suitability for use in oxygenation reactions. In addition, Griesbeck and co-workers have studied the selectivity of the Schenck-ene photooxygenation of an γ,δ-unsaturated ketone in microemulsion compared to acetonitrile.[16] This study shows that the use of microemulsions provide an environmental influence that may affect the selectivity of reactions.

Results and discussion

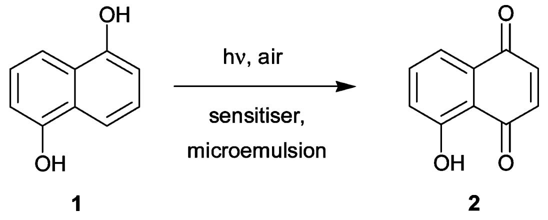
To demonstrate the use of microemulsions as green media for photooxygenation reactions, the conversion of 1,5-dihydroxynaphthalene (**1**) to Juglone (**2**, 5-hydroxy-1,4-naphthoquinone) was selected as a model reaction (Scheme 1). Under conventional conditions, *i.e.* using alcohols as reaction solvents, **2** has been obtained in yields up to 58% using artificial light illumination.[4c]

Green microemulsions of water in ethyl acetate, using sodium dodecyl sulfate and an alcoholic co-surfactant, were investigated and shown to be suitable solvents for the dye-sensitised photooxygenation. These exhibited an excellent solubilising ability

---

[a] *Dublin City University, School of Chemical Sciences and NCSR, Dublin 9, Ireland*
[b] *James Cook University, School of Pharmacy and Molecular Sciences, Townsville, QLD 4811, Australia.*
E-mail: michael.oelgemoeller@jcu.edu.au; Fax: +61 7 4781 6078; Tel: +61 7 4781 4543

Downloaded by City College of New York on 24 November 2010
Published on 03 September 2010 on http://pubs.rsc.org | doi:10.1039/C004869K



Scheme 1 Synthesis of Juglone **2**.

for all the reagents, which is attributed to the presence of both hydrophilic and hydrophobic regions in the medium, as depicted in Fig. 1.

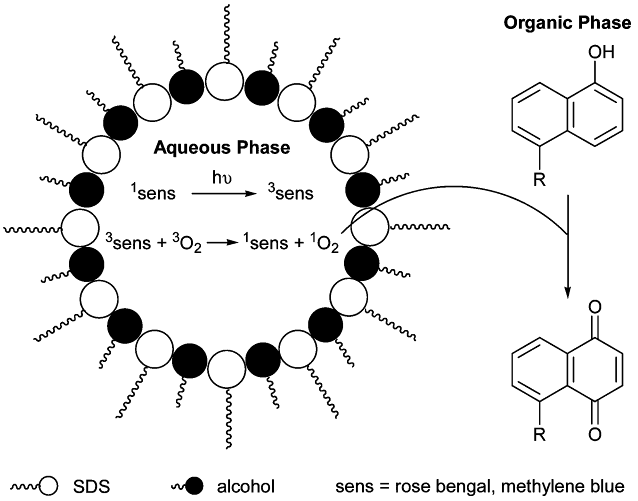


Fig. 1 A schematic of a microemulsion using RB or MB as a sensitiser.

The basic composition of the microemulsions used is water in ethyl acetate. To form homogeneous solutions, a surfactant is added, in this case sodium dodecyl sulfate (SDS). In addition, a co-surfactant is used. The ratio of the components determines whether or not a microemulsion is obtained. The influence of solutes is important, and so optimisation of the ratio of components was initially carried out, as shown in Table 1. Early investigations looked at the use of *n*-butanol as a co-surfactant as this was the co-solvent reported in previous green microemulsions.[15a] The substitution of *n*-butanol with *t*-amyl alcohol was studied, as this solvent has previously been used by us in photooxygenation reactions.[4a] Finally, the use of ethanol was investigated, which proved to be the most effective co-surfactant as it resulted in the use of less surfactant, as well as being more volatile and therefore offering ease of removal when compared to high boiling *n*-butanol or *t*-amyl alcohol. This is consistent with previous reports by Aubry, stating that the use of isopropyl alcohol offers similar advantages over *n*-butanol. The optimum ratio of sodium dodecyl sulfate–ethanol–ethyl acetate–water was found to be 3.1/7.9/73.3/15.7% by weight (Table 1, entry 10). Microscopy (Leica TCS, 40× and 63× dry lenses) of the solutions showed that less than 1% of the solution consisted of aggregates greater than 1 μm, indicating that nanosized droplets were indeed formed.

Following the identification of stable microemulsions, their stability in the presence of starting materials and sensitisers was assessed. This was achieved by the addition of **1** (1 mmol) and a sensitiser (rose bengal, methylene blue or tetraphenylporphyrin, 25 μmol) to the microemulsions (20 ml). The addition of these substances did not impact on the stability of the microemulsions. Despite the ionic nature of both rose bengal and methylene blue, the microemulsions remained stable, thus indicating their suitability for photooxygenation experiments. To confirm that the photooxygenation of **1** could be achieved in microemulsions, these solutions were irradiated for 4 h using a 500 W halogen lamp and the presence of **2** was determined by TLC.

As microemulsions are complex systems, optimisation of the work-up was necessary. For *t*-amyl alcohol-based microemulsions, **1** was irradiated for 4 h in a Schlenk flask with a 500 W halogen lamp in the presence of a sensitiser while the solution was being purged with air. The progress of the reaction was monitored by TLC analysis.

Initial work-up procedures looked at direct evaporation of the liquid components, followed by washing with cyclohexane[15] or directly introducing the residue onto a silica column to separate the product and surfactant. The former furnished **2** in a low yield of 20%, while the latter procedure gave **2** only in trace amounts. The use of Soxhlet extraction was also investigated, but **2** was again only obtained in trace amounts. Matrix effects caused by the surfactant thus appear to prevent or limit isolation of the product.[17] As an alternative, the use of multiple ethyl acetate–water extractions was investigated. Preliminary results showed that this protocol was suitable (Table 2, entry 1), but complete removal of SDS was not achieved and subsequent column chromatography was required.

To optimise the work-up for ethanolic microemulsions, the recovery of independently synthesised **2** was assessed using three procedures, namely extraction using ethyl acetate, washing with cyclohexane and washing with toluene (Table 3). Toluene

Table 1 Optimisation of the ratio of components for microemulsions

Entry	% SDS	Co-surfactant	% Co-surfactant	% EtOAc	% H_2O	Appearance
1	7.5	*n*-BuOH	7.5	70.0	15.0	Clear, homogeneous
2	7.3	*n*-BuOH	9.8	68.3	14.6	Clear, homogeneous
3	7.1	*n*-BuOH	11.9	66.7	14.3	Cloudy, no bilayer
4	7.5	*t*-AmOH	7.5	70.0	15.0	Clear, homogeneous
5	7.3	*t*-AmOH	9.8	68.3	14.6	Clear, homogeneous
6	7.1	*t*-AmOH	11.9	66.7	14.3	Clear, homogeneous
7	7.5	EtOH	7.5	70.0	15.0	Cloudy, no bilayer
8	7.7	EtOH	5.1	71.8	15.4	Cloudy, no bilayer
9	5.1	EtOH	7.7	71.8	15.4	Cloudy, no bilayer
10	3.1	EtOH	7.9	73.3	15.7	Clear, homogeneous

Downloaded by City College of New York on 24 November 2010
Published on 03 September 2010 on http://pubs.rsc.org | doi:10.1039/C004869K

Table 2 Optimisation of the work-up for *t*-amyl alcohol-based microemulsions

Entry	Work-up	Yield of **2** (%)
1	Extraction using ethyl acetate	57
2	Evaporation, washing with cyclohexane then filtration	20
3	Evaporation, Soxhlet extraction using cyclohexane	trace
4	Evaporation, direct column chromatography	trace

Table 3 Optimisation of the work-up for ethanolic microemulsions

Entry	Work-up	Recovery of **2** (%)	% SDS[a]
1	Break emulsion with brine, extraction using ethyl acetate	93	8
2	Break emulsion with brine, dry organic residue, wash with cyclohexane	93	2
3	Break emulsion with brine, dry organic residue, wash with toluene	92	3

[a] Determined by integration of selected signals in the ^{1}H NMR spectrum of the product.

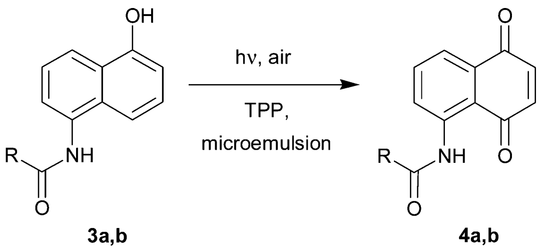
was chosen to wash the residue after evaporation of the liquid components (Table 3, entry 3) as the partition of SDS into toluene is zero.[18]

In each case, there was residual sodium dodecyl sulfate present. However, the use of cyclohexane washing gave the highest recovery with the lowest percentage of contaminant. This may be removed by further washings or by column chromatography.

Using the photooxygenation of **1**, the use of different sensitisers in microemulsions with ethanol (Table 4, entries 1–4) and *t*-amyl alcohol (Table 4, entries 5–7) as co-surfactants was probed. In all cases, the work-up procedure consisted of multiple ethyl acetate and water extractions, followed by column chromatography using a mixture of ethyl acetate and cyclohexane. For reactions using ethanol-based microemulsions, **2** was isolated in yields of 18–58%, while using *t*-amyl alcohol gave 39–85% yields.

Due to its poor solubility in polar solvents, photooxygenations using tetraphenylporphyrin (TPP) are traditionally performed in halogenated solvents such a dichloromethane. For the synthesis of **2**, however, alcohols are generally required as a co-solvent to ensure the solubility of starting material **1**.[4c] A comparison photooxygenation reaction of 1 using TPP as sensitiser in a mixture of dichloromethane and methanol (9 : 1) gave an isolated yield of **2** of 79%. Due to their excellent solubilising properties, microemulsions thus enable the use of TPP in a benign, non-chlorinated environment. TPP is likely to bind to the hydrocarbon tail of the surfactant and is thus localized at the interface of the microemulsion.[15b] As a result, TPP gave the highest conversions and isolated yields of 58 and 85% (Table 4, entries 3 and 7).

The optimised procedure was consequently applied to two other 1-naphthol derivatives (Scheme 2). Photooxygenations of 5-acetamido-1-naphthol (**3a**; R = CH_3) and 5-benzoylamido-1-naphthol (**3b**; R = Ph) furnished the corresponding 5-amido-1,4-naphthoquinones **4a** and **4b** in moderate yields of 36 and 32%, respectively.



Scheme 2 The photooxygenation of 1-hydroxy-5-amidonaphthalenes **3a** and **3b**.

Conclusions

The use of ethanolic microemulsions of water in ethyl acetate with sodium dodecyl sulfate as a co-surfactant have been demonstrated as excellent reaction media for the dye-sensitised photooxygenation reactions of selected 1-naphthols. These offer excellent solubilising abilities and, in particular, enable the use of TPP as a sensitiser in a non-chlorinated environment. Hence, the developed procedure represents another example of green photochemistry.[2,19] Isolating the products, however, remains a key challenge, and isolated yields are currently lower compared to common organic solvent systems.

Experimental

General procedure for the preparation of microemulsions

Sodium dodecyl sulfate, ethyl acetate and the co-surfactant were stirred together at room temperature (16–25 °C) to form a slurry. Water was added to this and the resulting mixture was stirred

Table 4 Sensitiser study in *t*-amyl alcohol-based and ethanolic microemulsions

Entry	Sensitiser	Co-surfactant	Conversion of **1** (%)	Isolated yield of **2** (%)
1	Rose bengal	EtOH	44	23 (53[a])
2	Methylene blue	EtOH	33	18 (55[a])
3	Tetraphenylporphyrin	EtOH	70	58 (83[a])
4	(none)	EtOH	8	7 (87[a])
5	Rose bengal	*t*-AmOH	n.d.[b]	52
6	Methylene blue	*t*-AmOH	n.d.[b]	39
7	Tetraphenylporphyrin	*t*-AmOH	n.d.[b]	85

[a] Yield based on conversion. [b] Not determined.

Published on 03 September 2010 on http://pubs.rsc.org | doi:10.1039/C004869K
Downloaded by City College of New York on 24 November 2010

vigorously for 15 min. The resulting microemulsions have been shown to be stable for more than 3 months.

General procedure for photooxygenation reactions

1,5-Dihydroxynaphthalene **1** (0.5 mmol) and the sensitiser (25 μmol: 25 mg RB, 8 mg MB or 15 mg TPP) were dissolved in 50 ml of microemulsion (Table 1, entries 6 or 10). The clear solution was irradiated using a 500 W halogen lamp in a Pyrex Schlenk flask equipped with a cold finger and a reflux condenser for 4 h at ambient temperature while purging with a gentle stream of air. Following irradiation, the reaction mixture was subjected to one of the work-up procedures outlined in Table 2 or Table 3, and the resultant crude product was further purified by column chromatography (SiO_2, cyclohexane : ethyl acetate 3 : 1) to give pure **2**.

Acknowledgements

This research project was financially supported by the Irish Research Council for Science, Engineering and Technology (IRCSET) and the Environmental Protection Agency (EPA, 2007-PhD-ET-7). The authors thank Dr Peter J. Dunn (Pfizer) for the generous donation of *t*-amyl alcohol and Dr Finbarr O'Sullivan (NICB) for help with the microscopy.

Notes and references

1 (*a*) P. Anastas and N. Eghbali, *Chem. Soc. Rev.*, 2010, **39**, 301–312; (*b*) E. S. Beach, Z. Cui and P. T. Anastas, *Energy Environ. Sci.*, 2009, **2**, 1038–1049; (*c*) J.-P. Lange, *ChemSusChem*, 2009, **2**, 587–592; (*d*) P. T. Anastas and M. M. Kirchhoff, *Acc. Chem. Res.*, 2002, **35**, 686–694; (*e*) P. Tundo, P. T. Anastas, D. S. Black, J. Breen, T. Collins, S. Memoli, J. Miyamoto, M. Polyakoff and W. Tumas, *Pure Appl. Chem.*, 2000, **72**, 1207–1228.

2 (*a*) A. Albini and M. Fagnoni, in *Green Chemical Reactions (NATO Science for Peace and Security Series, Series C: Environmental Security)*, ed. P. Tundo and V. Esposito, Springer, Dordrecht, 2008, pp. 173–189; (*b*) C. L. Ciana and C. G. Bochet, *Chimia*, 2007, **61**, 650–654; (*c*) J. Mattay, *Chem. Unserer Zeit*, 2002, **36**, 98–106; (*d*) M. Oelgemöller, C. Jung and J. Mattay, *Pure Appl. Chem.*, 2007, **79**, 1939–1947; (*e*) M. Oelgemöller, C. Jung, J. Ortner, M. Mattay, C. Schiel and E. Zimmermann, *The Spectrum*, 2005, **18**, 28–33.

3 (*a*) B. Murphy, P. Goodrich, C. Hardacre and M. Oelgemöller, *Green Chem.*, 2009, **11**, 1867–1870; (*b*) F. Friedrichs, B. Murphy, D. Nayrat, T. Ahner, M. Funke, M. Ryan, J. Lex, J. Mattay and M. Oelgemöller, *Synlett*, 2008, 3137–3140; (*c*) P. A. Waske, J. Mattay and M. Oelgemöller, *Tetrahedron Lett.*, 2006, **47**, 1329–1332; (*d*) M. Oelgemöller, C. Schiel, R. Fröhlich and J. Mattay, *Eur. J. Org. Chem.*, 2002, 2465–2474; (*e*) C. Schiel, M. Oelgemöller and J. Mattay, *Synthesis*, 2001, 1275–1279; (*f*) C. Schiel, M. Oelgemöller, J. Ortner and J. Mattay, *Green Chem.*, 2001, **3**, 224–228; (*g*) C. Schiel, M. Oelgemöller and J. Mattay, *J. Inf. Rec.*, 1998, **24**, 257–260.

4 (*a*) E. Haggiage, E. E. Coyle, K. Joyce and M. Oelgemöller, *Green Chem.*, 2009, **11**, 318–321; (*b*) M. Oelgemöller, N. Healy, L. de Oliveira, C. Jung and J. Mattay, *Green Chem.*, 2006, **8**, 831–834; (*c*) O. Suchard, R. Kane, B. J. Roe, E. Zimmerman, C. Jung, P. A. Waske, J. Mattay and M. Oelgemöller, *Tetrahedron*, 2006, **62**, 1467–1473; (*d*) M. Oelgemöller, C. Jung, J. Ortner, J. Mattay and E. Zimmermann, *Green Chem.*, 2005, **7**, 35–38; (*e*) D. T. Santos, J. Q. Albarelli, K. Joyce and M. Oelgemöller, *J. Chem. Technol. Biotechnol.*, 2009, **84**, 1026–1030.

5 (*a*) R. H. Thomson, *Naturally Occurring Quinones IV: Recent Advances*, Blackie Academic & Professional, London, 1997; (*b*) R. H. Thomson, *Naturally Occurring Quinones III: Recent Advances*, Chapman & Hall, London, 1987; (*c*) J. Bérdy, A. Aszalos, M. Bostian and K. L. McNitt, *CRC Handbook of Antibiotic Compounds. Quinone and Similar Antibiotics*, vol. 3, CRC Press, Boca Raton, 1980; (*d*) R. H. Thomson, *Naturally Occurring Quinones*, 2nd edn, Academic Press, New York, 1971.

6 O. A. Kholdeeva, O. V. Zalomaeva, A. N. Shmakov, M. S. Melgunov and A. B. Sorokin, *J. Catal.*, 2005, **236**, 62–68.

7 W. M. Owton, *J. Chem. Soc., Perkin Trans. 1*, 1999, 2409–2420.

8 (*a*) A. W. Jensen and C. Daniels, *J. Org. Chem.*, 2003, **68**, 207–210; (*b*) J. Cossy and D. Belotti, *Tetrahedron Lett.*, 2001, **42**, 4329–4331; (*c*) D. Murtinho, M. Pineiro, M. M. Pereira, A. M. d'A. Rocha Gonsalves, L. G. Arnaut, M. da Graça Miguel and H. D. Burrows, *J. Chem. Soc., Perkin Trans. 2*, 2000, 2441–2447; (*d*) A. S. Amarasekara, *Synth. Commun.*, 1999, **29**, 3063–3066; (*e*) H. M. Chawla, K. Kaul and M. Kaul, *Indian J. Chem., Sect. B*, 1993, **32**, 733–737; (*f*) S. Croux, M.-T. Maurette, M. Hocquaux, A. Ananides, A. M. Braun and E. Oliveros, *New J. Chem.*, 1990, **14**, 161–167; (*g*) H. Möhrle and H. Folttmann, *Arch. Pharm.*, 1988, **321**, 167–170; (*h*) G. Wurm and U. Geres, *Arch. Pharm.*, 1985, **318**, 931–937; (*i*) H. J. Duchstein and G. Wurm, *Arch. Pharm.*, 1984, **317**, 809–812; (*j*) J. Griffiths, K. Y. Chu and C. Hawkins, *J. Chem. Soc., Chem. Commun.*, 1976, 676–677.

9 K. Alfonsi, J. Colberg, P. J. Dunn, T. Fevig, S. Jennings, T. A. Johnson, H. P. Kleine, C. Knight, M. A. Nagy, D. A. Perry and M. Stefaniak, *Green Chem.*, 2008, **10**, 31–36.

10 (*a*) A. Astarita, F. Cermola, M. DellaGreca, M. R. Iesce, L. Previtera and M. Rubino, *Green Chem.*, 2009, **11**, 2030–2033; (*b*) N. Inoue, T. Ishioka and A. Harata, *Chem. Lett.*, 2009, **38**, 358–359; (*c*) E. Baciocchi, C. Chiappe, T. Del Giacco, C. Fasciani, O. Lanzalunga, A. Lapi and B. Melai, *Org. Lett.*, 2009, **11**, 1413–1416.

11 (*a*) A. G. Griesbeck, A. Bartoschek, T. T. El-Idreesy, O. Höinck and C. Miara, *J. Mol. Catal. A: Chem.*, 2006, **251**, 41–48; (*b*) A. G. Griesbeck and A. Bartoschek, *Chem. Commun.*, 2002, 1594–1595.

12 (*a*) R. A. Bourne, X. Han, A. O. Chapman, N. J. Arrowsmith, H. Kawanami, M. Poliakoff and M. W. George, *Chem. Commun.*, 2008, 4457–4459; (*b*) R. A. Bourne, X. Han, M. Poliakoff and M. W. George, *Angew. Chem., Int. Ed.*, 2009, **48**, 5322–5325; (*c*) X. Han, R. A. Bourne, M. Poliakoff and M. W. George, *Green Chem.*, 2009, **11**, 1787–1792.

13 The degradation of 1-naphthoate and 2-naphthoate by rose bengal-sensitised photooxidation has been studied previously: M. Luiz, M. A. Biasutti and N. A. García, *Redox Rep.*, 2004, **9**, 199–205.

14 (*a*) K. Holmberg, *Eur. J. Org. Chem.*, 2007, 731–742; (*b*) J. H. Fendler, *J. Phys. Chem.*, 1980, **84**, 1485–1491.

15 (*a*) V. Nardello, M. Hervé, P. L. Alsters and J.-M. Aubry, *Adv. Synth. Catal.*, 2002, **344**, 184–191; (*b*) V. Nardello, L. Caron, J.-M. Aubry, S. Bouttemy, T. Wirth, C. R. Saha-Möller and W. Adam, *J. Am. Chem. Soc.*, 2004, **126**, 10692–10700; (*c*) L. Caron, V. Nardello, J. Mugge, E. Hoving, P. L. Alsters and J.-M. Aubry, *J. Colloid Interface Sci.*, 2005, **282**, 478–485; (*d*) J.-M. Aubry, W. Adam, P. L. Alsters, C. Borde, S. Queste, J. Marko and V. Nardello, *Tetrahedron*, 2006, **62**, 10753–10761; (*e*) L. Caron, V. Nardello, P. L. Alsters and J.-M. Aubry, *J. Mol. Catal. A: Chem.*, 2006, **251**, 194–199; (*f*) P. L. Alsters, W. Jary, V. Nardello-Rataj and J.-M. Aubry, *Org. Process Res. Dev.*, 2010, **14**, 259–262.

16 A. G. Griesbeck and M. Cho, *Tetrahedron Lett.*, 2009, **50**, 121–123.

17 Similar matrix effects are known for ionic liquids. See reference ref. 3*a*.

18 J. M. Pollard, A. J. Shi and K. E. Goklen, *J. Chem. Eng. Data*, 2006, **51**, 230–236.

19 For further examples, see: (*a*) N. Hoffmann, *Pure Appl. Chem.*, 2007, **79**, 1949–1958; (*b*) M. Veerman, M. J. E. Resendiz and M. A. Garcia-Garibay, *Org. Lett.*, 2006, **8**, 2615–2617; (*c*) A. V. Samoshin and V. V. Samoshin, *J. Undergrad. Chem. Res.*, 2006, **2**, 13–16; (*d*) A. G. Griesbeck, N. Maptue, S. Bondock and M. Oelgemöller, *Photochem. Photobiol. Sci.*, 2003, **2**, 450–451; (*e*) A. G. Griesbeck, W. Kramer and M. Oelgemöller, *Green Chem.*, 1999, **1**, 205–207.