Tetrahedron Letters, Vol.31, No.11, pp 1563-1566, 1990
Printed in Great Britain

0040-4039/90 $3.00 + .00
Pergamon Press plc

PHOTOLYSIS OF 1,4-DIPROPYLBENZOBICYCLO[2.2.2]OCT-5-ENE-2,3-DIONE. INTERMEDIACY OF 1,4-DIPROPYL-2,3-DIHYDRONAPHTHALENE

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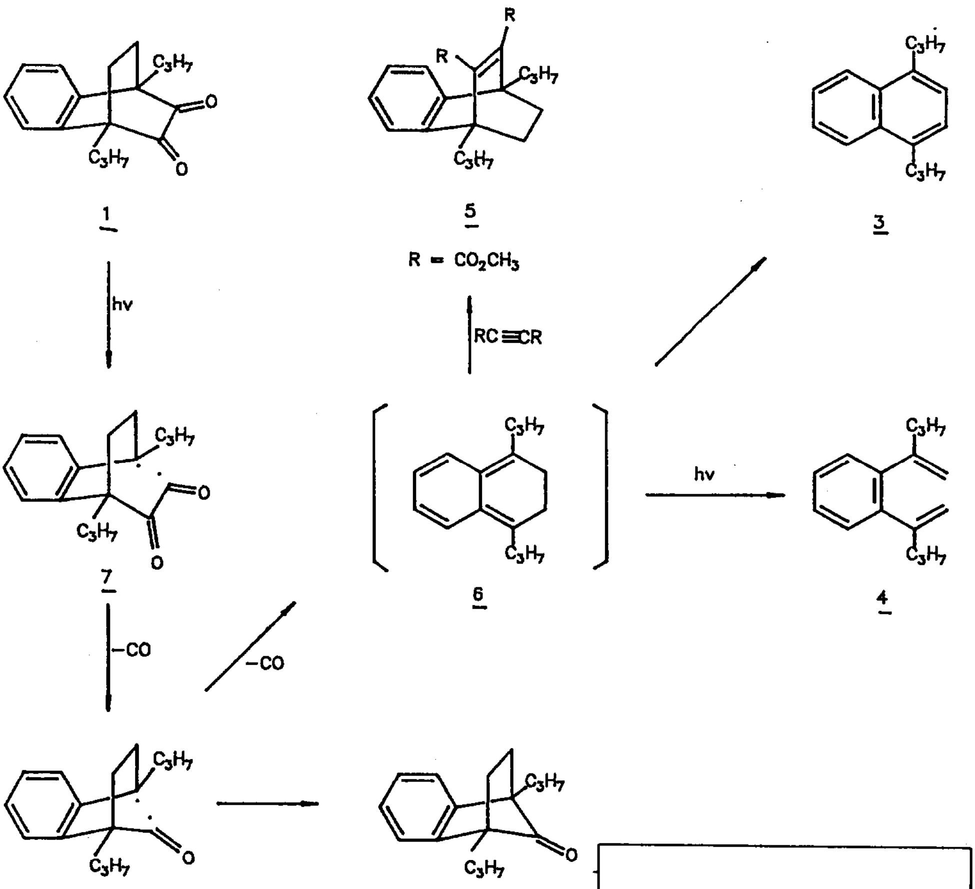
Abstract: The title α-diketone (1) was irradiated (λ>340 nm) in a degassed benzene solution to afford a bicyclic ketone (2), 1,4-dipropylnaphthalene (3), and *o*-divinylbenzene (4); 1,4-dipropyl-2,3-dihydronaphthalene (6) being an intermediate which was trapped with dimethyl acetylenedicarboxylate to give the Diels-Alder adduct (5), and characterized by its visible absorption spectrum and its ^{1}H nmr signals.

o-Quinodimethanes,[1] also called *o*-xylylenes, which are reactive intermediates have been extensively investigated from theoretical[2], physical organic[2,3] and synthetic[1b,4] viewpoints since first suggested by Cava[5] in 1957. 2,3-Dihydronaphthalenes which are cyclic *o*-quinodimethanes have however received less attention. Although they have been trapped in some cases by dienophiles to yield benzobicyclo[2.2.2]octane derivatives[1c,6], their characterization has been only limited to some sterically stabilized systems, such as 1,2,3,4,4a,9a-hexahydro-*N*-methyl-9,10-diphenylanthracene-4a,9a-dicarboximide.[7] Among a variety of methods, the extrusion reactions involving the loss of small molecules such as N_2, CO, and SO_2 from cyclic systems are often used for the generation of *o*-quinodimethanes.[1a,1b] Warrener[8] has reported that the photolysis of benzobicyclo-[2.2.1]hepten-2,3-diones gives isoindenes as intermediates. During the course of our continuing interest in studying the photochemistry of α-diketones[9], we have examined the photolysis of 1,4-dipropylbenzobicyclo[2.2.2]oct-5-ene-2,3-dione, 1 and wish to report herewith the results.

α-Diketone 1 was prepared by the Diels-Alder reaction of 3,6-dipropyl-*o*-benzoquinone[10] with benzyne prepared in situ[11] followed by catalytic hydrogenation of the adduct. Irradiation (λ>340 nm, a Hanovia medium pressure mercury lamp through a uranium glass filter) of a carefully degassed (three freeze-pump-thaw cycles) benzene solution (6.67×10^{-3}M) of 1 afforded a colorless mixture containing the bicyclic ketone 2[12] (23%), 1,4-dipropylnaphthalene 3[13] (5%), and *o*-divinylbenzene 4 (70%) based on ^{1}H nmr (400 MHz) analysis. The products were separated by silica gel column chromatography and repeated thin layer chromatography on silica gel impregnated with 5% silver nitrate, and their structures were established by their spectroscopic data. The increase in the yield of 3 was accompanied with the decrease in that of 4 when the degassing was not thorough. When irradiation of 1 was carried out in the presence of dimethyl acetylenedicarboxylate in benzene, the Diels-Alder adduct 5 was isolated in a 32% yield after chromatography. The formation of 5 revealed the intermediacy of 1,4-dipropyl-2,3-dihydronaphthalene 6.



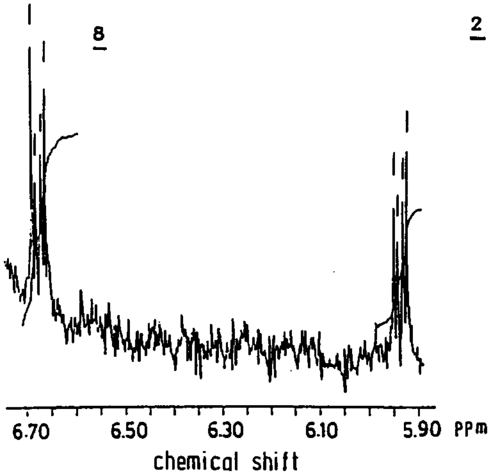


Figure 1. The ^{1}H nmr spectrum of the olefinic protons of 6.

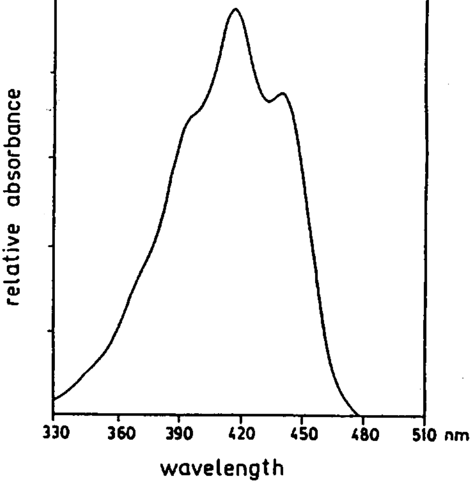


Figure 2. The visible absorption spectrum of 6.

Attempt to isolate 6 was not successful because it was readily oxidized, but it could be detected by means of ^1H nmr and visible absorption spectra. Very weak signals of AA'BB' pattern centered at δ 5.93 and 6.68 ppm (Figure 1) attributed to the olefinic protons[14] in 6 were observed when the irradiation (457.9 nm Ar^+ laser) in C_6D_6 solution ($4.32\times10^{-2}M$) was followed by ^1H nmr (400 MHz) analysis. As both 1 and 6 absorb visible light in about the same region, the visible spectrum of 6 was obtained in the following manner. A benzene solution of 1 ($4.89\times10^{-3}M$) sealed in a pyrex cuvette was irradiated (λ=470 nm, from a 1000 W mercury-xenon lamp and isolated with a monochromator) for a period of time and monitored by visible absorption spectra. The final irradiated solution was then allowed to contact with air and the spectrum was measured. Since 6 decolorized in contact with air, the balance between the spectra before and after contact with air gave the visible spectrum of 6 as shown in Figure 2. The spectrum is similar to those of other o-quinodimethanes.[3a,3b,15] In separate studies, visible spectral analysis indicated that 2,3-dihydronaphthalene 6 was quite stable in the absence of air on heating at ca. 46°C in the dark, but was readily decolorized photochemically, presumably leading to the formation of 4. It is not clear at the present stage whether the formation of 3 takes place via the oxidation of 6 by a trace amount of oxygen in the irradiated system or via other dehydrogenation process.

Based on the above experimental facts, a plausible working hypothesis to account for the formation of the products from photolysis of 1 is depicted in the scheme. Norrish type I cleavage of the excited state of 1 generates diradical 7 which loses subsequently a molecule of carbon monoxide to give diradical 8. The latter diradical may undergo either ring closure to produce 2 or extrusion of another molecule of carbon monoxide to yield 6 which may subsequently undergo photochemical electrocyclic transformation in a conrotatory mode to afford 4.

Acknowledgement: The financial support of this research work by the National Science Council of the Republic of China is gratefully acknowledged.

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(Received in Japan 4 January 1990)