Journal of Photochemistry and Photobiology A: Chemistry 141 (2001) 147–151

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.nl/locate/jphotochem

Photosynthesis of rose oxide by concentrated sunlight in the absence of singlet oxygen

Haluk Dincalp, Siddik Içli*

Department of Chemistry, Faculty of Science, Ege University, Bornova, 35100 Izmir, Turkey

Received 22 March 2001; received in revised form 18 April 2001; accepted 20 April 2001

Abstract

Rose oxide was photosynthesized in aerated acetonitrile solutions from citronellol via aromatic diimide (dehydroabietyl perylene diimide and *n*-butyl naphthalene diimide (BUNAP)) singlet photosensitizers under sodium light (0.2–0.4 sun) and concentrated sun light (90–100 sun). The yield of formation of rose oxide is high by concentrated sun light, with respect to sodium light irradiation. It was shown that, (I) super oxide anion radical results in the production of rose oxide from citronellol as seen previously with singlet oxygen; (II) photo- and thermal-stable aromatic diimides are capable of producing rose oxide in high yield by 100-fold concentrated sun light conditions. The addition of cupric and ferric ions to acetonitrile solutions lowered the yield of rose oxide formation. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Super oxide anion radical; Perylene diimide; Naphthalene diimide; Solar concentrator

---

1. Introduction

The production of fine chemicals under sun light is a prospective goal for photochemical applications. Photosynthesis, by direct sun light, is unreliable because of the short duration of effective sun light and the unpredictable and rare occasions of clear skies. Photochemical processes proceed faster by concentrated sun light, but only inorganic photosensitizers are known to be photostable for applications at high intensities of solar radiation [1]. On the other hand, there are numerous photosynthesis of fine organic chemicals by photooxidations, which are accomplished by employing organic photosensitizers under laboratory conditions. These photosensitizers (i.e. rose bengal, methylene blue, eosine, fluoresine, etc.) degrade readily by direct and/or concentrated sun light.

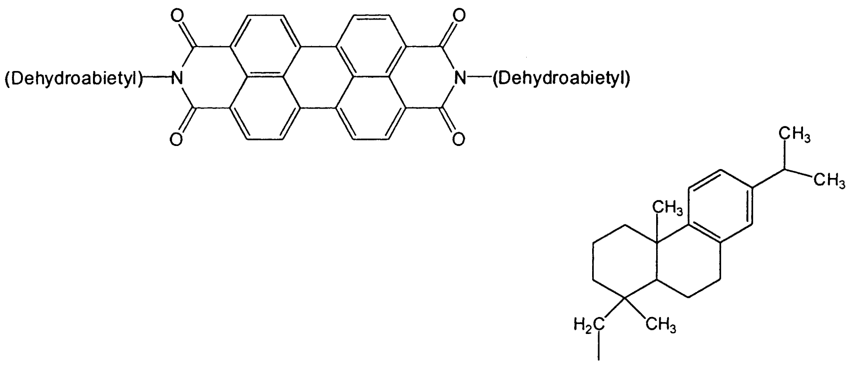
It is well known that rose oxide, a valuable perfume additive, was first photosynthesized from citronellol under visible light by Schenk et al. [2]. This is a singlet oxygen photooxidation reaction in the presence of rose bengal, which is a triplet photosensitizer. Hydroperoxides, formed by the so-called ene reaction of singlet oxygen in methanol solution, are reduced to diols with sodium sulfite, the resulting diols are converted to an isomeric rose oxide mixture upon heating in acidified solution. Numerous authors have repeated and studied this reaction with other triplet sensitizers, such as methylene blue, thionine, and pyrene under visible light from lamps [3–6]. These reports have pointed out that the application of artificial light sources, or even direct sunlight are insufficient for the scales required for an industrial photochemical production of rose oxide. Scharf first reported an increased rate of photoproduction of rose oxide by concentrated sunlight, 10–100 sun, employing various triplet sensitizers, such as fluorescein, eosine, erythrocyte B, rose bengal, phenothiazine, methylene blue and porphirines, in numerous organic solvents [7,8]. All of the organic triplet photosensitizers used were observed to be unstable by concentrated sunlight, and therefore the additional of fresh sensitizer was required during the reaction. This obligation, during the course of the reaction, is disadvantageous for a bulk production of this perfume additive. This high rate of consumption of the pigment results in problems during purification.

We report here a novel photooxidation reaction of citronellol, under sodium lamp irradiation and by concentrated sunlight by the use of aromatic diimides, which are singlet photosensitizers. This novel method resulted allowed the bulk production of rose oxide in the absence of pigment impurities. Perylene diimides and naphthalene diimides are known to be extremely stable under solar irradiations and their singlet excited state processes result in the production of super oxide anion radical as the only transient oxidant, which mediates the photooxidations [9,10,11].

---

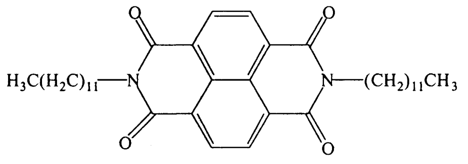
* Corresponding author. Tel.: +90-2323884000; fax: +90-2323888264.
E-mail address: icli@bornova.ege.edu.tr (S. Içli).

PII: S1010-6030(01)00457-9



Dehydroabietyl

N,N'-di-Dehydroabietyl perylene diimide - ABIPER



N,N'-di(n-Butyl) naphthalene diimide

2. Experimental details

2.1. Materials

A water cooled pyrex photoreactor equipped with a Philips-son-T plus-400 W sodium lamp was used for simulation of sun light (0.2–0.4 sun) under laboratory conditions, as described earlier [1]. Concentrated sunlight experiments were performed using a Fix Focus FF 3.5, HTC GmbH (Germany) instrument with a reflective usable surface reflector area of 2.66 m^2, covered with a reflective aluminized polymer film, at focal length of 0.65 m [1]. The intensity of concentrated sun light was determined by using Vilbert Loumart radiometers at 254 and 312 nm radiation wavelengths, and comparing the measured intensities with the intensity of direct sunlight (1 sun) using same radiometers. Irradiation intensity was adjusted to vary between 90 and 100 sun at the focal point of the concentrator under experiment conditions. The radiation intensity striking the sample was measured before and after each experiment. In order to compare results, the irradiation intensity was kept between 90 and 100 sun by adjustments at the focal point of the solar concentrator.

The intensity of the radiation emitted by the 400 W Philips sodium lamp source was also measured using Vilbert Loumart radiometers, at 312 and 365 nm radiation wavelengths, and the measured intensities were compared to direct sunlight (1 sun). The effective radiation intensity striking the cylindrical glass photoreactor was found to be about 0.2 sun at 4 cm distance between photoreactor and 400 W sodium lamp. Concentrated sun light experiments were done during the months of April–November, and between 11.00 and 15.00 h. Aeration in photoreactor was accomplished by using of a small aquarium pump. *n*-Dehydroabietyl perylene bis-diimide (ABIPER) and *n*-butyl naphthalene bis-diimide (BUNAP) were synthesized as described [9,10]. Both of these compounds have the highest solubilities in acetonitrile solutions with respect to other perylene and naphthalene diimide derivatives. Acetonitrile (Lab-Scan) and chloroform (Fluca) were both HPLC grade. Cupric pivalate was prepared by the treatment of pivalic acid with cupric hydroxide, and ferric myristate by the treatment of myristic acid with ferric hydroxide. All other chemicals (HCl, H_2SO_4, anhydrous $CaCl_2$, Na_2SO_3, ethyl acetate, *n*-hexane) were used as received.

Distilled water was used for the preparation of all solutions. GC-Mass spectrometry analysis were done using an HP 6890 instrument equipped with a mass selective detector and HP-5MS phenyl methyl siloxane capillary column, at an initial oven temperature of 40°C and maximum temperature of 280°C, at 6.5 psi pressure. (−)-Citronellol, (−)*cis* and (−)*trans*-rose oxide isomers, and the diols (2,6-dimethyl-2-octene-2,8-diol and 2,6-dimethyl-2-octene-4,6-diol) were detected via mass spectra by the observation of their characteristic molecular ions as shown below

Citronellol, detection time; 16–17 min and *m*/*e* (natural abundance): 156 (5, mp); 138 (10); 123 (25); 109 (20); 95 (40); 81 and 82 (50); 69 (100, bp).

Rose oxide, detection time; 13–14 min and *m*/*e* (natural abundance): 154 (10, mp); 140 (15); 139 (100, bp); 97 (5); 83 (20); 69 (45).

Diols, detection time; 19–24 min and *m*/*e* (natural abundance): 172 (2, mp); 154 (4); 139 (8); 121 (5); 111 (6); 99 (9); 86 (15); 71 (100, bp); 69 (35); 55 (35).

Some photolysis reactions shown additional products at ratios of 1–12% of the total detected mass at detection time ranging from 22 to 26 min. Analysis of the mass spectra for these products did not reveal the molecular structures of these compounds.

2.2. Solar irradiations

Solar irradiations in the photoreactor under sodium lamp and by concentrated sun light were done under similar conditions as described below. The duration of photolysis times were determined by examining the decrease of citronellol and increase of product formation via thin layer chromatography, during the course of the reaction.

2.2.1. Experiment conditions:

About 1–2 mg of the photosensitizers ABIPER or BUNAP were dissolved in 100 ml acetonitrile ($\sim 10^{-5}$ M), the color of the resulting solutions were light bright orange. If 2–5 mg cupric pivalate was added the color of the solution changed to blue-green, if 2–5 mg ferric myristate was added the color changed to dark orange-brown. (−)-Citronellol, 3.65 ml (0.02 mol) was added to these solutions, and then poured into the photoreactor. The reaction products were analyzed during photolysis with sodium lamp or concentrated sun light (see Section 2.2). Following the photolysis, the photolysis solutions were mixed with sodium sulfite, 6.30 g per 100 ml water. The mixture was stirred at room temperature for 6 h and the products were extracted with chloroform. The chloroform phase was dried over anhydrous $CaCl_2$, acidified, and stirred at room temperature overnight.

3. Results and discussions

3.1. Irradiations under sodium lamp

It was shown earlier that a 400 W sodium lamp light is an efficient simulator for direct solar irradiation. Irradiation of citronellol in the presence of ABIPER under sodium light for 14 h resulted in the nearly complete reaction of (−)-citronellol and the formation of both (−)*cis* and (−)*trans*-rose oxide isomers (53.4 and 25.6%) and the diols (20.1%) as the major products, determined by GC–MS analysis (Table 1). Singlet oxygen photooxidations of citronellol are reported to present similar ratios of formation of rose oxide and the diols [2–6]. This work alone proves that the perylene diimide, which produces only super oxide anion radical under photolysis, is capable of formation of rose oxide in absence of singlet oxygen. Scheme below outlines the mechanism of formation rose oxide The photolysis mechanism is similar to that deduced for photooxidation of α-terpinene with phenyl perylene diimide [11]. Hydroperoxyl products, as found in singlet oxygen photooxidations, are reduced to alcohols by sodium sulfide and the acidification resulted in production of rose oxide.

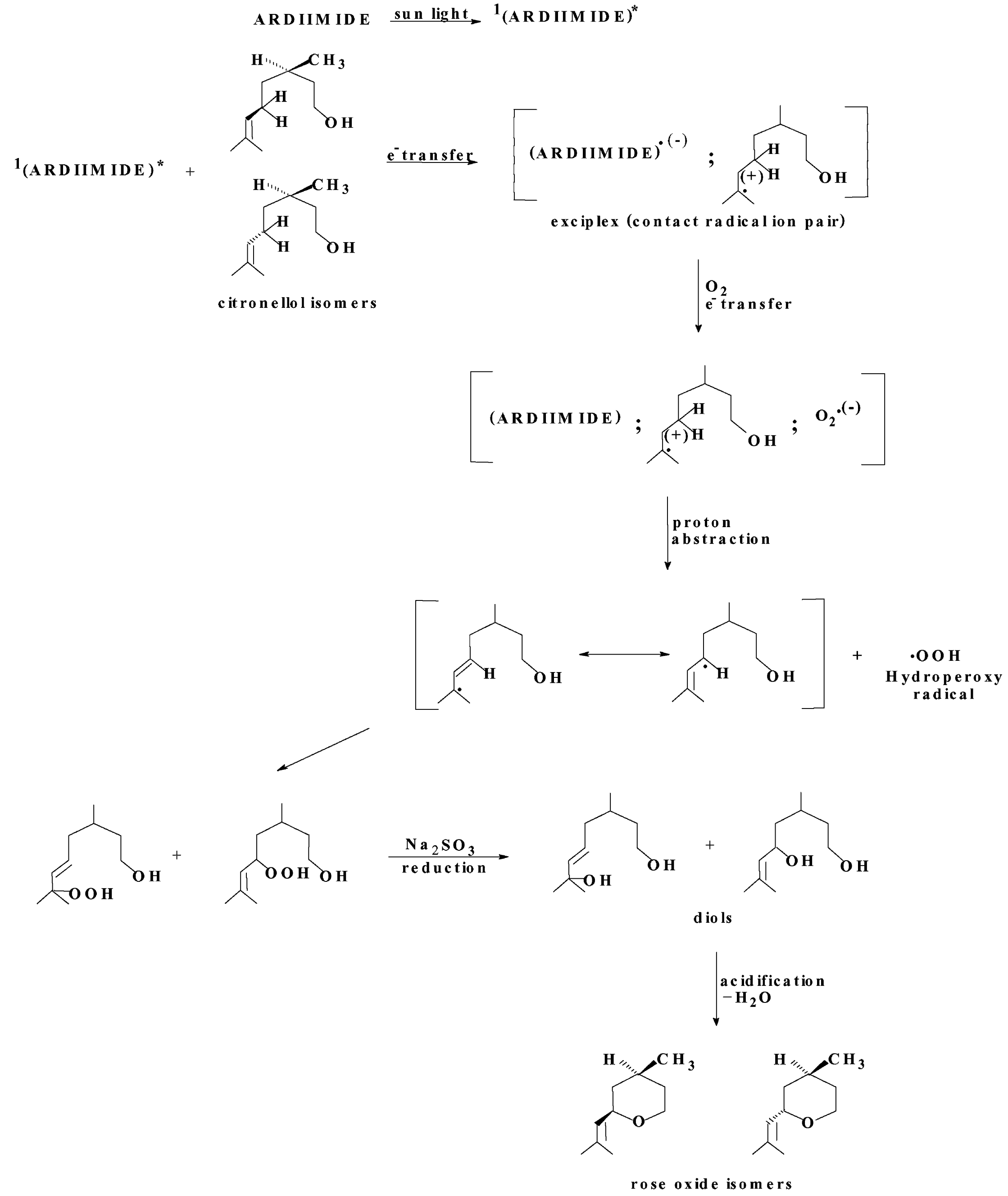
Sodium lamp photooxidation of citronellol in presence of BUNAP yielded total of 19.4% ratio of rose oxide isomers after 38 h of irradiation (Table 1). The naphthalene diimides only absorb at or below 377 nm wavelength, in contrast to visible range absorption of perylene diimides (480–530 nm). It is expected that BUNAP is unable to produce the super oxide anion radical intermediate in sufficient concentration under sodium lamp irradiation. The intensity of the radiation below 400 nm is very low by direct sun light and under sodium lamp.

3.2. Irradiations by concentrated sun light

Irradiation of citronellol in presence of ABIPER by concentrated sun light of 90–100 sun resulted in a higher yield of rose oxide formation with respect to sodium lamp irradiation, as expected. Rose oxide *cis* and *trans* isomers are found to form in total of 82.2% yield after only 2 h of irradiation (Table 1). The initial concentration ABIPER was 10–20 ppm, and during irradiations no additional perylene diimide was added. The colour of the solution did not fade during this time either. This result proves that the perylene diimide photosensitizer has remarkable stability by 100-fold concentrated sun light and is an excellent photo-

Table 1
Yields in % ratios of (−)-citronellol, (−)*cis* and (−)*trans*-rose oxide isomers and diols by GC–MS analysis after photolysis of (−)-citronellolol in acetonitrile solution in the presence of (A) dehydroabietyl perylene diimide, ABIPER and (B) BUNAP photosensitizers

Irradiation source	Photolysis period (h)	Rosexide (%) (−)*cis* and (−)*trans*	Diols (%)	(−)-Citronellol (%)
(A) Photosensitizer, ABIPER				
Sodium lamp	14	53.4; 25.6	20.1	0.8
Concentrated sun light	0.5	2.8; 0.1	5.0	88.6
Concentrated sun light	1.0	32.5; 15.0	16.4	20.0
Concentrated sun light	2.0	76.0; 6.2	5.9	3.2
(B) Photosensitizer, BUNAP				
Sodium lamp	38	11.4; 8.0	36.7	28.0
Concentrated sun light	0.25	8.0; 5.2	6.5	78.8
Concentrated sun light	0.50	37.5; 16.1	12.8	29.6
Concentrated sun light	1.0	53.9; 23.1	19.6	0.7



Scheme 1.

catalyst for the solar photosynthesis of bulk amounts of fine chemicals.

Another remarkable result is observed when ABIPER is replaced by BUNAP. Naphthalene diimide is seen to produce rose oxide *cis* and *trans* isomers, in total of 77% yield, by 1 h of concentrated sun light (90–100 sun) which is comparable to the yield obtained with perylene diimide, under the same conditions. Only the optical purity of the rose oxide isomers was seen to differ; in the case of ABIPER, 76.0/6.2, with respect to BUNAP, 53.9/23. (Table 1). It is difficult to explain the different ratios of isomers with ABIPER and BUNAP. It may be that one isomer is sterically preferred in contact radical ion pair forms with ABIPER (see Scheme 1). As reported earlier, our concentrated sun light equipment has an aluminium reflection mirror which reflects the solar radiation below 400 nm. BUNAP is expected to absorb irradiation in sufficient amount to catalyze the reaction when the sun light is concentrated 90–100 times. A similar observation by concentrated sun light was detected for ZnO [1]. Naphthalene diimides are non-fluorescent compared to perylene diimides, but the photooxidation mechanism is shown to be same [10]. Naphthalene diimides are as stable as the

Table 2
Yields in % ratios of (−)-citronellol, (−)*cis* and (−)*trans*-rose oxide isomers and diols by GC–MS analysis after photolysis of (−)-citronellolol in acetonitrile solution in presence of (A) dehydroabietyl perylene diimide, ABIPER/cupric pivalate and (B) dehydroabietyl perylene diimide, ABIPER/ferric myristate photosensitizer mixtures

Irradiation source	Photolysis period (h)	Rosexide (%) (−)*cis* and (−)*trans*	Diols (%)	(−)-Citronellol (%)
(A) Photosensitizer, ABIPER/Cu^{2+}				
Concentrated sun light	0.5	7.8; 3.1	1.4	84.2
Concentrated sun light	1.0	9.2; 3.2	1.2	83.8
Concentrated sun light	2.0	11.2; 4.9	2.0	81.1
(B) Photosensitizer, ABIPER/Fe^{3+}				
Concentrated sun light	0.5	11.1; 0.8	3.9	79.7
Concentrated sun light	1.0	22.1; 4.1	10.0	58.6
Concentrated sun light	2.0	53.4; 5.8	4.6	35.7

perylene diimides by concentrated sun light, but less toxic and probably also less expensive to synthesize. These properties may make for the use of naphthalene diimides in solar photosynthesis applications by concentrated sun light conditions more advantageous compared to the perylene diimides.

3.3. Irradiations by concentrated sun light in presence of Cu^{2+} and Fe^{3+}

It has reported earlier that aromatic diimides in the presence of cupric, Cu^{2+}, and ferric, Fe^{3+}, ions photooxidize olefinic substrates in better yields, compared to aromatic diimides alone [9,10]. To study this we have photooxidized citronellol with ABIPER in the presence of cupric and ferric ions. 20–50 ppm of cupric pivalate or ferric myristate was added to the citronellol/ABIPER solutions in acetonitrile. Photolysis was carried out by concentrated sun light under identical conditions. The results are seen in Table 2. Cupric ions/ABIPER gave a low yield of formation of rose oxide isomers (total 16.1%), and more than 80% of the citronellol starting material remained unreacted after 2 h of irradiation under 90–10 sun. The ferric ion/ABIPER combination gave a better yield of rose oxide isomers (total 59.2%), but 35.7% of the citronellol starting material remained after 2 h of irradiation under 90–10 sun. These results are in contrast to increased yield of formation of benzaldehyde from styrene from aromatic diimides in the presence of cupric or ferric ions [10]. The differences between the structures of styrene and citronellol, such as presence of hydroxyl groups in citronellol, may have caused conflicting results on photooxidation. The aromatic diimides, ABIPER or BUNAP, alone, are seen to be the best photosensitizers to produce rose oxide by concentrated sun light.

4. Conclusion

The formation of the fine chemical rose oxide, a valuable perfume additive, from citronellol by concentrated sun light in the presence of catalytic amounts of aromatic diimide photosensitizers introduces a novel era of solar chemical production. The application of this photooxidation method to other terpenes (i.e. α-pinene, β-pinene, etc.), and olefinic structures could result in the production of other fine chemicals by concentrated sun light and may create a profitable method for the use solar energy.

Acknowledgements

We thank to Alexander von Humboldt Foundation (AvH) for providing Symposium presentation support. We acknowledge the project support funds provided by the Research Center of Ege University (EBILTEM), the State Planning Organization of Turkey (DPT) and the Scientific Research Council of Turkey (TUBITAK). We are also indebted to Mr. Robert Stackow for his work on this manuscript and to Miss Deniz Ungor for GC–MS spectra measurements.

References

[1] B. Dindar, S. Icli, J. Photochem. Photobiol.: A Chem. 140 (2001) 263.

[2] G. Ohloff, E. Klein, G.O. Schenk, Angew. Chem. 73 (1961) 78.

[3] M.G. Casarotto, G.J. Smith, J. Photochem. Photobiol.: A Chem. 40 (1987) 87.

[4] R.S. Davidson, J.E. Pratt, Tetrahedron Lett. 23 (36) (1982) 3729.

[5] R.S. Davidson, J.E. Pratt, Tetrahedron 46 (1984) 999.

[6] M. El Bouamri, J.P. Gorrichon, A.M. Braun, E. Oliveros, J. Photochem. Photobiol.: A Chem. 54 (1991) 619.

[7] H.-D. Scharf, E. Esser, W. Kuhn, R. Pelzer, US Patent 5,620,569 (1997) Processes for the photooxidation of terpene olefins, Haarman & Reimer GmbH, 15 April 1997.

[8] B. Pohlmann, H.D. Scharf, U. Jarolimek, P. Mauermann, Solar Energy 61 (1997) 159.

[9] S. Icli, S. Demiç, B. Dindar, A.O. Doroshenko, C. Timur, J. Photochem. Photobiol: A Chem. 136 (1-2) (2000) 15.

[10] S. Alp, S. Erten, C. Karapire, B. Köz, A.O. Doroshenko, S. Içli, J. Photochem. Photobiol: A Chem. 135 (23) (2000) 103.

[11] L. Chen, L.A. Lucia, E.R. Gaillard, H. Icil, S. Icli, D.G. Whitten, J. Phys. Chem. A102 (1998) 9095.