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Sustainable photochemistry: solvent-free singlet oxygen-photooxygenation of organic substrates embedded in porphyrin-loaded polystyrene beads†

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A solvent-free photooxygenation process that uses organic substrates embedded in porphyrin-loaded polystyrene beads as solid support is described and applied for ene- and [4+2]-cycloaddition reactions involving singlet oxygen ($^1\Delta_g$).

Among all processes that are discussed as suitable for sustainable chemistry, photooxygenation is one of the most appealing because this reaction uses only visible light, oxygen, dye and the substrate. Like its natural oxygen-producing antagonist, photosynthesis, photooxygenation is an archetype of a green chemical process.[1] The type II process involves singlet oxygen ($^1\Delta_g$), formed by energy-transfer from an electronically excited dye molecule.[2] This process is the cleanest way to oxygenated products with excellent chemo-, regio- and stereoselectivity pattern and (as one of few photochemical reactions) is used for industrial applications.[3–5] Severe problems, however, stem from the chemical setup: (a) the dye contaminates the product and has to be removed after reaction by chromatography or distillation; (b) solvents show conflicting properties, *i.e.* singlet oxygen is short-lived in environmentally friendly solvents (4 μs in water) and long-lived in problematic solvents like halogenated hydrocarbons (0.06 s in tetrachloromethane);[6] (c) pure oxygen is not applicable for industrial applications and also air-purging is elaborate. Here we show experimentally that these disadvantages can be circumvented by using a routine protocol by which porphyrin dyes are embedded in polystyrene beads, substrate and product are loaded and extracted by use of environmentally friendly solvents and visible irradiation is performed under an atmosphere of air.

From a synthetic point of view, the ene-[3] and the [4 + 2]-cycloaddition[4] reaction are the most important chemical reactions of organic substrates with singlet oxygen resulting in the formation of allylic hydroperoxides and endoperoxides, respectively, important intermediates in the synthesis of oxyfunctionalized products such as allylic alcohols, epoxy alcohols, vicinal diols, 1,4-diols, saturated polyols and many more[4,5] The fundamental rules for green chemistry are nicely achieved with respect to the theoretical framework and have been exemplarily demonstrated decades ago. In reality, photooxygenation is much less ‘green’ than possible due to solvent effects, product stability, safety precautions, and sensitizer recovery and separation, respectively. One solution to the long-standing problem of sensitizer dye recovery is the use of covalently polymer-bound singlet oxygen sensitizers such as the commercially available polystyrene-immobilized rose bengal (Sensitox®)[7] and many more. Most sensitizer systems are, however, not very useful in nonpolar solvents due to severe dye-bleaching and/or bleeding. A series of classical dyes and also C_{60} have been immobilized and used for photooxidation in aqueous suspensions.[8,9] For organic synthesis, these systems have not yet been applied successfully. An attractive alternative would be the use of dyes non-covalently embedded in confined media where loading and unloading of substrate and product, respectively, occurs simply by washing. This approach is suggested by the zeolite photooxygenation protocol as elaborated by Ramamurthy *et al.*[10] Here, however, the confined media is highly polar and protic which is disadvantageous for the singlet oxygen lifetime and the use of nonpolar sensitizers with high singlet oxygen quantum yields (Φ_Δ).

Therefore, we followed another route and used commercially available‡ polystyrene beads (60 ± 15 μm diameter) crosslinked with divinylbenzene as solid support. These beads are known to have easily modifiable space structures which can be controlled by polymer swelling with an appropriate nonpolar solvent.[11] By this swelling process, the nonpolar sensitizer (meso-arylated porphyrins) is introduced into the polymer beads (120 ± 25 μm diameter, after swelling with ethyl acetate) and, due to its extreme low solubility in more polar solvents, is fixed in the polymer network. The polystyrene beads were loaded with the sensitizer by swelling with a solution of catalytic amounts *meso*-tetraphenylporphyrin (TPP) or tetratolylporphyrin (TTP) in EtOAc with subsequent evaporation of the excess solvent. Subsequently, the beads were treated with a solution of the substrate dissolved in a minimum amount of ethyl acetate and by evaporation of the excess transfer solvent, a layer of sandy solid is obtained that was irradiated in a loosely covered petri dish by means of a sodium street lamp or a halide lamp, respectively (Fig. 1). It is worth mentioning, that the dye is nearly insoluble in most substrates investigated herein.

By repeated washing with ethanol, the product was extracted from the polymer beads. The dyestuff stayed nearly completely in the solid support and substrate loading could be repeated. We investigated two modes of singlet oxygen reactions, ene- and [4 + 2]-cycloadditions and checked whether the reactivity and selectivity behaviour is comparable to solution photochemistry. The highly reactive substrates α-pinene (**1**) and the alcohol from sorbic acid (**3**) gave, in excellent yields, the singlet oxygen products **2** and **4**, respectively. The regiochemical sensitive probes 1-methylcyclohexene (**5**) and citronellol (**7**) gave the hydroperoxide mixtures **6a–c** and **8a**,**b** in the same composition (by NMR of the crude reaction mixture) as in nonpolar solvents

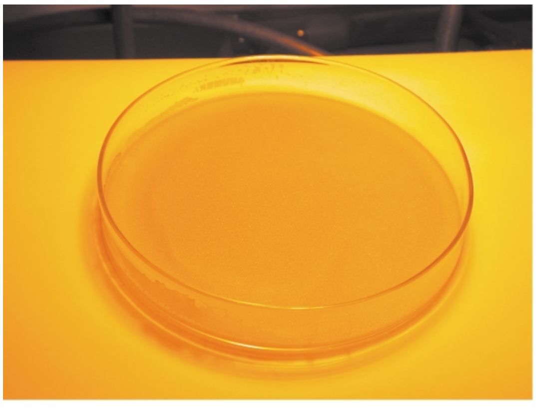

Fig. 1 Porphyrin- and citronellol loaded polystyrene beads irradiated by a halide lamp.

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† Dedicated to Professor Waldemar Adam on the occasion of his 65th birthday and his retirement from the stage of photooxygenation chemistry.

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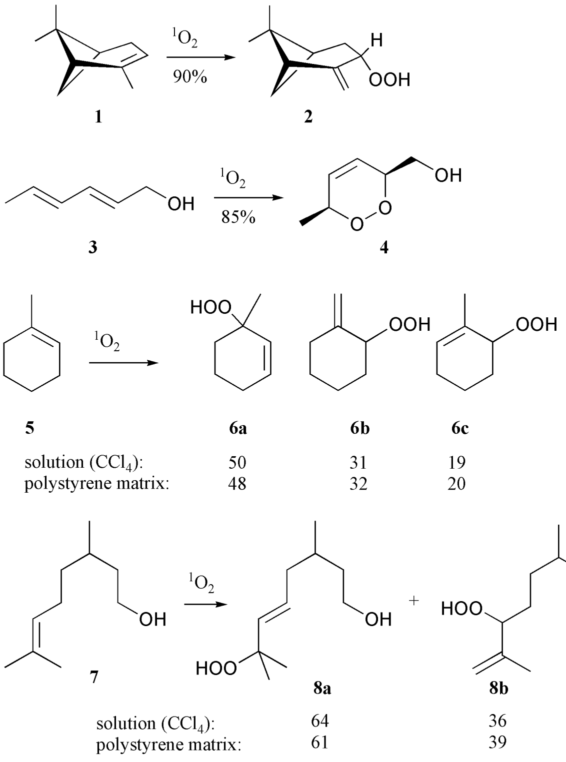
(Scheme 1). As an important industrial process rose oxide is synthesized from **7** in annual multi-ton quantities.

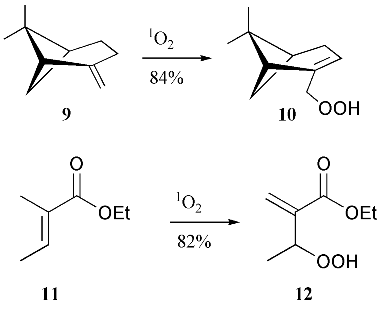
The loading, photolysis and unloading process was repeated five times for the citronellol system without noticeable slowdown of the photooxygenation efficiency. By this procedure, as much as 1 gram of substrate per 1 gram of polystyrene was converted into the corresponding products. The degree of conversion under these conditions is comparable to liquid-phase photooxygenation in tetrachloromethane or fluorinated hydrocarbons as solvents. This comparison, however, is somewhat unfair for the solid support reaction, because no oxygen or air was purged through the reaction medium as is the case for liquid-phase photooxygenation. The notoriously less reactive substrates β-pinene (**9**, the industrial precursor for the synthesis of myrtenol) and ethyl tiglate (**11**) were likewise transformed into the corresponding allylic hydroperoxides **10** and **12**, respectively (Scheme 2). The β-pinene reaction can be driven to complete conversion which is problematic under liquid-phase reactions where secondary processes compete after moderate conversions.



	6a	6b	6c
solution (CCl_4):	50	31	19
polystyrene matrix:	48	32	20

	8a	8b
solution (CCl_4):	64	36
polystyrene matrix:	61	39

Scheme 1



Scheme 2

One way of looking at these processes is as a solvent-free photooxygenation where the lifetime of the excited singlet oxygen is solely determined by the chemical and physical deactivation induced by the substrate molecule itself. The singlet oxygen lifetime has been determined for polystyrene (τ_Δ = 19 s) and resembles that in toluene solution.[12] The porphyrin sensitizers, however, are nearly insoluble in the substrates which indicates that they are strongly embedded in the polymer matrix with the liquid substrate filling the free space. Thus, singlet oxygen is generated by energy transfer probably at the polymer walls and then diffuses into the substrate and reacts. In one way or another, this is a more loosely defined system as *e.g.* the intra/extra-micelle or membrane systems, where energy transfer to and chemical reaction with singlet oxygen occurs in different spacial areas of the supporting matrices.[13]

From a practical point of view, our procedure has major advantages over the 'classical' Type II photooxygenation protocol: the photochemical reactions proceed solvent-free and only little amounts of ethyl acetate and ethanol are needed for loading and deloading, respectively. Loading could also be performed in many cases by directly using the liquid substrate which further reduces the amount of solvent. The molar sensitizer–substrate ratio can be as low 1 : 10000 and applied several times without loss in activity. This technique in combination with the use of solar radiation is a further step to more green photochemistry applications.[14]

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Notes and references

‡ Polystyrene beads were purchased from Acros Organics (100–200 mesh) copolymerized with 1% of divinylbenzene. TTP and TPP were purchased from Porphyrine Systems. The amount of dyestuff was 0.1 weight-% with respect to the polymer matrix.

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