

Photochemical Reactions of α -Terpinene and Acenaphthene under Concentrated Sunlight

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α -Terpinene was successfully dehydrogenated to *p*-cymene in photocatalytic reaction with benzophenone and cupric ions under 40 suns concentrated sunlight irradiation, proving that photodehydrogenation reactions may be employed for the synthesis of fine chemicals under sunlight. Acenaphthene dehydrogenation under concentrated sunlight resulted in the minor formation of acenaphthylene and the quantitative formation of acenaphthenone when the solution was aerated. Stable benzylic-type radical intermediates are thought to lower the yield of dehydrogenation reactions.

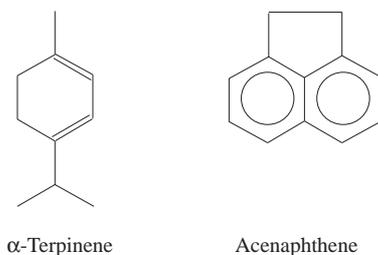
Key Words: Photodehydrogenation, solar irradiation, hydrogen abstraction, benzophenone, α -terpinene, acenaphthene.

Introduction

It is well known that the benzophenone triplet ($n-\pi^*$) excited state has a radical character, similar to alkoxy radicals, and abstracts hydrogen from a suitable donor molecule¹. The primary product of hydrogen abstraction by benzophenone is the ketyl radical and the radical of the hydrogen donor molecule. Secondary dimerisation and/or disproportionation reactions of both radicals result in the formation of products. Kochi has shown that alkyl radicals can be converted to alkenes and ketyl radicals to ketones in the presence of Cu(II) ions². Similarly, Jones et al. have shown that cyclohexane is quantitatively converted to cyclohexene using photoexcited benzophenone in the presence of cupric ions³. The photodehydrogenation of N-alkyl substituted pyrrolidines was reported to occur in low yields under similar conditions but in the absence of cupric ions⁴. Hydrogen evolution from the photolysis of alcohol solutions of benzophenone in the presence of Pt has been presented by Graetzel⁵. Further attempts to produce hydrogen in these benzophenone/Pt photocatalytic systems gave extremely low yields of evolution^{6,7}.

The efficient conversion of abietic acid to dehydroabietic acid follows a similar mechanism⁸, and in this report it was noted that the photodehydrogenation reaction could be accomplished in sunlight. The

radiation intensity of direct sunlight shorter than 400 nm is low. Photodehydrogenation reactions proceeded by excitation benzophenone at 350 nm would proceed at lower yields under direct sunlight in comparison to irradiations with a medium pressure mercury lamp. We now report the successful photocatalytic dehydrogenation reactions of α -terpinene and acenaphthene under concentrated sunlight. These photodehydrogenation reactions may open the route of a novel solar photosynthesis method for fine chemicals.

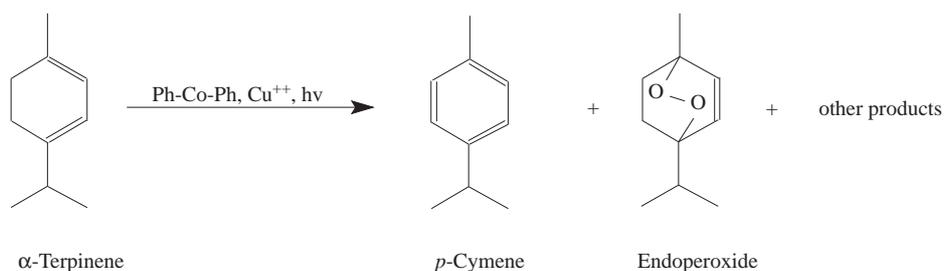


Experimental details

Apparatus and Materials

Irradiations using a HPK 125 W Phillips mercury lamp were carried out using a pyrex reactor fitted with a water-cooled jacket. For the simulation of sunlight under laboratory conditions we used a Philips-son-T plus 400 W sodium lamp (0.2-0.4 sun) in a similar reactor⁹. Concentrated sunlight experiments were performed with a Fix Focus FF 3.5 – HTC GmbH (Germany) instrument with a reflective usable surface reflector area of 2.66 m², covered with a reflective aluminized polymer film, at a focal length of 0.65 m. The intensity of concentrated sunlight was determined as described in the literature⁸. Irradiation intensity was adjusted to vary between 40 and 150 suns at the focal point of the concentrator under experimental conditions. Research-grade α -terpinene and acenaphthene obtained from Aldrich, acetonitrile from Lab-Scan, and chloroform from Fluka were all HPLC grade. Cupric pivalate was prepared by the treatment of pivalic acid with cupric hydroxide. GC-Mass spectrometry analysis was carried out on a Hewlett-Packard 6890 instrument equipped with a mass selective detector and HP-5MS phenyl methyl siloxane capillary column, at an initial temperature of 40°C rising to a maximum temperature of 280°C over 2 h. NMR spectra were recorded on a Jeol 400 spectrometer with tetramethylsilane as an internal standard. IR spectra were obtained using a Perkin-Elmer 1600 spectrometer.

Photodehydrogenation of α -terpinene



Irradiations using mercury and sodium lamps

Reactions were carried out in the pyrex photoreactors using the lamps described above. The photoreactions were monitored using TLC. GC-MS and/or ^1H NMR spectroscopy were used for product analysis.

Medium pressure mercury lamp: α -Terpinene (820 mg, 6 mmol), benzophenone (17 mg, 0.1 mmol) and cupric pivalate (8 mg, 0.03 mmol) were dissolved in 3% v/v CD_3CN in CDCl_3 (25 ml). The blue-green solution was degassed under argon and irradiated for 15 min. Periodically, the reaction was stopped for an aeration/degassing cycle in order for the oxidation of cuprous ions to cupric ions. The ^1H NMR spectrum of the solution after five such cycles showed that the ratio of *p*-cymene to α -terpinene is 97:3, respectively.

Sodium lamp: α -Terpinene (1.67 g, 12 mmol), benzophenone (50 mg, 0.3 mmol) and cupric pivalate (32 mg, 0.12 mmol) were dissolved in acetonitrile (50 mls). The blue-green solution was degassed under nitrogen and irradiated with the 400 W sodium lamp. The GC/MS analysis of the solution following nine such cycles showed that the yield of *p*-cymene is 13.5% with 77.4% unreacted α -terpinene and 9.1% unidentified products.

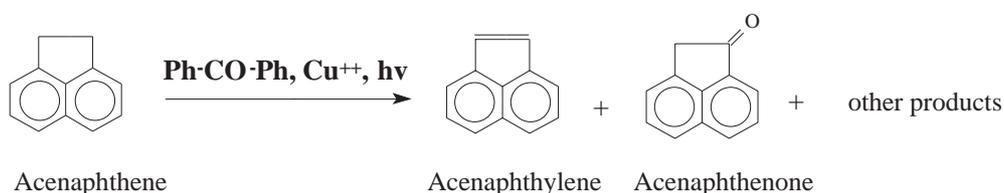
The same experiment was done in CCl_4 solution and the product mixture was analysed at proton NMR. The integral ratios of proton signals revealed that the ratio of *p*-cymene to α -terpinene is about 17:83, respectively.

Concentrated sunlight

The reaction solution of α -terpinene, benzophenone and cupric pivalate was prepared as described above but with CCl_4 as the solvent. The solution was placed in a water-cooled photoreactor at the focal point of the solar collector. The sunlight intensity was 40 suns and this was maintained throughout the reaction. The aeration/degassing cycle was executed eight times for a total irradiation period of 4 h. After this time, the *p*-cymene yield was 46.6% with 27.1% unreacted α -terpinene and 26.3% other products. The α -terpinene and *p*-cymene have retention times less than 9 min and the component eluting at 14.2 min had a molecular ion of 168, which may be attributed to α -terpinene endoperoxide (2.9%). The remaining components have higher molecular weights and may be derived from photooxidation processes.

Integral ratios of proton signals at NMR spectrum revealed that the ratio of *p*-cymene to α -terpinene is about 67:33, respectively.

Photodehydrogenation of acenaphthene



Irradiations of acenaphthene in the presence of benzophenone and cupric pivalate under mercury and sodium lamps, and the analysis of products by GC-MS, showed that acenaphthene remains unreacted in a photolysis medium. Irradiations of acenaphthene in the presence of benzophenone and cupric pivalate yielded products only under concentrated sunlight.

The nitrogen-degassed acenaphthene/benzophenone/cupric pivalate solution was irradiated under 15 suns. The product formation was monitored by TLC with the solvent system hexane to acetone to chloroform (1:0.1:0.1) over a period of 7 d; this represented a total irradiation time of 30 h. GC-MS analysis revealed that 5.0% of the acenaphthalene remained, but that the product (95%) was acenaphthenone. This was confirmed by IR spectroscopy.

Acenaphthenone, $C_{12}H_8O$, GC-MS; detection time at 26.12 min and m/e(natural abundance): 168(100, molecular peak and base peak).

Acenaphthene, $C_{12}H_{10}$, GC-MS; detection time at 21.79 min and m/e(natural abundance): 154(100, molecular peak and base peak).

In a second experiment, the nitrogen-degassed solution of the reactants was irradiated under 110 suns for 7.5 h continuously with no aeration-deaeration cycles. GC-MS analysis revealed that a small amount of acenaphthylene (0.8%) had formed but that 97% of the acenaphthene had not reacted. This experiment was repeated under similar conditions for 15.5 and 20 h which yielded 1.5% and 2.2% acenaphthylene respectively.

Acenaphthylene, $C_{12}H_8$, GC-MS; detection time at 20.19 min and m/e(natural abundance): 152(100, molecular peak and base peak).

Results and Discussion

In the present work we showed that α -terpinene can be dehydrogenated photochemically in high yield to give *p*-cymene under medium-pressure mercury lamp irradiation (Table). Simulated sunlight radiation using a 400 W sodium lamp is also effective but less efficient, giving 13.5% conversion after 4.5 h. The photolysis of α -terpinene is expected to follow the mechanism outlined below. At the end of each cycle the blue-green cupric ions have been converted into yellow-brown cuprous ions. On aeration of the solution, the cuprous ions are oxidised back to cupric ions and benzophenone is reformed from the ketyl radical.

Table. Yields on dehydrogenation photolysis of α -terpinene and acenaphthene under mercury lamp, sodium lamp and concentrated sun light.

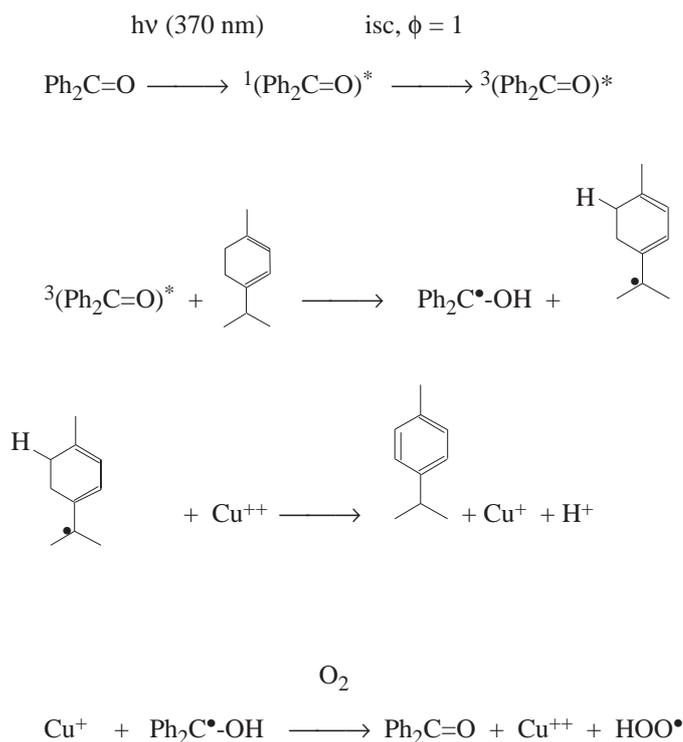
A - Photolysis of α -terpinene

Irradiation Source	Photolysis Period (h)	α -Terpinene	<i>p</i> -Cymene
<i>Mercury Lamp</i>	1	3%	97%
<i>Sodium Lamp</i>	4.5	77.4%	13.5%
Concent. Sunlight 40 suns	4	27.1%	46.6%

B - Photolysis of acenaphthene

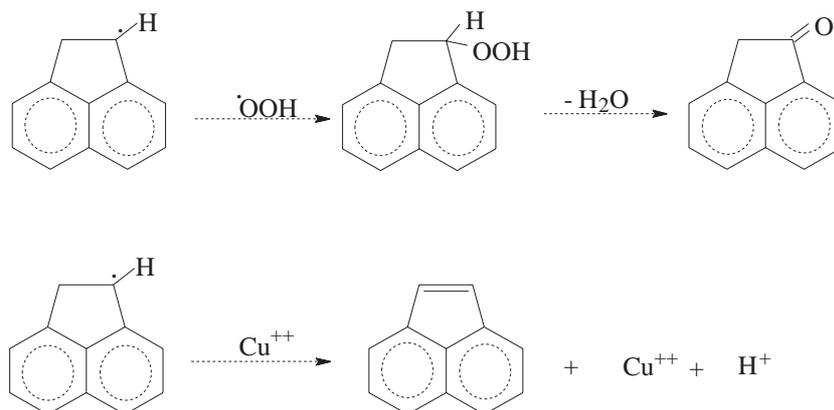
Irradiation Source	Photolysis Period (h)	Acenaphthene	Acenaphthylene	Acenaphthenone
<i>Mercury Lamp</i>	1	100%	-	-
<i>Sodium Lamp</i>	2	100%	-	-
Concent. Sunlight 15 suns	30	5.0%	-	95.0%
Concent. Sunlight 110 suns	7.5*	97%	0.8%	-
Concent. Sunlight 110 suns	15.5*	95%	1.5%	-
Concent. Sunlight 110 suns	20*	89%	2.2%	-

*in the absence of aeration-deaeration steps, continuous irradiation.



The hydroperoxyl radicals formed during the aeration process may contribute to hydrogen abstraction in the second step of the mechanism and may increase the yield of dehydrogenation. Photolysis under concentrated sunlight results in the formation of oxygenated products at a rate of 26.3%; among these one product in 2.9% yield is tentatively identified on GC-MS analysis as α -terpinene endoperoxide. This result indicates that the hydroperoxyl radicals may not only cause the dehydrogenation but also the oxidation reactions. The photodehydrogenation process is initiated by triplet benzophenone abstracting hydrogen from α -terpinene. Direct sunlight and the emission of a sodium lamp have a low intensity at wavelengths shorter than 400 nm, which is the likely cause of lower yield of *p*-cymene formation in these systems. Concentrated sunlight, however, gives much higher yields (46.6%) of *p*-cymene in eight cycles.

It can be seen from the data in Table that α -terpinene is photodehydrogenated to *p*-cymene more easily than acenaphthene to acenaphthylene and/or acenaphthenone since the cyclic allylic radical of α -terpinene formed from hydrogen abstraction by triplet benzophenone readily aromatize to give *p*-cymene¹⁰. Indeed, hydrogen abstraction from the cyclohexadiene radical to give benzene is known to be a highly exothermic reaction^{2,11}. On the other hand, the acenaphthene carbon radical in conjugation with aromatic rings is expected to be more stable than the cyclohexadiene radical, and may not dehydrogenate as readily as α -terpinene. The formation of acenaphthenone in a 95% yield can be explained by the reaction of the stable acenaphthene radical as it reacts readily with hydroperoxyl radicals to give a ketone, rather than undergoing dehydrogenation in the presence of cupric ions. In addition, the five-membered ring in acenaphthene has a steric strain; formation of a new double bond will increase the steric strain. On the other hand, *p*-cymene formation from α -terpinene is a sterically favoured reaction.



The irradiation of acenaphthene in the absence of oxygen for 7.5 h under 110 suns concentrated sunlight gave only 0.8% of acenaphthylene and this was only slightly increased by more prolonged irradiation. In summary, acenaphthene is unreactive to benzophenone photodehydrogenation under short UV and direct solar irradiation, but reacts under concentrated sunlight.

Conclusion

Concentrated sunlight increases the yield of the photodehydrogenation reaction, but also causes the formation of photooxygenated products at the aeration steps, which are required to reform the cupric ions from cuprous ions and the benzophenone from ketyl radicals. Photodehydrogenation reactions under concentrated solar irradiation give good yields with allylic type radicals, but give poorer yields in the presence of benzylic type radicals.

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