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Ionic liquid soluble photosensitizers

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Abstract—The preparation and investigation of triplet photosensitizers designed to be preferentially soluble in room-temperature ionic liquids are reported. Photosensitizers prepared by covalent attachment of 1-methylimidazole to aryl ketones are soluble in ionic liquids and remain in the ionic liquid layer when the solution is extracted with an organic solvent. The photosensitized isomerization of *trans*-β-ionol to *cis*-β-ionol was efficiently carried out in ionic liquid solution with the product ionol being extracted and the sensitizer/ionic liquid mixture being re-used in additional photosensitization reactions. The scope and utility of the sensitizers in sensitizing other reactions are discussed.

1. Introduction

Ionic liquids have found increasing use in organic chemistry as chemists have improved their ability to tailor these solvents to a particular need.[1] Among the specialized ionic liquids developed are those that carry catalysts and reagents.[2] Ionic liquids have been designed for specific chemical function, such as fixing carbon dioxide.[3] Although ionic liquids are often discussed as a uniform class of material in the literature, the physical properties and chemical behavior of ionic liquids cannot be narrowly defined and may vary significantly from one ionic liquid to another.[4] Ionic liquids may be soluble in water, organics, or both.[1] Furthermore, ionic liquids may dissolve a wide range of solutes.[1] When partitioned against an organic solvent, ether for instance, many ionic species are retained in the ionic liquid layer. This property is useful in that it allows the rapid separation of neutral organics from charged molecules. This technique is often used to separate a metal catalyst or other reagent following a reaction in an ionic liquid.[2] Several examples using homogenous supports in ionic liquids have appeared in the last few years.[5] A substrate is loaded onto a support that is preferentially soluble in an ionic liquid, which then becomes a fluid solid support. The substrate then undergoes a series of transformations, until the final product is cleaved from the support and extracted with an organic solvent. Though fewer examples are known, homogenously supported reagents have also been reported.[2] The idea is analogous to work done in fluorous media where a perfluorinated catalyst or reagent is used to carry out a transformation on a 'normal' organic substrate.[6] After the reaction, the catalyst can easily be separated from the substrate/product by extraction.

While studying photochemical reactions in ionic liquids, we noted that ionic liquids are excellent media in which to perform anaerobic reactions.[7] The negligible vapor pressure of the ionic liquids allows solutions to be degassed readily without numerous cycles of freeze–pump–thaw. If none of the reagents or reactants are volatile, the reaction mixture can simply be placed on a vacuum line prior to irradiation. A number of reports discussing photochemistry in ionic liquids have appeared in the past several years.[8] These observations led to the idea of an ionic liquid containing a photosensitizing chromophore so that the ionic liquid itself might be a photosensitizer. Photochemical energy transfer in ionic liquids has been reported previously.[9] Unfortunately, all attempts at preparing such a liquid have failed, as the chromophore invariably rendered the salt a solid. However, the ability of ionic liquids to retain other ionic compounds suggested the idea of doping an ionic liquid with a sensitizer bearing a charge, thereby making it preferentially soluble in the ionic liquid. The result would be a homogenously supported photosensitizer. We sought to attach a dialkylimidazolium cation to a photosensitizer and then use a solution of this new sensitizing salt dissolved in an ionic liquid to carry out a photosensitized reaction. If successful, the photoproduct could be separated from the sensitizer by extraction, leaving the ionic liquid/sensitizer mixture to be reused.

A suitable photosensitizer would need three properties: (1) a partition coefficient of zero between an ionic liquid and an

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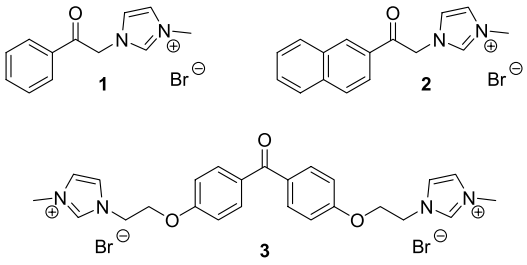


Chart 1.

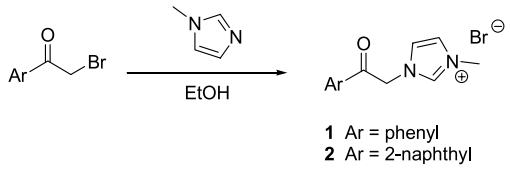
organic solvent, (2) photochemical inertness, other than triplet energy transfer, and (3) ease of preparation. We chose the common ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]) and diethyl ether as representative example of an ionic liquid/organic solvent pair. The sensitizers prepared are shown in Chart 1.

2. Results and discussion

Our first target was acetophenone **1**, which was readily prepared by treating 1-methylimidazole with phenacyl bromide in ethanol (Scheme 1). Acetophenones have been widely used as triplet sensitizers and absorb well at $\lambda >$ 300 nm, which is critical in protecting the ionic liquid itself from excitation. Compound **1** was soluble in [bmim][BF_4] and insoluble in diethyl ether. When **1** was dissolved in [bmim][BF_4] (1 mg/mL) and extracted three times with an equivalent volume of diethyl ether, no **1** was present in the combined ether layers. Thus, **1** fulfilled two of the three criteria listed above.

Unfortunately, **1** did not meet criterion 2, photochemical inertness. In the photosensitized isomerization of *trans*-β-ionol,[10] **1** invariably led to complex mixtures and low mass recoveries. Isomerization of the ionol was observed, but it was clear that a number of other undesired processes were occurring. In retrospect, these side reactions might have been anticipated. Acetophenone triplets are highly reactive as hydrogen abstractors and electron acceptors. In addition, the expulsion of leaving groups from the α position following photoinduced electron transfer has also been observed in related systems.[11] Consistent with the latter reaction, acetophenone was observed in small amounts in the organic extracts from these attempted photoisomerizations. Decomposition of **1** could also be surmised because isomerization in recycled [bmim][BF_4]/**1** mixtures was markedly less efficient.

Both hydrogen abstraction and expulsion of leaving groups, such as the alkylimidazole in **1**, from α-positions are efficient processes in n,π^* triplets. Considering this reactivity, we next prepared two additional photosensitizers, **2** and **3**. Sensitizer **2** was prepared by alkylation



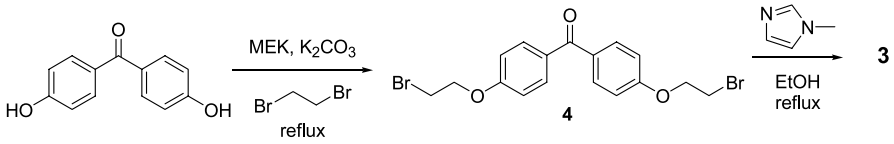
Scheme 1.

of 1-methylimidazole with 2-bromoacetonaphthone (Scheme 1). Sensitizer **3** was prepared as shown in Scheme 2. Alkylation of 4,4′-dihydroxybenzophenone with excess 1,2-dibromoethane gave **4** in 66% yield. Dibromide **4** was then used to alkylate 1-methylimidazole to give **3** in 68% yield. The chromophore in both **2** and **3** was modified such that the lowest triplet state should be the π,π^* configuration. Also, imidazole expulsion was not possible in **3**. As was the case with **1**, neither **2** nor **3** was soluble in diethyl ether.

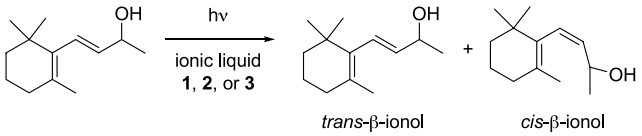
Both **2** and **3** sensitized the isomerization of *trans*-β-ionol (Scheme 3) when irradiated with a medium pressure Hg lamp with a UO_2 doped glass filter ($\lambda > 350$ nm). In degassed methanol, the photostationary state achieved in sensitization with **3** was 65% *cis*-β-ionol (see below). This photostationary state was reached in 48 h when 5 mol% of **3** (relative to ionol) was used. Under the same conditions, sensitizer **2** gave a photostationary state of 100% *cis*-β-ionol, which was reached in 24 h.

Irradiation of *trans*-β-ionol in the [bmim][BF_4]/**2** or [bmim][BF_4]/**3** (5 mol% of **2** or **3** in each case) mixture led to formation of *cis*-β-ionol much more effectively than in reactions with **1**. Interestingly, the reaction was much slower in the ionic liquid than in methanol when sensitized with **3**, though no similar reduction in the rate of reaction with **2** was observed in going from methanol to ionic liquid. In all cases, the β-ionol product could be easily extracted from the ionic liquid, with recovered yields between 85 and 100%. No sensitizer was observed in any ether extracts.

The sensitizer/ionic liquid mixture could be recycled several times with no noticeable effect on rate, photostationary state composition or yield. Three successive 24 h runs were conducted using **2** (5 mol%) in 10 mL [bmim][BF_4]. In each case, the composition of β-ionol after 24 h of irradiation ($\lambda > 350$ nm) was 100% *cis*. By simple extraction, pure β-ionol could be obtained from the ionic liquid. Yields for the three runs were 92, 89 and 83%. Between each run, the recovered ionic liquid was concentrated in vacuo. A ^{1}H NMR spectrum of the ionic liquid portion after each run indicated pure [bmim][BF_4] (the sensitizer was present in too low concentration to be seen by NMR). For the fourth attempt, the ionic liquid layer from the third reaction was allowed to sit unused for ten days at ambient temperature and in room light prior to the sensitization reaction. Again,



Scheme 2.



Scheme 3.

the isomerization was complete in less than 24 h and the yield of *cis*-β-ionol was 97%. The variation in actual recovered yields was slight and was consistently between 80 and 100%.

In all cases described thus far, diethyl ether was used as the organic solvent in extracting ionol from the ionic liquid. Attempts to extract the ionic liquid ([bmim][BF_4]) with benzene or ethyl acetate were problematic, as the ionic liquid itself was partially soluble in the organic solvent. This led to significant quantities of ionic liquid, and some sensitizer, crossing into the organic layer. Significant accumulation of the organic solvent in the ionic liquid layer also occurred, requiring removal of the solvent under reduced pressure. Though the suitability of an organic solvent will vary according to the ionic liquid used, in most cases, ether or hexane will be the most effective extraction solvent.

Recoveries of β-ionol from reactions sensitized by **3** in [bmim][BF_4] were also high (>80%). However, these reactions were very slow when irradiated at $\lambda>350$ nm. The photostationary state (88% *cis*) was only reached after 410 h. The reduced rate is best explained by the relative absorptivities of **2** and **3**. Benzophenone **3** absorbs strongly between 260 and 320 nm ($\varepsilon_{313}=5000$) but poorly at 350 nm ($\varepsilon=28$). At the principal emission line of the filtered lamp (366 nm), **3** has practically no absorbance. In contrast, **2** absorbs very well between 300 and 350 nm ($\varepsilon_{350}=1410$ and $\varepsilon_{366}=41$). The rate of sensitization using **3** did appear to be slower in [bmim][BF_4] than in organic solvent, as the photostationary state using 4,4′-dimethoxybenzophenone (an analog of **3**) in benzene was reached in only 72 h ($\lambda>$ 350 nm). In methanol, a photosensitization reaction using **3** did not proceed to the usual photostationary state. Instead, this reaction stopped after approximately a 3:1 ratio of *cis* to *trans*-β-ionol had been obtained. When this reaction was concentrated, NMR analysis indicated an absence of **3**, which had apparently undergone photoreduction by the solvent, as determined by the aromatic signals moving upfield by 0.1–0.4 ppm.

Figure 1 shows a comparison of rates of ionol isomerizaton in [bmim][BF_4] and methanol, using **2** as the sensitizer. No significant difference in the rate of sensitization in the two solvents was observed. The rate appeared to slow as the reaction progressed when the reaction was conducted in methanol. However, consumption of **2** was not detected when the residue was analyzed following removal of the methanol.

The usefulness of **2** and **3** in ionic liquids other than [bmim][BF_4] was also examined. Two additional ionic liquids were chosen: 1-butyl-4-methylpyridinium tetrafluoroborate ([BuPic][BF_4]) and *N*-butyl-*N*-methylpyrrolidinium triflimide ([BMPyr][Tf_2N]). The sensitization of ionol

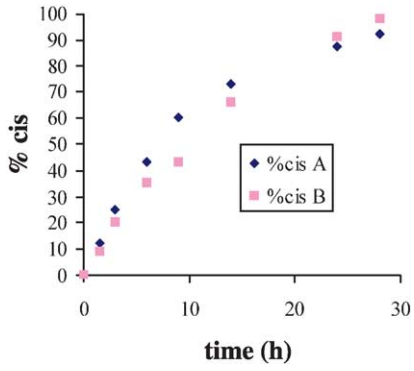
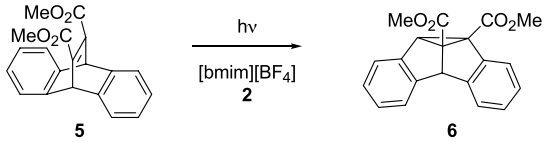


Figure 1. Amount of *cis*-ionol present in reactions sensitized by **2** in methanol (A) and in [bmim][BF_4] (B). The two samples were irradiated using a medium pressure Hg lamp and UO_2 filter ($\lambda>350$ nm).

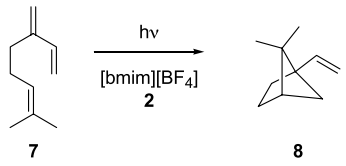
isomerization using **2** was tested in both solvents. This reaction gave a very complex mixture when carried out in [BuPic][BF_4]: GC analysis registered 13 volatile products in greater abundance than the total amount of ionol. However, after 24 h ($\lambda>350$ nm), the ionol was 87% *cis*, indicating that the sensitized isomerization did occur. NMR confirmed that a complex mixture had resulted. We have observed numerous undesired photoreactions in pyridinium based ionic liquids.[7a] Given our past results and the recent data, we suggest avoiding pyridinium based ionic liquids as solvents for photoreactions, unless a specific interaction with the solvent is desired.

Photoisomerization reactions (5 mol% **2**) run in [BMPyr][Tf_2N] proceeded smoothly. In our first attempt, isomerization was complete after 24 h and *cis*-β-ionol was recovered in 87% yield. The recovered [BMPyr][Tf_2N] was used in a second reaction, and again, isomerization went to completion in 24 h with 91% recovery of *cis*-β-ionol. This ionic liquid was not as attractive for use in the sensitized ionol isomerization because of its higher hydrophobicity relative to [bmim][BF_4]. Extraction with ether was impossible, as the ether dissolved significant quantities of the ionic liquid, contaminating the recovered ionol with both [BMPyr][Tf_2N] and sensitizer **2**. Instead, hexane was used to extract the ionol from the ionic liquid.

Other sensitized photoreactions were examined to determine the scope of the ionic liquid soluble photosensitizers. The sensitized di-π-methane rearrangement of **5**[12] was successfully carried out by irradiation ($\lambda>350$ nm) of a solution of **2** in [bmim][BF_4] for 18 h (Scheme 4). The solution was prepared and irradiated exactly as were the ionol photoisomerization reactions. The starting dibenzobarrelene was remarkably soluble in the ionic liquid, 75 mg of **5** dissolving readily in 10 mL of [bmim][BF_4]. The product, **6**,[13] was extracted from the ionic liquid with ether and recovered in 87% yield. No starting material remained and no other products were extracted with the product.



Scheme 4.



Scheme 5.

In contrast, the sensitized photolysis of myrcene (**7**) did not proceed when irradiated similarly in [bmim][BF_4] (Scheme 5).[14] Extraction of the ionic liquid with ether following photolysis gave a complex mixture of products that could not be separated, though signals of the desired product (**8**) were identified in a ^{1}H NMR spectrum of the crude product. An explanation for this result could be found in the behavior of the hydrocarbon upon addition to the ionic liquid; when myrcene is added to [bmim][BF_4] (or other ionic liquids), visible globules form. The insolubility of myrcene in the ionic liquid most likely produces a higher effective concentration than indicated by the relative amounts of substrate and solvent. Liu and Hammond reported that at higher concentrations photosensitization of myrcene led to dimerization, rather than photocyclization.[14] We believe that in this case, the phase separation that occurs between myrcene and [bmim][BF_4] results in dimerization and oligomerization in addition to the desired reaction. Thus, ionic liquids are suitable solvents for photosensitization reactions only when they dissolve the substrates at reasonable concentrations. Unfortunately, use of the more hydrophobic ionic liquid, [BMPyr][Tf_2N], did not provide improvement in the sensitized photoisomerization of myrcene.

3. Conclusion

Imidazole-tagged aryl ketones have been developed that can efficiently sensitize photochemical reactions in ionic liquids. The product can be isolated simply by extraction of the ionic liquid solution with an appropriate organic solvent, with the sensitizer remaining in the ionic liquid layer. The ionic liquid/sensitizer mixture can be recycled a number of times with little loss of energy transfer efficiency or recovered yield of the product. Due to apparent participation of the solvent, [BuPic][BF_4] was not an effective ionic liquid for these reactions. The most effective combination was acetonapthone **2** in [bmim][BF_4], using ether as the solvent for extraction, though this will likely vary according to reaction and substrate. This method is effective for rapid isolation of product and as a means of avoiding chromatography of sensitive photoproducts in cases where photosensitization via energy transfer is required.

4. Experimental

4.1. General methods

^{1}H NMR (300, 500 MHz) and ^{13}C NMR (75, 125 MHz) spectra were recorded on Bruker Avance 300 and 500 MHz spectrometers. Unless otherwise indicated, all reagents and solvents were obtained commercially and used without further purification: all compounds were purchased from Sigma-Aldrich or Fisher Scientific. CH_2Cl_2 was distilled over calcium hydride. Thin-layer chromatography was performed on silica gel (250 μm thickness doped with fluorescein) unless otherwise indicated. The chromatograms were visualized with UV light (254 nm) unless otherwise indicated. GC analyses were conducted on an Agilent 6890 GC and analytes detected by FID following elution from a 30 m β-cyclodextrin column (Supelco 24304). Elemental analyses were performed by Atlantic Microlabs, Inc. in Norcross, GA. High-resolution mass spectrometry was performed at Ohio State University by the laboratory of Christopher Hadad in Columbus, OH. Photochemical reactions were conducted using a 450 W medium pressure Hg vapor lamp (Hanovia) in conjunction with a UO_2 doped glass filter.

4.1.1. 3-Phenacyl-1-methylimidazolium bromide (1). Phenacyl bromide (15.0 g, 76 mmol) was dissolved in ethanol (300 mL) and the solution cooled to 0 °C by an external ice/water bath. 1-Methylimidazole (6.2 mL, 84 mmol) was added dropwise to the stirring reaction mixture via addition funnel. The resulting solution was allowed to warm to ambient temperature with the bath. After 36 h, solvent was removed in vacuo to give a yellowish sludge. The sludge was poured into rapidly stirring diethyl ether and a white precipitate formed. The precipitate was collected and triturated extensively with ether and dried in vacuo to give the desired salt as a yellow powder (19.2 g, 68 mmol, 90%). ^{1}H NMR (300 MHz, CD_3OD) δ 4.01 (s, 3H), 6.00 (s, 2H (exchanges with CD_3OD)), 7.63 (m, 5H), 8.08 (s, 1H), 8.11 (s, 1H), 8.99 (s, 1H (exchanges with CD_3OD)); ^{13}C NMR (75 MHz, CD_3OD) δ 192.1, 139.4, 135.7, 135.2, 130.2, 129.4, 125.4, 124.5, 56.3, 36.8. HRMS calcd for $C_{12}H_{13}N_2O^+$: 201.102239. Found: 201.10241.

4.1.2. 3-Acenapthyl-1-methylimidazolium bromide (2). 2′-Bromo-2-acetonaphthone (2.49 g, 10 mmol) was dissolved in ethanol (50 mL). To this stirring solution was added 1-methylimidazole (0.836 mL, 10.5 mmol). The reaction mixture warmed during addition of 1-methylimidazole; an ice/water bath was used to keep the reaction cool. After addition was complete, the bath was removed and the mixture allowed to warm to ambient temperature overnight. Solvent was removed in vacuo to give a yellow-orange powder. The residue was recrystallized from boiling $CHCl_3$ to give the desired salt as small yellow crystals (2.41 g, 7.3 mmol, 73%). ^{1}H NMR (300 MHz, CD_3OD) δ 4.02 (s, 3H), 6.15 (s, 2H (exchanges with CD_3OD)), 7.68 (m, 4H), 7.99 (m, 4H), 8.74 (s, 1H), 9.01 (s, 1H, exchanges with CD_3OD)); ^{13}C NMR (75 MHz, CD_3OD) δ 191.3, 139.5, 137.7, 134.0, 132.5, 130.9, 130.5, 130.0, 129.4, 129.0, 128.7, 125.4, 124.6, 124.3, 56.3, 36.8. HRMS calcd for $C_{16}H_{15}N_2O^+$: 251.117889. Found: 251.11685.

4.1.3. 4,4′-(2-Bromoethoxy)benzophenone (4). To a stirring solution of 4,4′-dihydroxybenzophenone (2.14 g, 10 mmol) in MEK (200 mL) was added K_2CO_3 (3 g, 22 mmol) followed by 1,2-dibromoethane (38 g, 200 mmol) in one portion. The solution was heated to reflux for 5 h. TLC indicated no starting material remained. The solution was filtered through a plug of basic alumina, which was

washed with MEK (100 mL). The filtrate was concentrated to give a white solid (2.82 g, 6.6 mmol, 66%), which was used without further purification. An analytically pure sample of **4** was obtained by recrystallization from hot ethanol. Mp 124–126 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.68 (t, 4H, $J=6.6$ Hz), 4.38 (t, 4H, $J=6.6$ Hz), 6.98 (d, 4H, $J=9.0$ Hz), 7.78 (d, 4H, $J=9.0$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.2, 161.3, 132.3, 131.3, 114.2, 67.9, 28.6. Anal. Calcd for $C_{21}H_{16}Br_2O_3$: C, 47.69; H, 3.77; Br, 37.33. Found: C, 48.06; H, 3.72; Br, 36.99.

4.1.4. 4,4′-(2-(1-Methylimidazolium)ethoxy)benzophenone dibromide (3). To a stirring solution of **4** (2.28 g, 5.4 mmol) in MEK (50 mL) was added 1-methylimidazole (7 mL, 84 mmol) in one portion. The solution was heated to reflux for 72 h. Solvent was removed in vacuo to give a gummy residue that was partitioned between EtOAc (50 mL) and water (100 mL). The layers were separated and the aqueous layer washed repeatedly (5×50 mL) with EtOAc. The aqueous layer was then dried in vacuo to give an amorphous paste that was crystallized from ethanol/EtOAc to give the desired salt (2.18 g, 3.68 mmol, 68%). ^{1}H NMR (300 MHz, CD_3OD) δ 3.99 (s, 6H), 4.52 (m, 4H), 4.74 (m, 4H), 7.11 (m, 4H), 7.71 (m, 8H), 9.18 (s, 2H, exchanges with CD_3OD)); ^{13}C NMR (75 MHz, CD_3OD) δ 196.2, 162.8, 138.3, 133.0, 132.6, 125.0, 124.2, 115.5, 67.6, 36.7, 33.9. HRMS calcd for $C_{25}H_{28}BrN_4O_3Na^+$: 511.133928. Found: 511.13426.

4.2. Method for photoisomerization of ionol

To 10 mL RTIL was added a measured amount of sensitizer followed by 100 μL *trans*-β-ionol (94 mg, 0.48 mmol). The mixture was then vigorously stirred while evacuated on a high-vacuum line (50 mTorr). The solution was stirred for 1 h or until the sensitizer was fully dissolved, whichever took longer. The solution was then irradiated with a medium pressure Hg lamp through Pyrex and a UO_2 doped glass filter ($\lambda>350$ nm). Photolyses were followed by removal of 500 μL aliquots from the reaction mixture, extraction of the aliquot with 500 μL diethyl ether and GC analysis of the extract. For preparatory scale reactions, the photolysis mixture was extracted three times with an equivalent volume of diethyl ether, the combined organic extracts washed with 10 mL water and conc. in vacuo.

4.3. Method for sensitized di-π-methane of dibenzobarrelene 5.[13]

To 10 mL [bmim][BF_4] was added 16 mg of **2** (0.05 mmol) and the solution stirred vigorously while being gently heated until the sensitizer had dissolved. To the resulting solution was added **5** (75 mg, 0.23 mmol).[12] The mixture was then evacuated on a high-vacuum line (50 mTorr) for 3 h. The solution was then irradiated with a medium pressure Hg lamp through Pyrex and a UO_2 doped glass filter ($\lambda>$ 350 nm) while being vigorously stirred for 18 h. The photolysis mixture was extracted four times with 20 mL of diethyl ether, the combined organic extracts washed with 10 mL water and conc. in vacuo to give **6** (65 mg, 0.20 mmol, 87%). The ^{1}H NMR spectrum for **6** isolated from ionic liquid supported reactions matched exactly that of **6** made by literature methods.[13]

4.4. Method for sensitized photolysis of myrcene

To 10 mL [bmim][BF_4] was added 15 mg of **2** (0.05 mmol) and the solution stirred vigorously while being gently heated until the sensitizer had dissolved. To the resulting solution was added 125 μL of freshly distilled myrcene (100 mg, 0.74 mmol). The mixture was then evacuated on a high-vacuum line (50 mTorr) for 30 min. The solution was then irradiated with a medium pressure Hg lamp through Pyrex and a UO_2 doped glass filter ($\lambda>350$ nm) while being vigorously stirred for 24 h. The photolysis mixture was extracted three times with 15 mL of diethyl ether, the combined organic extracts washed with 10 mL water and conc. in vacuo to give the crude product.

Acknowledgements

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References and notes

1. (a) Welton, T. *Chem. Rev.* **1999**, *99*, 2071–2083. (b) Dupont, J.; de Souza, R. F.; Suarez, P. A. Z. *Chem. Rev.* **2002**, *102*, 3667–3692.
2. (a) Baleizao, C.; Gigante, B.; Garcia, H.; Corma, A. *Tetrahedron Lett.* **2003**, *44*, 6813–6816. (b) Audic, N.; Clavier, H.; Mauduit, M.; Guillemin, J.-C. *J. Am. Chem. Soc.* **2003**, *125*, 9248–9249. (c) Geldbach, T. J.; Dyson, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 8114–8115. (d) Handy, S. T.; Okello, M. *J. Org. Chem.* **2005**, *70*, 2874–2877. (e) Qian, W.; Jin, E.; Bao, W.; Zhang, Y. *Angew. Chem., Int. Ed. Engl.* **2005**, *44*, 952–955.
3. Bates, E. D.; Mayton, R. D.; Ntai, I.; Davis, J. H., Jr. *J. Am. Chem. Soc.* **2002**, *124*, 926–927.
4. Anderson, J. L.; Ding, J.; Welton, T.; Armstrong, D. W. *J. Am. Chem. Soc.* **2002**, *124*, 14247–14254.
5. (a) Handy, S. T.; Okello, M. *Tetrahedron Lett.* **2003**, *44*, 8399–8402. (b) Anjaiah, S.; Chandrasekhar, S.; Gree, R. *Tetrahedron Lett.* **2004**, *45*, 569–571. (c) de Kort, M.; Tuin, A. W.; Kuiper, S.; Overkleeft, H. S.; van der Marel, G. A.; Buijsman, R. C. *Tetrahedron Lett.* **2004**, *45*, 2171–2175.
6. (a) Dandapani, S.; Curran, D. P. *J. Org. Chem.* **2004**, *69*, 8751–8757. (b) Matsugi, M.; Curran, D. P. *Org. Lett.* **2004**, *6*, 2717–2720. (c) Curran, D. P.; Fischer, K.; Moura-Letts, G. *Synlett* **2004**, *8*, 1379. (d) DiMagno, S. G.; Dussault, P. H.; Schultz, J. A. *J. Am. Chem. Soc.* **1996**, *118*, 5312–5313.
7. (a) Jones, P. B.; Reynolds, J. L.; Brinson, R. G.; Butke, R. A. *ACS Symp. Ser.* **2003**, *856*, 370–380. (b) Reynolds, J. L.; Erdner, K. R.; Jones, P. B. *Org. Lett.* **2002**, *4*, 917–919.
8. (a) Paul, A.; Mandal, P. K.; Samanta, A. *Chem. Phys. Lett.* **2005**, *402*, 375–379. (b) Ding, J.; Desikan, V.; Han, X. X.; Xiao, T. L.; Ding, R. F.; Jenks, W. S.; Armstrong, D. W. *Org. Lett.* **2005**, *7*, 335–337. (c) Ozawa, R.; Hamaguchi, H. *Chem. Lett.* **2001**, *7*, 736–737. (d) Lee, C.; Winston, T.; Unni, A.; Pagni, R. M.; Mamantov, G. *J. Am. Chem. Soc.* **1996**, *118*,

4919–4924. (e) Muldoon, M. J.; McLean, A. J.; Gordon, C. M.; Dunkin, I. R. *Chem. Commun.* **2001**, 2364–2365. (f) Gordon, C. M.; McLean, A. J.; Muldoon, M. J.; Dunkin, I. R. *ACS Symp. Ser.* **2003**, *856*, 357–369. (g) Gordon, C. M.; McLean, A. J.; Muldoon, M. J.; Dunkin, I. R. *ACS Symp. Ser.* **2003**, *818*, 428–443.

9. Alvaro, M.; Ferrer, B.; Garcia, H.; Narayana, M. *Chem. Phys. Lett.* **2002**, *362*, 435–440.
10. Ramamurthy, V.; Liu, R. S. H. *J. Am. Chem. Soc.* **1976**, *98*, 2935–2942.
11. (a) Zhang, W. Q.; Feng, K. S.; Wu, X. S.; Martin, D.; Neckers, D. C. *J. Org. Chem.* **1999**, *64*, 458–463. (b) Sarker, A. M.; Kaneko, Y.; Neckers, D. C. *J. Photochem. Photobiol.* **1999**, *121*, 83–90.
12. Diels, O.; Alder, K.; Beckmann, S. *Ann.* **1931**, *486*, 191–202.
13. (a) Ciganek, E. *J. Am. Chem. Soc.* **1966**, *88*, 2882–2883. (b) Huelsduenker, A.; Ritter, A.; Demuth, M. *Sol. Therm. Energy Util.* **1992**, *6*, 443–450.
14. Liu, R. S. H.; Hammond, G. S. *J. Am. Chem. Soc.* **1967**, *89*, 4936–4944.