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# Surfactant-type catalysts in organic reactions

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This paper is dedicated to Smaeel Ghaderi on the occasion of his 53rd birthday and also in recognition of his outstanding contributions to the chemical industry

**Contents**

## 1. Introduction

One of the biggest challenges in modern chemistry is to find environmentally friendly processes while carrying out already known chemical reactions. On the other hand, acid- and base-catalysed reactions are by far the most numerous and best-studied reaction types,[1–7] in which organic functional groups undergo an array of different transformations with nucleophilic reagents in the presence of acids or bases as catalysts. It is a widely accepted belief, however that Lewis acid-catalysed reactions must be carried out in

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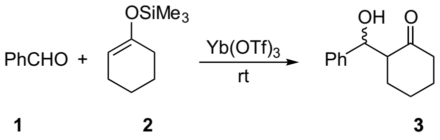
the absence of water or even under strictly anhydrous conditions. Very frequently, the presence of even trace quantities of water stops the Lewis acid-catalysed reaction completely, because the most common Lewis acid catalysts react immediately with water and instantaneously or progressively decompose to form hydroxides or oxides, losing immediately or gradually their Lewis acid activity. The hydrolysis of anhydrous metal halides such as $AlCl_3$, $TiCl_4$, and $BCl_3$ is a paradigmatic example of the dramatic negative influence of the presence of water (Scheme 1).

$$MX_n + nH_2O \longrightarrow M(OH)_n + nHX$$

**Scheme 1.**

From the point of view of green chemistry, water would be the perfect solvent to carry out chemical reactions, provided that it dissolves the reagents and products and that no polluted waste waters are dispersed.[8–10] Additionally, in many cases, due to hydrophobic effects, using water as a solvent not only accelerates the reaction rates, but also enhances the reaction selectivities, even when the reactants are sparingly soluble or insoluble in this medium.[7]

Recently, various kinds of protonic and Lewis acids have been found to retain that catalytic activities in aqueous media and, in particular, many of them are not only compatible with water, but are also activated by water. Rare earth metal salts such as $Sc(OTf)_3$ and $Yb(OTf)_3$ can be used for aqueous organic reactions. As an example, $Yb(OTf)_3$ is found to be highly effective for catalysing the Mukaiyama aldol reaction of benzaldehyde **1** with silyl enol ether **2** to give the alcohol product **3** in aqueous solution and is much less effective in dry organic solvents (Scheme 2).[11] The enhancement of the reaction rate by water is very likely due to the change of the acid catalyst's structure and activity caused by water, or to the regeneration of the active catalyst from the corresponding intermediate, which is faster in water than in dry organic solvents.



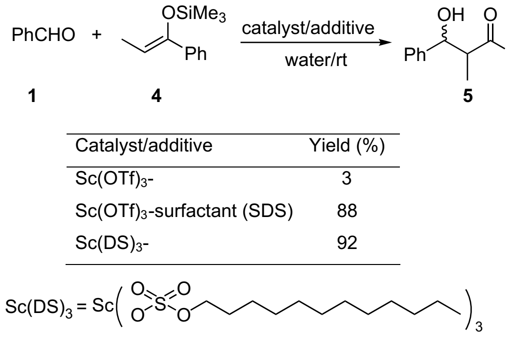
| | |
|---|---|
| $H_2O$/THF (1/4) | 91% |
| THF | 10% |

**Scheme 2.**

One of the major drawbacks of using water as a solvent is the low solubility of most organic substrates in this medium. This problem could be overcome by the use of an organic solvent as a co-solvent (Scheme 2) or by employing surfactants, which solubilise organic substances in water.

While the reaction of benzaldehyde **1** with silyl enol ether **4** gives almost no desirable aldol product **5** in the presence of a catalytic amount of $Sc(OTf)_3$ in water, a high yield of the corresponding aldol adduct is obtained when the reaction is carried out in the presence of a catalytic amount of $Sc(OTf)_3$ and sodium dodecyl sulfate (SDS; a surfactant) in water (Scheme 3).[12] Recently, a new type of catalyst, a Lewis acid-surfactant-combined catalyst (LASC), has been developed. This acts both as a Lewis acid to catalyse the reaction and as a surfactant to solubilise organic substrates in water. Scandium tris(dodecyl sulfate) $Sc(DS)_3$ is a good example, because it is very effective for catalysing the reaction of benzaldehyde **1** with silyl enol ether **2** in water (Scheme 3).[11,12]

The aim of this review is to show the applications of surfactant-type acids and bases in organic reactions in a dual role both as a catalyst to activate the substrate molecules and as a surfactant to increase the concentration of organic reactants to form micelle particles in water.



| Catalyst/additive | Yield (%) |
|---|---|
| $Sc(OTf)_3$- | 3 |
| $Sc(OTf)_3$-surfactant (SDS) | 88 |
| $Sc(DS)_3$- | 92 |

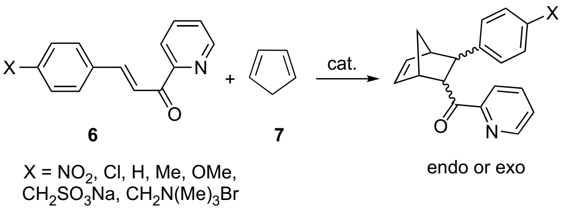
**Scheme 3.**

## 2. Surfactant-type Lewis acids

### 2.1. Metal dodecyl sulfates[13]

The syntheses of metal dodecyl sulfates, such as $Cu(DS)_2$ and $Zn(DS)_2$, have been first reported by Mutuura et al. via the addition of sodium dodecyl sulfate (NaDS) to a solution of the metal nitrate or chloride.[14–16]

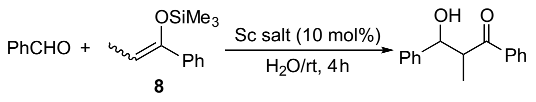
In an interesting study, Otto and co-workers have found that, in contrast to SDS, cetyltrimethylammonium bromide (CTAB) or dodecyl heptaoxyethylene ether ($C_{12}E_7$), $Cu(DS)_2$ micelles catalyse the Diels–Alder reaction between **6** and **7** with extremely high efficiency, leading to rate enhancements of up to $1.8\times10^6$, compared to the uncatalysed reaction. This results primarily from the essentially complete complexation of **6** to the copper ions at the micellar surface (Scheme 4).[17]



**Scheme 4.**

In this field, the pioneering work of Kobayashi's group started with the synthesis of several types of scandium alkyl sulfates and sulfonates. Their research has shown that, with $Sc(DS)_3$, the aldol condensation proceeded more efficiently than with other scandium sulfonates and sulfates under aqueous conditions (Table 1).[18]

**Table 1**
Effect of alkyl chains of Sc salts[a]



| R | $Sc(OSO_3R)_3$ | $Sc(OSO_2\text{-}p\text{-}R\text{-}Ph)_3$ | $Sc(OSO_2R)_3$ |
|---|---|---|---|
| $C_{10}H_{21}$ | — | 55 | 60 (0.7 μm)[b] |
| $C_{11}H_{23}$ | — | — | 68 |
| $C_{12}H_{25}$ | 92 | 91 | 83 (1.1 μm)[b] |
| $C_{13}H_{27}$ | — | — | 76 |
| $C_{14}H_{29}$ | 73 | 33 | 19 (0.4 μm)[b,c] |
| $C_{16}H_{33}$ | — | 14 | 12 |

[a] Numbers shown in the columns are isolated yields (%).

[b] Particle sizes of the dispersions.

[c] The dispersion system was stable within a few minutes. A quick measurement of this system has indicated that its particle size was 0.4 μm.

Kobayashi's group also found that $Sc(DS)_3$ worked well in water rather than in organic solvents. The effect of solvents on the aldol reaction of **8** with benzaldehyde is shown in Table 2.[18]

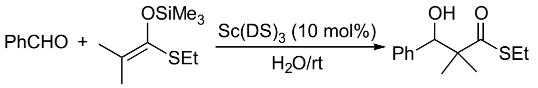
**Table 2**
Effects of solvents[a]

| Solvent | Yield (%) | Solvent | Yield (%) |
|---|---|---|---|
| $H_2O$ | 92 | $CH_2Cl_2$ | 2 |
| MeOH | 4 | THF | Trace |
| DMF | 14 | $Et_2O$ | Trace |
| DMSO | 9 | Toluene | Trace |
| MeCN | 3 | Hexane | 4 |

[a] While $Sc(DS)_3$ is dissolved in MeOH, DMF, DMSO, and THF, it is not dissolved or slightly dissolved in other solvents.

In the other work Kobayashi et al. show that the reactivity of scandium tris(dodecyl sulfate) in aldol reactions of aldehydes with silyl enolates enhances remarkably in the presence of Brønsted acids such as HCl (Table 3).[19]

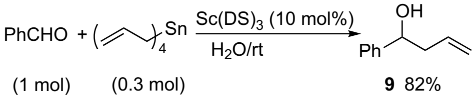
**Table 3**
Effect of Brønsted acids on LASC-mediated aldol reactions in water



| Additive (%) | Time (min) | Yield (%) |
|---|---|---|
| — | 5 | 16 |
| TsOH (10) | 5 | 52 |
| TfOH (10) | 5 | 51 |
| HCl (10) | 5 | 67 |
| HCl (10) | 15 | 88 |
| TsOH (10)[a] | 5 | 0 |
| HCl (10)[a] | 5 | 0 |

[a] In the absence of $Sc(DS)_3$.

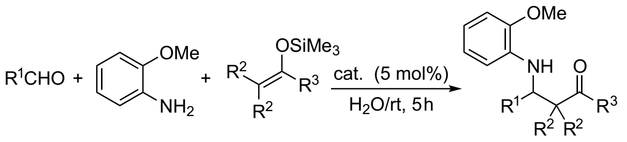
The LASC-catalysed reaction is also applicable for transformations using organometallics. The utility of organometallic reagents is now well recognised in organic synthesis and, recently, much attention has been focused on the reactions of allyl organometallics with carbonyl compounds in water-containing solvents.[20,21] By using $Sc(DS)_3$, Kobayashi and his group have attained Lewis acid-catalysed allylation reactions in water (Scheme 5). Tetraallyltin was found to be the allylating reagent of choice, and the corresponding homoallylic alcohol **9** was obtained in 82% yield.[21] Other metal dodecyl sulfates such as those of lanthanide(III) or copper(II), have also been used for the same reaction.[21]



**Scheme 5.**

Scandium tris(dodecyl sulfate) as well as copper bis(dodecyl sulfate) were found to catalyse three-component Mannich-type reactions of aldehydes, amines, and silyl enolates in water. A copper-based LASC gave better yields than $Sc(DS)_3$. The results are shown in Table 4. Not only benzaldehyde, but also heteroaromatic, α,β-unsaturated, and aliphatic aldehydes, reacted smoothly to afford the desired adducts in high yields. The three-component reactions proceed via the formation of imines, which are activated by a catalytic amount of the Lewis acidic metal cation in water. It should be noted that the dehydrative formation of the imines occurred smoothly in water, and that water-labile imines reacted efficiently to afford the desired Mannich-type adducts in high yields.[20]

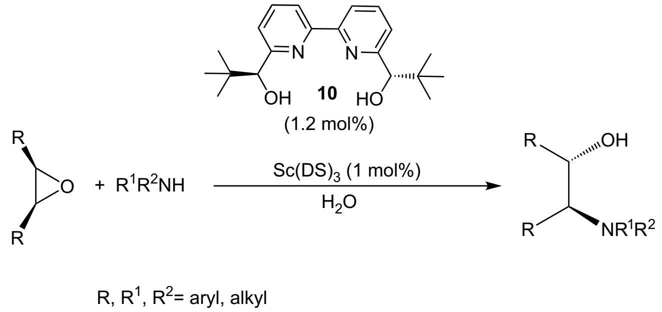
**Table 4**
Three-component Mannich-type reactions in water



| $R^1$ | $R^2$ | $R^3$ | Cat. | Yield (%) |
|---|---|---|---|---|
| Ph | H | Ph | $Cu(DS)_2$ | 85 |
| Ph | Me | OMe | $Cu(DS)_2$ | 90 |
| Ph | Me | OMe | $Sc(DS)_3$ | 72 |
| 2-Furyl | Me | OMe | $Cu(DS)_2$ | 85 |
| PhCH=CH | Me | OMe | $Cu(DS)_2$ | 73 |
| $(Me)_2CHCH_2$ | Me | OMe | $Cu(DS)_2$ | 93[a] |

[a] Reaction carried out at 0 °C.

A catalytic asymmetric ring opening of *meso*-epoxides with aromatic amines has been developed in the presence of scandium tris(dodecyl sulfate) and a chiral bipyridine ligand **10**, to afford β-amino alcohols in high yields and excellent enantioselectivities (Scheme 6).[22]

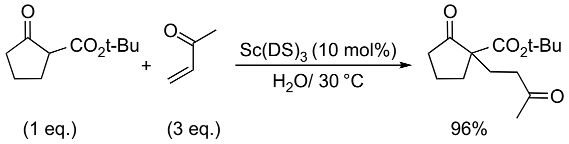


**Scheme 6.**

Additionally, in the presence of a catalytic amount of $Sc(DS)_3$ and a chiral bipyridine ligand, asymmetric ring opening of *meso*-epoxides with aromatic *N*-heterocycles, an alcohol and thiols proceeded smoothly to afford the corresponding products in moderate-to-good yields (34–85%) with high-to-excellent enantioselectivities (74–96% ee).[23]

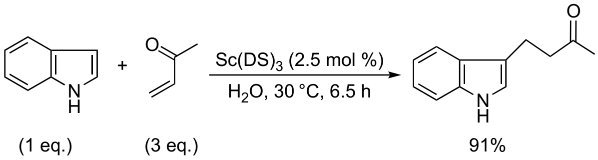
Catalytic asymmetric aldol reactions in water without the use of organic solvents have been carried out by using a combination of copper bis(dodecyl sulfate) and a chiral bis(oxazoline) ligand to afford the desired products in high yields with good enantiomeric excesses.[24]

Michael reactions are one of the most useful types of carbon–carbon bond-forming reactions in organic synthesis, and Lewis acid-catalysed versions have been developed to solve problems, which are often observed in traditional, base-catalysed Michael reactions. $Sc(DS)_3$ can be also applied to Michael reactions in water, as shown in Scheme 7.[25]



**Scheme 7.**

Similarly, the reactions of indoles with electron-deficient olefins were catalysed by $Sc(DS)_3$ (Scheme 8).[26] As for electron-deficient olefins, not only enones, but also β-nitrostyrene, were successfully used. It is noteworthy that solid substrates such as indole and β-nitrostyrene as well as liquid substrates reacted smoothly.

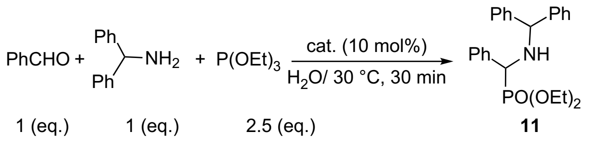


**Scheme 8.**

Firouzabadi et al. have synthesised aluminium tris(dodecyl sulfate) trihydrate ($Al(DS)_3 \cdot 3H_2O$) for the first time and investigated its successful application in the Michael addition of indoles and pyrrole to α,β-unsaturated electron-deficient compounds under aqueous media at room temperature. In this study, they found that the catalytic activity of $Al(DS)_3 \cdot 3H_2O$ is greater than that of $Sc(DS)_3$.[27] $Al(DS)_3 \cdot 3H_2O$ was also employed efficiently as a catalyst for the conversion of epoxides into thiiranes with thiourea in water at room temperature in excellent yields.[28] Regio- and chemoselective ring opening of structurally diverse epoxides with aromatic and aliphatic amines was performed using water as medium in the presence of $Al(DS)_3 \cdot 3H_2O$ at room temperature.[28]

Three-component reactions of aldehydes, amines and triethyl phosphate have been effectively catalysed by $Sc(DS)_3$ to give the corresponding α-amino phosphonates in high yields in water at room temperature.[29] In Table 5, the reaction of benzaldehyde, benzhydrylamine and $P(OEt)_3$ has been tested as a model reaction in the presence of various catalysts in water. When $Sc(DS)_3$ was used as a catalyst, the reaction proceeded smoothly to afford the desired product **11** in good yield (entry 1). On the other hand, sodium dodecyl sulfate (SDS) or scandium triflate gave **11** in very low yields (entries 2 and 3). These results indicate that both the Lewis acidic cation and the anionic surfactant are indispensable for the efficient catalysis. $Sc(DS)_3$ was far superior to dodecylbenzenesulfonic acid (DBSA) in this reaction (entry 4). Furthermore, the reaction under neat conditions without any solvents proceeded slowly (entry 5), indicating that water as a solvent plays an essential role for acceleration of the reaction. It was found that the reaction with $HOP(OEt)_2$, which has been used as a phosphorus nucleophile in the Lewis acid-catalysed synthesis of α-amino phosphonates in organic solvents, scarcely proceeded (entry 6).

**Table 5**
Three-component synthesis of α-amino phosphonate **11** in water



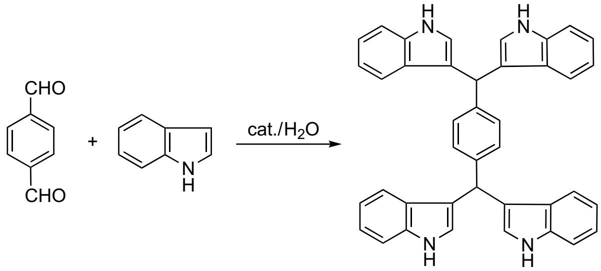
| Entry | Catalyst | Yield (%) |
|---|---|---|
| 1 | $Sc(DS)_3$ | 71 |
| 2 | SDS (30%) | 8 |
| 3 | $Sc(OTf)_3$ | 6 |
| 4 | DBSA | 18 |
| 5[a] | $Sc(DS)_3$ | 31 |
| 6[b] | $Sc(DS)_3$ | Trace |

[a] Under neat conditions.
[b] $HOP(OEt)_2$ was used, instead of $P(OEt)_3$.

For an investigation of the behaviour of other metal ions in these catalysts, Zolfigol and co-workers prepared a wide range of metal dodecyl sulfates by the reaction of sodium dodecyl sulfate and the corresponding metal nitrates (Table 6, entries 1–15). All of the prepared salts catalysed the condensation of indoles with aldehydes and ketones. Among these, zirconium tetrakis(dodecyl sulfate) in water, was superior to the other salts for this purpose. Bis- and tris-indolylmethanes were synthesised at room temperature in high yields by using $Zr(DS)_4$ under aqueous media (Scheme 9). $Zr(DS)_4$ has been recovered and re-used for a new run.[30]

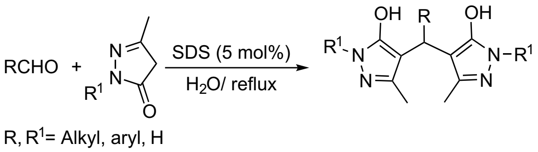
**Table 6**
Preparation of metal dodecyl sulfates

| Entry | Metal nitrate | Salt | Temp (°C) | Time (h) | Yield (%) | Colour of product |
|---|---|---|---|---|---|---|
| 1 | $Fe(NO_3)_3 \cdot 9H_2O$ | $Fe(DS)_3$ | 25 | 1 | 80 | Yellow |
| 2 | $Sr(NO_3)_2$ | $Sr(DS)_2$ | 25 | 0.5 | 85 | White |
| 3 | $Al(NO_3)_3 \cdot 9H_2O$ | $Al(DS)_3$ | 25 | 0.5 | 80 | White |
| 4 | $AgNO_3$ | Ag(DS) | 100 | 5 | 52 | Black |
| 5 | $Pb(NO_3)_2$ | $Pb(DS)_2$ | 25 | 1 | 90 | White |
| 6 | $Cd(NO_3)_2 \cdot 4H_2O$ | $Cd(DS)_2$ | 100 | 12 | 0 | — |
| 7 | $Mg(NO_3)_2 \cdot 4H_2O$ | $Mg(DS)_2$ | 100 | 12 | 0 | — |
| 8 | $Cu(NO_3)_2 \cdot 3H_2O$ | $Cu(DS)_2$ | 100 | 12 | 0 | — |
| 9 | $Zr(NO_3)_4$ | $Zr(DS)_4$ | 25 | 0.5 | 87 | White |
| 10 | $(NH_4)_2Ce(NO_3)_6$ | $Ce(DS)_4$ | 25 | 5 | 65 | Yellow |
| 11 | $Ca(NO_3)_2 \cdot 4H_2O$ | $Ca(DS)_2$ | 25 | 1 | 88 | White |
| 12 | $Zn(NO_3)_2 \cdot 4H_2O$ | $Zn(DS)_2$ | 100 | 12 | 0 | — |
| 13 | $Mn(NO_3)_2 \cdot 2H_2O$ | $Mn(DS)_2$ | 100 | 12 | 0 | — |
| 14 | $Co(NO_3)_2 \cdot 6H_2O$ | $Co(DS)_2$ | 100 | 12 | 20 | Grey |
| 15 | $Cr(NO_3)_3 \cdot 9H_2O$ | $Cr(DS)_3$ | 25 | 1 | 72 | Green |



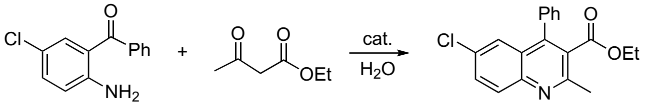
**Scheme 9.**

Electrophilic substitution reactions of indoles with various aldehydes were also carried out in water at room temperature in the presence of sodium dodecyl sulfate (SDS) to afford the bis(indolyl)methanes in excellent yields.[31] SDS also catalysed the condensation of 3-methyl-L-phenyl-5-pyrazolone or 3-methyl-1*H*-5-pyrazolone with aromatic and aliphatic aldehydes in water at reflux temperature, giving the 4,4′-alkylmethylene-bis(3-methyl-5-pyrazolones) in good-to-high yields (Scheme 10).[32]



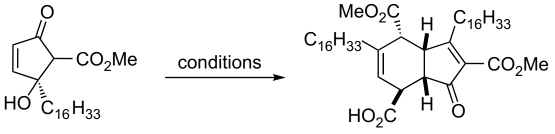
**Scheme 10.**

Polysubstituted quinolines have been synthesised from *o*-aminoaryl ketones or *o*-aminobenzonitrile and ketones or β-diketones in the presence of different metal dodecyl sulfates (Scheme 11).[33,34]



**Scheme 11.**

**Table 7**
Reaction conditions and isolated yields of **13**



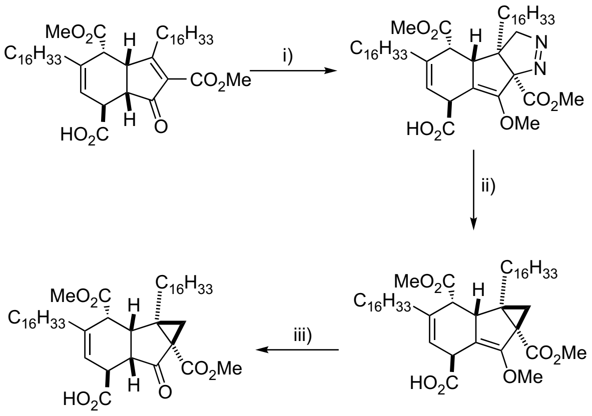
untenone A **12** manzamenone A **13**

| Entry | Conditions | Isolated yield (%) |
|---|---|---|
| 1 | Neat, ca. 70 °C, 24 h | 24–48 |
| 2 | $H_2O$, 25 °C, 39 h | — |
| 3 | SDS (2%), $H_2O$, 25 °C, 39 h | 46 |
| 4 | SDS (5%), $H_2O$, 25 °C, 39 h | 64 |
| 5 | SDS (5%), $H_2O$, 25 °C, 6 h | 75 |
| 6 | DBSA[a] (0.1 equiv), $H_2O$, 25 °C, 24 h | 68 |
| 7 | DBSA[a] (0.1 equiv), $H_2O$, 25 °C, 7.5 h | 69 |
| 8 | $Sc(DS)_3$ (0.1 equiv), $H_2O$, 25 °C, 24 h | 78 |
| 9 | $Sc(DS)_3$ (0.1 equiv), $H_2O$, 25 °C, 1 h | 73 |

[a] DBSA=Dodecylbenzene sulfonic acid.

Improved procedures exploiting surfactant catalysts have been developed for the conversion of (±)-untenone A **12** into (±)-manzamenone A **13** in an aqueous medium. Doncaster et al. investigated the use of $Sc(DS)_3$ as a catalyst for the conversion of **12** into **13** with very encouraging results. This LASC proved to be a more efficient catalyst with conversion of **12** into **13** being complete within 1 h at 25 °C. Using just 10 mol % of this catalyst, manzamenone A could be prepared reproducibly in yields of between 70 and 80% after chromatography (Table 7, entries 1–9).[35]

The consequent availability of (±)-manzamenone A has allowed the synthesis of a biologically interesting cyclopropyl analogue **14** (Scheme 12).[35]



**14**

**Scheme 12.** Synthesis of cyclopropyl analogue **14**. Reagents: (i) $CH_2N_2$, $Et_2O$, rt, 94%; (ii) neat, 125 °C, 4 h, 57%; (iii) HCl, $Et_2O$, rt, 24 h, 56%.

A Lewis acid–surfactant-combined catalyst (LASC) was tentatively used in a cationic polymerisation in a mini-emulsion of *p*-methoxystyrene (*p*-MOS). In the first part of the study, the initiating potential of ytterbium tris(dodecyl sulfate) ($Yb(DS)_3 \cdot 0.25H_2O$) was determined in the solution polymerisation of *p*-MOS initiated by the corresponding chlorinated adduct *p*-MOS–HCl. Mini-emulsion polymerisations of *p*-MOS performed using the same initiating system gave rise to oligomers, but the experimental conditions chosen could not detect the expected LASC-mediated cationic polymerisation process. Further studies showed that the LASC is located at the interface and acts only as a surfactant together with SDS. The polymerisation occurred due to the hydrolysis of *p*-MOS–HCl. The resulting acidification of the water phase leads to the transformation of SDS into its sulfuric acid form, acting as an inisurf according to an interfacial cationic polymerisation process.[36a] Surfactant-type iron(III) complex, $Fe_2O(DS)_4$, has been found to be effective for benzylic oxidation of simple aryl alkanes using aqueous *t*-butyl hydroperoxide (TBHP) as an oxidant.[36b]

## 2.2. Metal dodecanesulfonates

LASCs **15**–**19** have been used for the aldol reaction of benzaldehyde with silyl enol ether **4** in water. While **17** only slightly dissolved in water, stable dispersions were formed upon addition of the aldehyde with stirring or vigorous mixing (Fig. 1). It should be noted that hydrolysis of the silyl enol ether is not a severe problem under the reaction conditions, despite the water-labile nature of silyl enol ethers under acidic conditions. The results are summarised in Table 8. The dodecanesulfonate **17** was found to give the best results, and the LASCs with shorter or longer alkyl chains resulted in lower yields.[20]

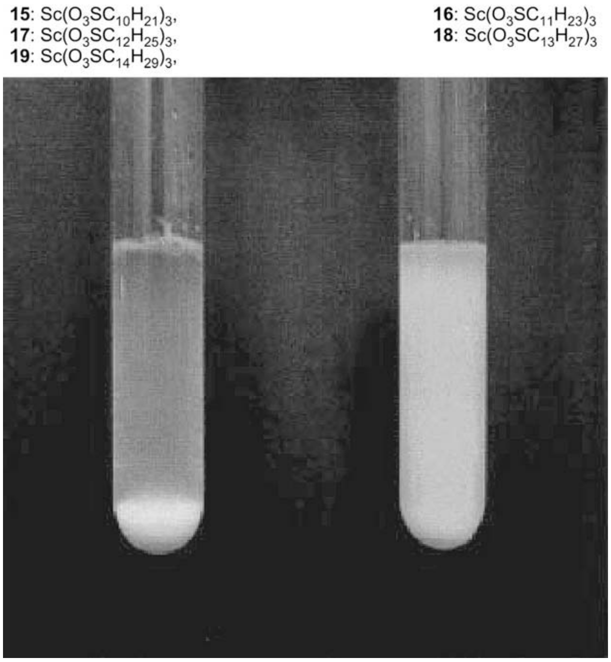
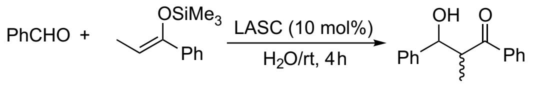


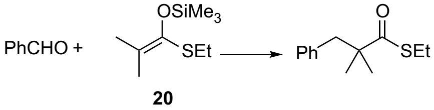
**Figure 1.** Mixtures of LASC **17** in water (left) and LASC **17** and benzaldehyde (1:10) in water (right).

**Table 8**
Effect of alkyl chain length of LASCs on aldol reactions in water



| LASC | Yield (%) |
|---|---|
| **15**: $Sc(O_3SC_{10}H_{21})_3$ | 60 |
| **16**: $Sc(O_3SC_{11}H_{23})_3$ | 68 |
| **17**: $Sc(O_3SC_{12}H_{25})_3$ | 83 |
| **18**: $Sc(O_3SC_{13}H_{27})_3$ | 76 |
| **19**: $Sc(O_3SC_{14}H_{29})_3$ | 19 |

Studies on the aldol reactions of benzaldehyde with a thioketene silyl acetal in water in the presence of various dodecanesulfonate salts as Lewis acid–surfactant-combined catalysts have revealed that the order of the catalytic ability of these salts at the initial stage of the reaction is Cu>Zn, Ag>Sc, Yb>Na>Mn, Co, and that the Sc and Yb salts afforded the aldol product in more than 90% final yields, due to their ability to suppress the hydrolysis of the thioketene silyl acetal **20** (Scheme 13, Fig. 2).[37]



Scheme 13.

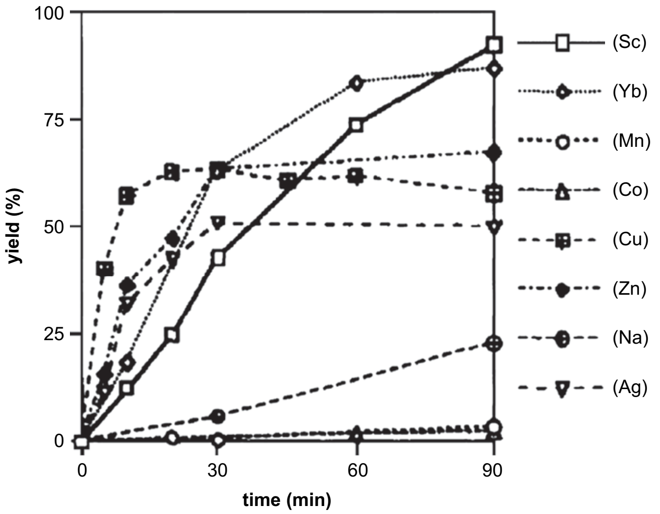


**Figure 2.** Plot of GC yield versus time for the aldol reaction of benzaldehyde with **20** in the presence of dodecanesulfonate salts in water.

The aldol condensation and Diels–Alder reaction in water in the presence of various dodecanesulfonate salts as Lewis acid–surfactant-combined catalysts have also been studied. In the aldol reactions, these salts differed from each other with respect to their catalytic ability at the initial stage of the reaction and the final yields of the aldol product, while the salts did not affect the reaction rates of the Diels–Alder reactions.[38]

## 2.3. Polymer-supported surfactant-type Lewis acid catalysts

One of the disadvantages of LASCs is that rather tedious procedures are needed to recover the catalyst. As a solution to this problem, Kobayashi and Nagayama have reported a novel polymer-supported scandium-based Lewis acid **21**, which shows a high activity in water and can be easily recovered and re-used. Their idea was to change the hydrophobic part of an LASC to polymer chains having spacers composed of alkylaromatic moieties and to develop a novel polymer-supported catalyst that can be used in water (Fig. 3).

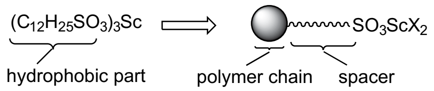
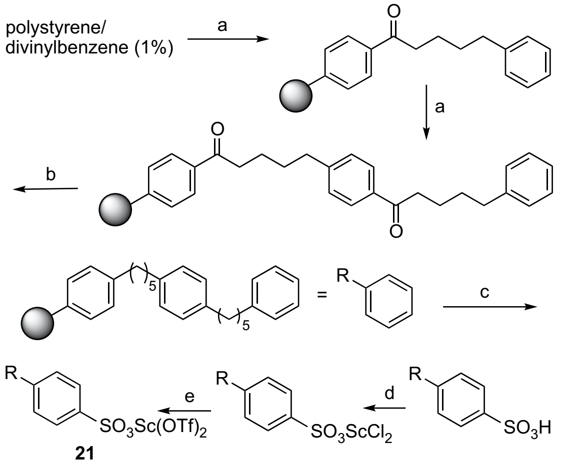


**Figure 3.** Representation of Lewis acid catalysts. Left: example LASC. Right: scandium-based active site is separated by an alkylaromatic spacer moiety from polymeric support.

The preparation of the polymer-supported scandium catalyst **21** was performed according to the method shown in Scheme 14.

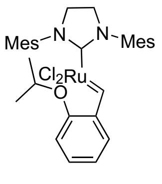
The catalytic activities of **21** have been first tested in the allylation reaction of carbonyl compounds with tetraallyltin, which are among the most fundamental and important carbon–carbon bond-forming reactions in organic synthesis. On the basis of these results, it was found that the reaction proceeded smoothly in the presence of 3.2 mol % of **21** in water at room temperature for 12 h, to afford the corresponding homoallylic alcohol in 92% yield. The catalyst has polymer chains and spacers, which help to form hydrophobic reaction fields in water. Several useful carbon–carbon bond-forming reactions such as Mukayama aldol condensations, Diels–Alder reactions and Strecker-type reactions of benzaldehyde, aniline, and tributyltin cyanide were performed successfully using catalyst **21**.[39]



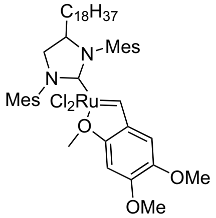
**Scheme 14.** Preparation of **21**. (a) $AlCl_3$, $Ph(CH_2)_4COCl/CS_2$; (b) $AlCl_3$, $LiAlH_4/Et_2O$; (c) $ClSO_3H/CH_2Cl_2$, $MeCO_2H$; (d) $ScCl_3/MeCN$; (e) $TfOH/CH_2Cl_2$.

## 2.4. Surfactant-type forms of Hoveyda's catalysts

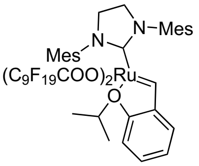
Hoveyda's catalyst **22** is a well-known catalyst used in metathesis reactions. Some catalysts bearing long alkyl chains (**23** and **24**) and analogous to this catalyst have been synthesised by Mingotaud and his group.



**22**

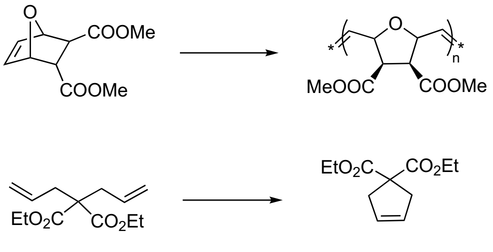


**23**



**24**

Both catalysts **23** and **24** are able to catalyse metathesis reactions efficiently, although catalyst **23** has a higher activity compared to **24**. Both form monolayers at the air–water interface, demonstrating their surface-active properties. In preliminary experiments in micelle solutions, it has been shown that they are useful inisurf molecules, enabling a ROMP (ring-opening metathesis polymerisation) process to be carried out in non-degassed water with well-defined catalysts. The polymerisation in this environmentally friendly medium is, furthermore, better controlled compared to that in homogeneous solutions. RCM (ring-closing metathesis) reactions also were shown to be very efficiently catalysed by catalyst **24** when mixed in with the micelles (Scheme 15).[40]

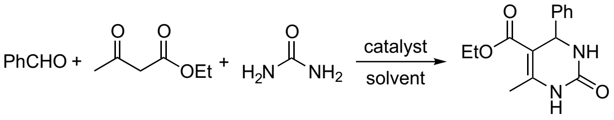


**Scheme 15.** ROMP and RCM reactions.

## 3. Surfactant-type Brønsted acids

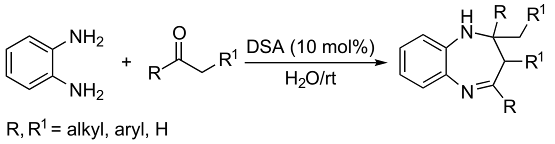
### 3.1. Dodecylsulfonic acid (DSA)

Dihydropyrimidinones[41,42] are classes of biologically important organic molecules. The dihydropyrimidinone (DHPM) scaffold is featured in a wide variety of bioactive molecules. A number of marine alkaloids with a broad spectrum of biological activities contain the DHPM framework as a part of their structures[43–45] and therefore, the synthesis of these materials is very important. A simple, efficient, mild and green method has been developed for the synthesis of 3,4-dihydropyrimidin-2-ones employing dodecylsulfonic acid as an excellent surfactant-type Brønsted acid catalyst under aqueous media at room temperature by Sharma et al. (Scheme 16).[46]



Scheme 16.

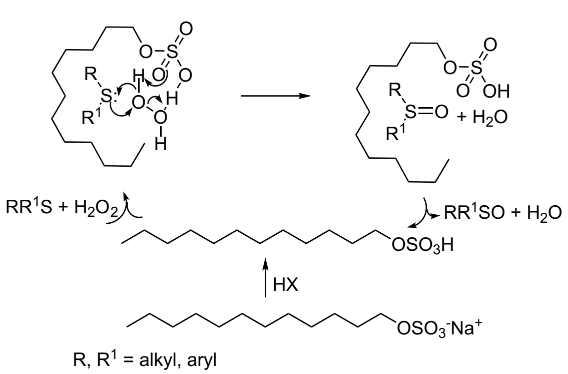
DSA has also been used successfully as a Brønsted acid catalyst in the condensation reaction of *o*-phenylenediamine with ketones having an α-hydrogen, leading to the product 1,5-benzodiazepines in a water medium at ambient temperature in high yields (Scheme 17).[46]



Scheme 17.

### 3.2. Dodecyl hydrogen sulfate

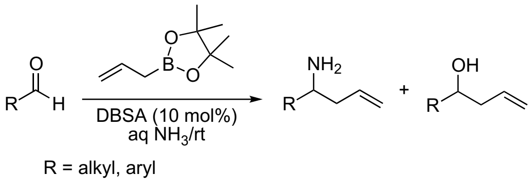
A high-yield and chemoselective oxidation of sulfides to sulfoxides with an aqueous solution of $H_2O_2$ (35%) catalysed by in situ-generated dodecyl hydrogen sulfate as a Brønsted acid–surfactant in the absence of any organic co-solvents and under metal-free conditions was described by Firouzabadi et al. They showed the dual activity of dodecyl hydrogen sulfate in this reaction (Scheme 18).[47]



Scheme 18.

### 3.3. Dodecylbenzenesulfonic acid (DBSA)

Selective α-aminoallylation has been developed successfully by Kobayashi and his group by using commercial aqueous ammonia, aldehydes and allylboronates in the presence of dodecylbenzenesulfonic acid (DBSA) as additives (Scheme 19). It should be noted that the use of commercial aqueous ammonia makes the reaction easy and practical.[48]



Scheme 19.

Dehydration is a very common reaction in organic chemistry. It is difficult to carry out in water, because water molecules generated during the reaction must be removed to shift the equilibrium towards the side of the dehydrated product. With a surfactant-type acid catalyst, dehydration has been successfully developed in water. Emulsion droplets are formed in water in the presence of a surfactant-type catalyst and organic substrates. The emulsion droplets have a hydrophobic interior, which would concentrate acid catalysts onto the surface of the droplets and enhance the reaction rate towards the side of the dehydrated product. Water molecules generated during the reaction are, however, removed from the droplets, due to the hydrophobic nature of their interior, which shifts the equilibrium towards the desired side.

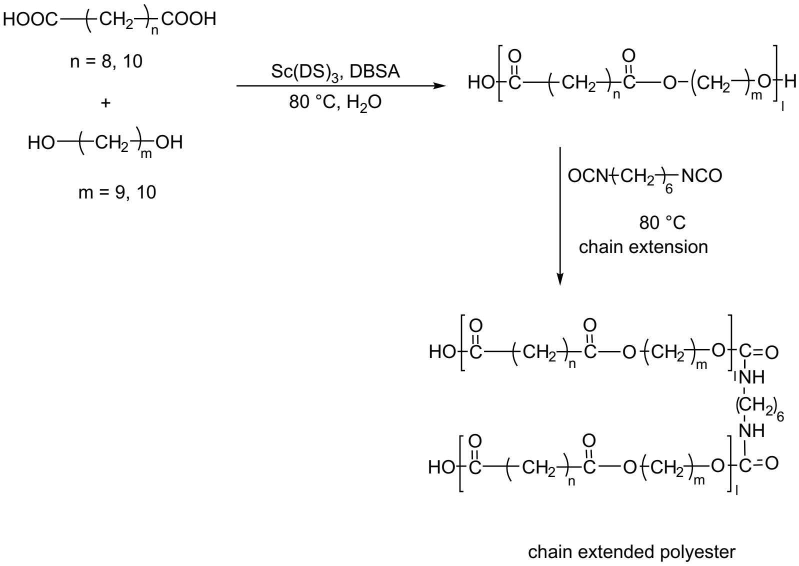
The dehydrative dimerisation/retro-Dieckmann reaction proceeded smoothly in water at 25 °C in the presence of 10 mol % of DBSA to give **13** in 68% yield after 24 h. Analysis of the time course of the reaction by $^1$H NMR indicated that it was complete after 7.5 h and manzamenone A **13** could be isolated in 69% yield after this time (Table 7, entries 6 and 7).[32]

A representative example of dehydration in water is protonic acid-catalysed dehydrative esterification. Dodecylbenzenesulfonic acid (DBSA), which acts as a protonic acid–surfactant-combined catalyst, is very effective for catalysing the esterification of acids with alcohols in water.[49,50] Besides the esterification, etherification and thioetherification also proceed smoothly in water using the catalyst DBSA. Dithioacetals are very useful in organic synthesis as powerful protective groups for carbonyl compounds. The DBSA-catalysed system is also applicable to dithioacetalisation in water, which yields dithioacetal products. The reaction proceeds very well not only for ketones, but also for aldehydes.[49–51]

A new protocol for the dehydrative nucleophilic substitution of benzyl alcohols with a variety of carbon- and heteroatom-centred nucleophiles using a dodecylbenzenesulfonic acid catalyst in water has been developed. The reaction system can be applied to the stereoselective C-glycosylation of 1-hydroxy sugars in water.[52]

1-Hydroxy sugars, such as *O*-benzyl-protected furanose and pyranose, reacted with alcohols and a nitrogen nucleophile in the presence of a catalytic amount of DBSA to afford the desired adducts in good yields. A detailed study of the glycosylation of 2-deoxy-D-ribofuranose showed that the hydrophobicity of the substrates was important to attain higher yields. Regarding the α/β-selectivities, D-ribose and D-mannose derivatives gave the products in high β- and α-selectivities, respectively.[53]

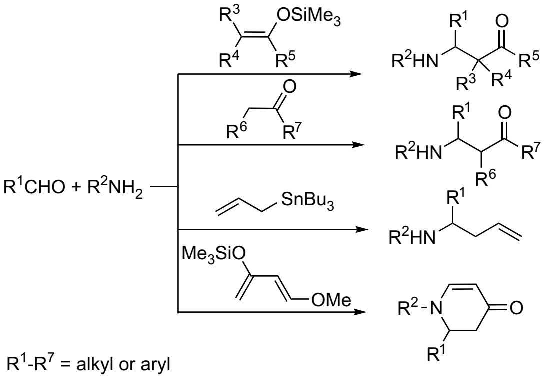
Direct dehydration polycondensation of dicarboxylic acids and alcohols has been carried out by surfactant-combined Brønsted and Lewis acids. This procedure did not require the removal of water, because the esterification was established at the interface of the emulsion in water. Emulsion polycondensations of 1,9-nonanediol (1,9-ND) and dodecanedioic acid (DDA) (molar ratio of dicarboxylic acid to diol=1:1) were carried out at 80 °C for 48 h in the presence of 16 wt % DBSA. The corresponding polyester ($MW=10.1\times10^3$) was obtained in an excellent yield (99%). Chain extension in the



Scheme 20.

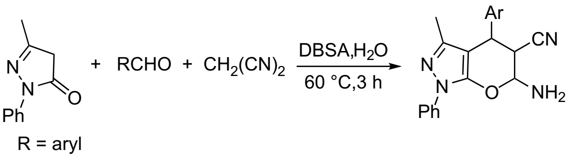
emulsion was carried out using hexamethylene diisocyanate as the chain extender (Scheme 20).[54]

Reactions of aldehydes, amines, and various nucleophiles such as silyl enolates,[55,56] ketones,[55,57] Danishefsky's diene, and allyltribuyltin in water were successfully carried out in the presence of *p*-dodecylbenzenesulfonic acid (Scheme 21).[55]



Scheme 21.

A three-component process for the one-pot synthesis of 6-amino-4-aryl-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazoles from 3-methyl-1-phenyl-2-pyrazolin-5-one, aromatic aldehydes and malononitrile using *p*-dodecylbenzenesulfonic acid as the catalyst (10 mol %) under aqueous media has been described (Scheme 22).[58]

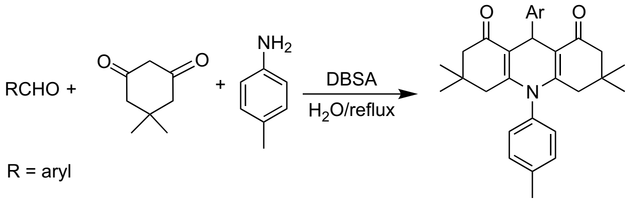


Scheme 22.

The synthesis of 2-amino-3-cyano-4-aryl-7,7-dimethyl-5-oxo-4*H*-5,6,7,8-tetrahydrobenzo[*b*]pyrans from aromatic aldehydes, malononitrile and 5,5-dimethyl-1,3-dioxocyclohexane using 4-dodecylbenzenesulfonic acid as the catalyst (10 mol %) has also been described.[59]

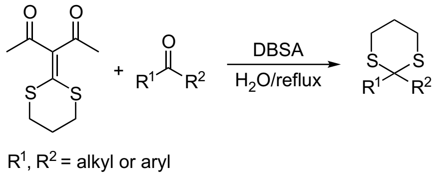
An approach to the synthesis of 3,3,6,6-tetramethyl-9-aryl-1,8-dioxo-octahydroxanthene derivatives from aldehydes and 5,5-dimethyl-1,3-dioxocyclohexane using DBSA as the catalyst (10 mol %) under ultrasound irradiation in water has been reported.[60]

The reaction of aromatic aldehydes, 5,5-dimethyl-1,3-cyclohexanedione and *p*-toluidine in water were successfully carried out (Scheme 23).[61]



Scheme 23.

A chemoselective thioacetalisation utilising 3-(1,3-dithian-2-ylidene)pentane-2,4-dione as a novel nonthiolic, odourless 1,3-propanedithiol equivalent catalysed by *p*-dodecylbenzenesulfonic acid in water has been developed (Scheme 24).[62]

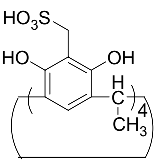


Scheme 24.

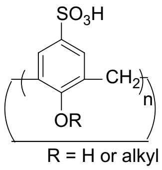
Solvent-free esterifications of various carboxylic acids and alcohols can be catalysed by the surfactant-combined catalysts, dodecylbenzenesulfonic acid (DBSA) and copper dodecylbenzenesulfonate (CDBS), in moderate-to-excellent yields at room temperature.[63]

### 3.4. Calix[*n*]arenes bearing sulfonic acids

Mannich-type reactions in water can be carried out in the absence of surfactants and organic solvents by calix[4]resorcinarenesulfonic acids. The water-soluble calix[4]resorcinarenesulfonic acid, 2,8,14,20-tetramethyl-5,11,17,23-tetrakis(sulfomethyl) calix-[4]resorcinarene **25a**, acts as an efficient inverse phase-transfer catalyst. It can be recovered as an aqueous solution and recycled after a simple extraction of the water-insoluble products.[64a]



**25a**



**25b**

The water-soluble calix[4]resorcinarenesulfonic acid would be expected to form host–guest complexes with nucleophile molecules in the organic–aqueous interfacial layer, and the attack of the nucleophile (silyl enolate or enol form of ketone) on the protonated imine would take place in the interfacial layer (Fig. 4).

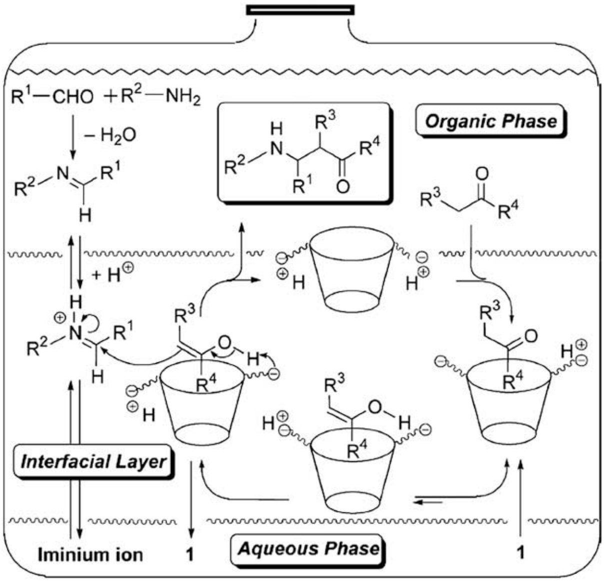
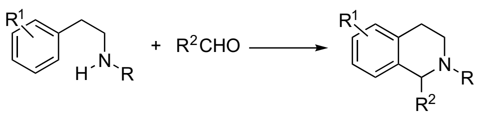


**Figure 4.** Possible mechanism of a Mannich-type reaction, catalysed by water-soluble calixarenesulfonic acid **25a**.

Calix[*n*]arene sulfonic acids **25b** bearing pendant aliphatic chains have also been developed as surfactant-type Brösted acid catalysts for allylic alkylation with allyl alcohols in water. The allylic alkylation products of aromatic compounds have been obtained in 60–94% yields. The water-solution of the surfactant-type catalyst has been recovered by means of simple extraction of water-insoluble products and centrifiguation, which could be reused in the next cycle directly.[64b]

## 3.5. Perfluorooctanesulfonic acid

Perfluorooctanesulfonic acid (PFOSA), as a Brønsted acid–surfactant-combined catalyst, efficiently catalyses the Pictet–Spengler reactions of β-arylethyl carbamate derivatives with aldehydes in water (Scheme 25). The present reaction is accelerated by the addition of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP).[65,66]



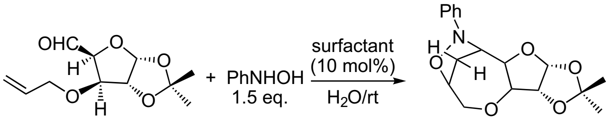
**Scheme 25.**

# 4. Quaternary ammoniums

## 4.1. Cetyltrimethylammonium bromide (CTAB)

A highly stereoselective surfactant-catalysed intramolecular nitrone (formed by dehydration in water) cycloaddition in aqueous media leading to the exclusive formation of a single isomer has been reported. Either an oxepane or pyran is formed from 3-*O*-allyl furanoside derivatives, which constitute the framework of a large number of biologically active compounds. By carrying out the model reaction shown in Table 9, it was found that the type of surfactant used influenced both the yield and the reaction time. Nonionic surfactants (entries 5, 6 and 8) were effective, but required a longer reaction time, an acidic surfactant (entry 7) reduced the yield, and anionic surfactants (entries 3 and 4) were slightly less effective than a cationic surfactant (entry 2). From these observations, it was concluded that CTAB is the most efficient surfactant for this reaction. When performing these reactions in water without surfactant, starting materials were recovered (entry 1).[67]

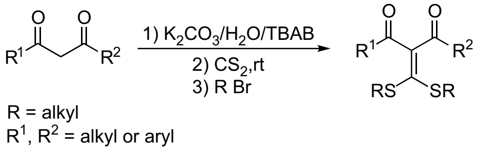
**Table 9**
Effect of surfactant on intramolecular nitrone cycloaddition in water



| Entry | Surfactant | Time (h) | Yield (%) | Entry | Surfactant | Time (h) | Yield (%) |
|---|---|---|---|---|---|---|---|
| 1 | — | 48 | 0 | 5 | Triton X-100 | 30 | 80 |
| 2 | CTAB | 8 | 79 | 6 | Tween-20 | 30 | 80 |
| 3 | SDS | 8 | 75 | 7 | DBSA | 16 | 61 |
| 4 | SDBS | 8 | 75 | 8 | Triton CF 10 | 36 | 79 |

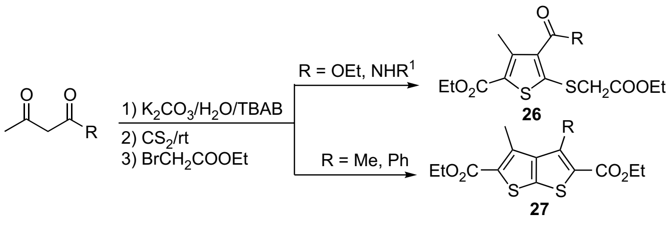
## 4.2. Tetrabutylammonium bromide

A clean, facile and practical synthesis of α-oxoketene *S*,*S*-acetals in water has been developed. Catalysed by tetrabutylammonium bromide (TBAB) at room temperature in water, a range of β-dicarbonyl compounds have been converted into the corresponding α-oxoketene *S*,*S*-acetals in very high yields. The catalyst in the aqueous phase can be recycled after separation of the organic products (Scheme 26).[68]



**Scheme 26.**

In this manner, when α-bromo esters were used instead of alkyl bromides polysubstituted thiophenes could be synthesised. Interestingly, β-keto esters and amides could be converted into polysubstituted thiophenes **26**. Polysubstituted thieno[2,3-*b*]-



**Scheme 27.**

**Table 10**
Catalytic activities in oxidation of various substrates to adipic acid

| Entry | Complex | Yield of adipic acid (%) | | | |
|---|---|---|---|---|---|
| | | Cyclohexene | Cyclohexanol | Cyclohexanone[a] | 1,2-Cyclohexanediol[b] |
| 1 | $[C_{16}H_{33}N(CH_3)_3]_2W_2O_3(O_2)_4$ | 77.8 | 51.8 | 60.3 | 81.4 |
| 2 | $[\pi\text{-}C_5H_5NC_{16}H_{33}]_2W_2O_3(O_2)_4$ | 78.3 | 51.2 | 60.7 | 83.3 |
| 3 | $[C_{16}H_{33}N(CH_3)_3]_2Mo_2O_3(O_2)_4$ | 0 | 27.9 | 0 | 23.6 |
| 4 | $[\pi\text{-}C_5H_5NC_{16}H_{33}]_2Mo_2O_3(O_2)_4$ | 15.2 | 23.5 | 37.4 | 48.3 |

All reactions performed at 90 °C using 30 wt % aq $H_2O_2$ for 20 h. Yield (based on substrate charged) refers to isolated product. Unless otherwise stated, *n*(substrate)/*n*(catalyst)/*n*($H_2O_2$) is 100:0.6:538 (mmol).

[a] Cyclohexanone=150 mmol.

[b] $H_2O_2$=400 mmol.

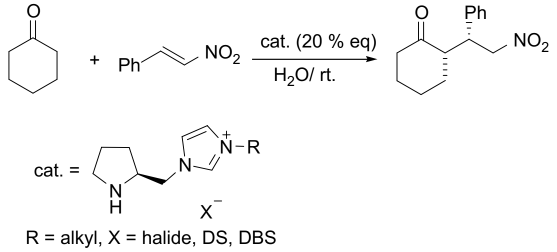
thiophenes **27** have been achieved in high yields from 1,3-dicarbonyl compounds catalysed by tetrabutylammonium bromide (TBAB) in the presence of $K_2CO_3$ in water (Scheme 27). TBAB in the aqueous phase can be recycled after the separation of organic products.[69]

### 4.3. Tetraalkylammonium peroxotungstates and peroxomolybdates

Some surfactant-type peroxotungstates and peroxomolybdates have been synthesised and characterised by Zhu and co-workers. Their studies indicated that the peroxotungstates catalysed the oxidation of cyclohexene and 1,2-cyclohexanediol to adipic acid with hydrogen peroxide without organic solvents and co-catalysts in excellent yields. Oxidation of cyclohexanol and cyclohexanone, however, gave only moderate yields (Table 10, entries 1 and 2). The peroxomolybdates were found to exhibit low activity (Table 10, entries 3 and 4).[70]

### 4.4. Imidazolium salts

In an interesting study, Luo and co-workers have used dodecyl sulfate (DS) and dodecylbenzenesolfunate (DBS) anions as counterions for chiral quaternary amines as surfactant-type asymmetric organocatalysts (STAO) that could catalyse efficiently Michael additions to nitroalkenes with high stereoselectivities in water without using any organic solvents or additional additives (Scheme 28).[71]



**Scheme 28.**

## 5. Summary and outlook

In summary, water has emerged as a versatile solvent for organic chemistry in recent years. Water as a solvent is not only inexpensive and environmentally benign, but it also plays a distinguished role in reactivity. Surfactant-type acids can catalyse organic reactions in water without using any harmful organic solvents. This review provides an introductory overview of this field. The types of organic reactions in water are now as diverse as those in organic solvents. It is worthy of note that completely new reactivities of reactions have been discovered in water. The wide application of aqueous organic reactions also provides a driving force for the future development of this area.

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