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Unpowered Mechanical Stirring of Reaction Media Using Renewable Stirring Fish (RSFs).

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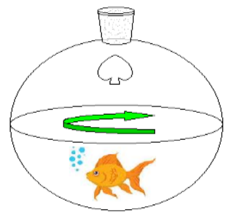
Abstract: The use of power-intensive mechanical stirring represents an obstacle to environmentally-sound chemistry. We present an efficient and visually appealing alternative.

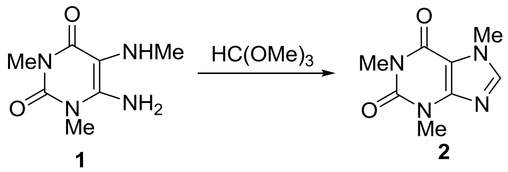


Introduction

Extensive research has been conducted into the development of environmentally sound methods for synthetic chemistry, in accordance with the principles of green chemistry.[1] Renewable starting materials,[2] recyclable solvents and reduced toxic waste streams have all been investigated in depth; however, this research effort has thus far failed to address the requirement for mechanical or magnetic stirring, usually powered by mains electricity and thus unsustainable. The present study details our development of an effective and environmentally friendly alternative, exploiting the autonomous stirring capability of Renewable Stirring Fish (RSFs).

Discussion

After initially disappointing results using Renewable Stirring Mammals,[3] we investigated the possibility of using RSFs, using the condensation of **1** with trimethyl orthoformate as a model reaction (Scheme 1).



Scheme 1

Although initially sluggish, the stirring rate increased exponentially as the reaction proceeded towards completion (Figure 1). Upon workup with an aqueous thiopental solution, the product could be isolated in excellent yield.

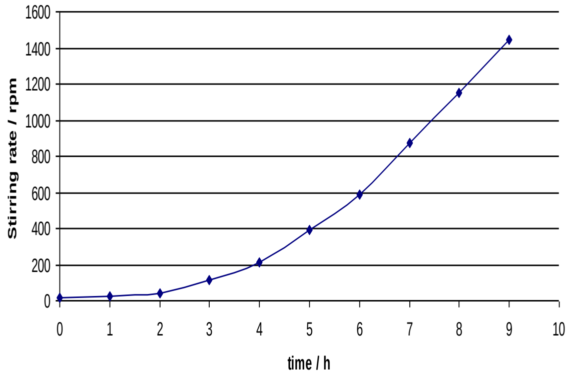


Figure 1

Next, we investigated the effect of solvent on the stirring rate, with some surprising results. Methanol, DMF, HMPA and acetonitrile proved to be incompatible with RSF stirring, leading rapidly to a stirring rate of 0 rpm. In ethanol, stirring was erratic; an initially rapid rate was followed by inversion of the RSF (Figure 2) and eventual deactivation. Water proved to be the most effective solvent, particularly at approximately neutral pH. RSFs could be recycled without loss of efficacy after use in aqueous solutions, but were deactivated after exposure to most organic solvents. Degassing the solvent was found to be detrimental to the stirring rate in all cases.

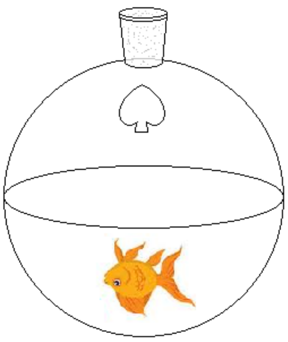


Figure 2. Effect of ethanolic solution on RSF.

Having established the optimal solvent, temperature was investigated. Increased reaction temperatures generally led to an increased stirring rate, although there was a drastic reduction at temperatures above 60 °C (Figure 3). Thus, the optimised conditions for condensation of **1** proved to be neutral aqueous solution at approximately 50 °C. Due to the wide range of RSFs available, scale-up of the method is relatively simple, although we note that the use of the Renewable Stirring Shark (RSS)[4] is inadvisable for large-scale work due to its poor safety profile.

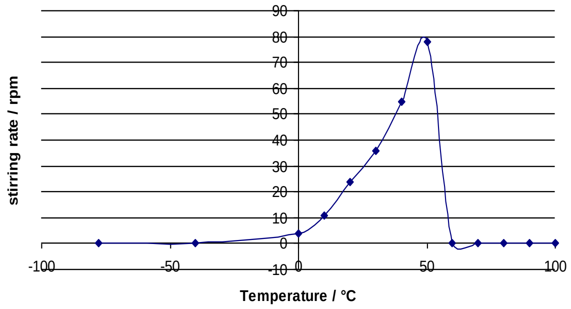


Figure 3. Stirring rate at various temperatures.

These conditions were applied to the RSF stirring of several reactions, and stirring rates were plotted, with mixed results (Figures 4-7). Interestingly, stirring could be considerably accelerated in some cases either by sonication or addition of pizza, as outlined in Figure 4 and Figure 6.

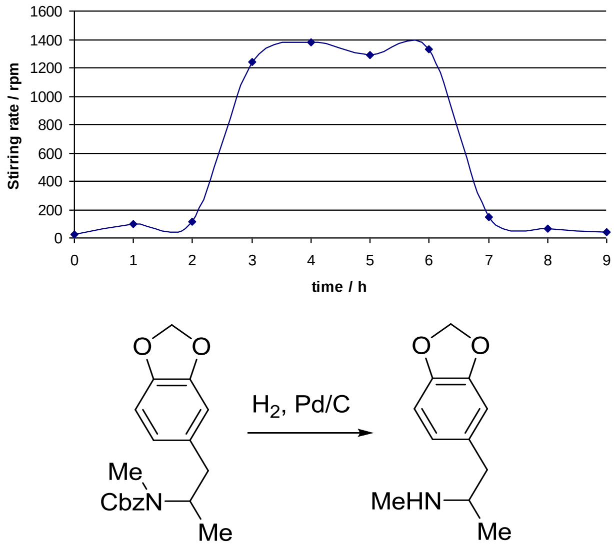


Figure 4. Note: reaction mixture sonicated with pounding techno, 3 h – 6 h.

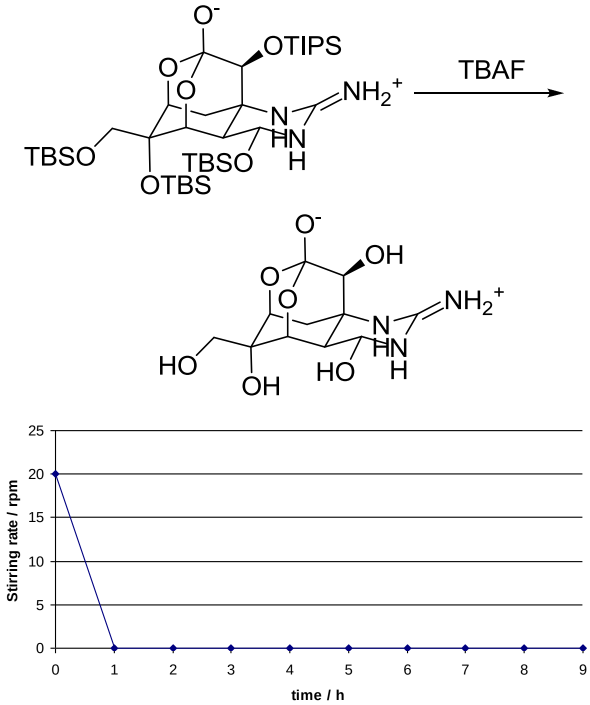


Figure 5

Current studies are directed towards the mechanisms underlying these synergistic effects, and will be reported in due course.

In summary, an effective new method for stirring of aqueous reaction mixtures is reported, requiring no external energy input. The stirrer units are renewable and widely available at extremely low cost.

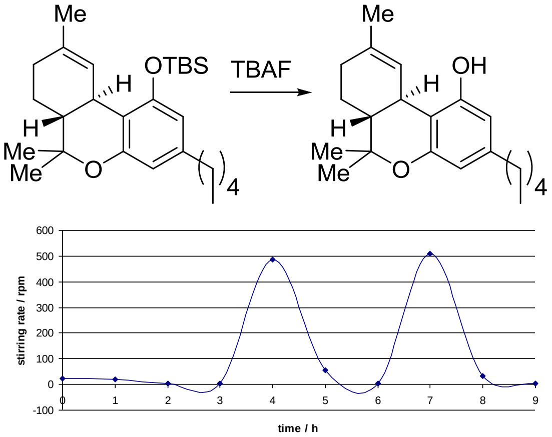


Figure 6. Note: pizza (1.0 slice) added at 4 h and 7 h.

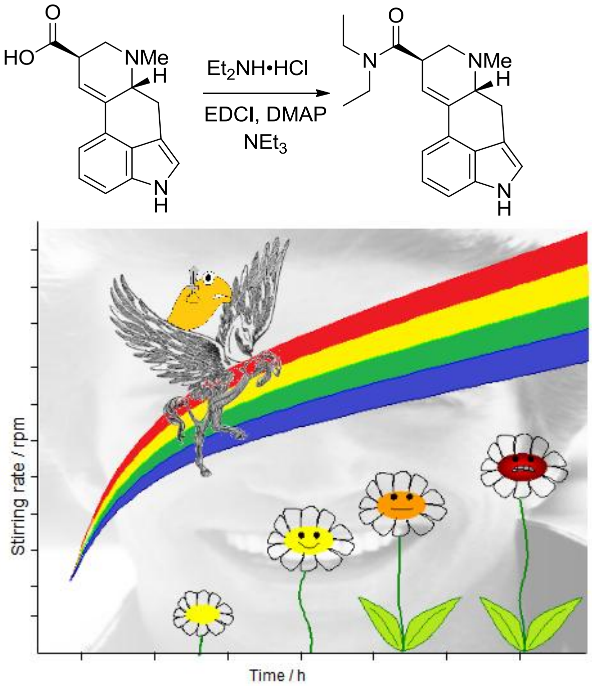


Figure 7

Acknowledgements
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General Experimental Details
RSFs were procured from various fairgrounds, lakes and rivers, and were used as received. All other reagents were synthesized by standard procedures or bought from commercial suppliers.

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