CHEMISTRY LETTERS, pp. 29-32, 1974. Published by the Chemical Society of Japan

PHOTOCHEMISTRY OF 1,2-DIPHENYLCYCLOBUTENE IN PROTIC SOLVENTS

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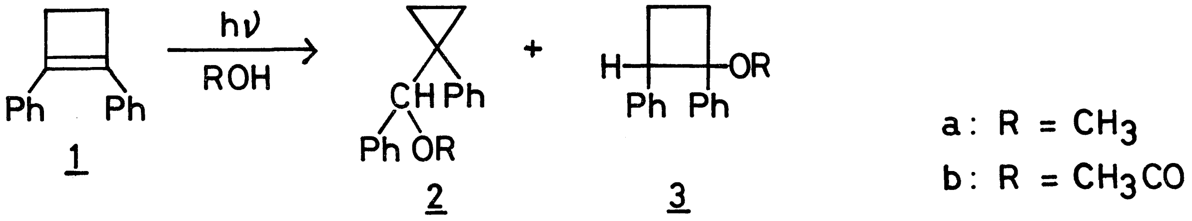
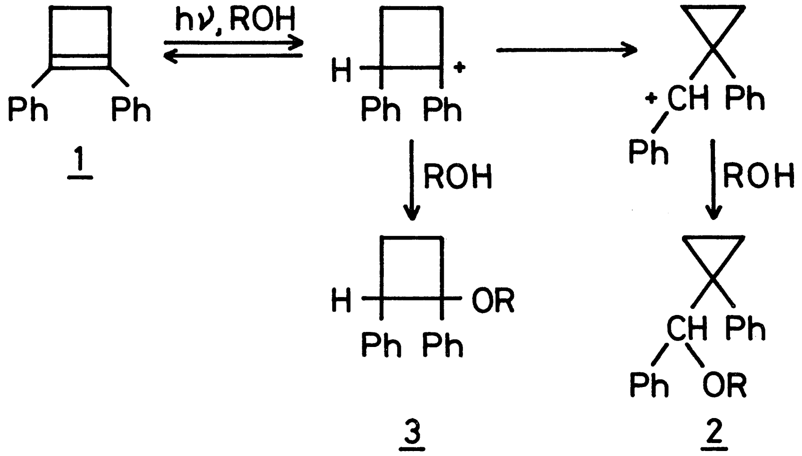
Irradiation of 1,2-diphenylcyclobutene (1) in methanol solution afforded a mixture of α-(1-phenylcyclopropyl)benzyl methyl ether and 1,2-diphenylcyclobutyl methyl ether. In acetic acid corresponding esters were obtained. Evidence supporting the involvement of a singlet species was obtained by the finding that the fluorescence of 1 is substantially quenched on addition of methanol to the solution of 1 in *n*-hexane.

Photochemical ionic additions to cycloolefins have been extensively studied in recent years, but only cyclohexenes, cycloheptenes, and cyclooctenes have been reported as reacting cycloolefins.[1] We wish to report here a photochemical ionic addition to cyclobutene, in which the rearrangement from a cyclobutyl cation to a cyclopropylmethyl cation is probably involved, and to present evidence that this addition reaction occurs exclusively by way of the singlet state in sharp contrast to the case of the cycloolefins described above.

A solution of 1,2-diphenylcyclobutene[2] (1, 5×10^{-5} M) in methanol, ethanol or acetic acid was irradiated with 330 nm light using a JASCO CRM-FA Spectro Irradiator. The uv bands of 1 at 227 and 297 nm decreased in intensity during irradiation. A typical example is shown for methanol in Figure 1. Three isosbestic points maintained their positions during the reaction, suggesting that this reaction is straightforward. In order to obtain reaction products, 1 (300 mg) in methanol (200 ml) was irradiated by a 500 W xenon lamp through a filter (Corning glass filter 0-54) for 18 hours. The reaction mixture was chromatographed over silica gel, and a colorless liquid (2a, bp ca. 270°, 26%), a white crystalline solid (3a, mp 91.5 - 92°, 15%), and 1 (40%) were obtained. 2a and 3a were deduced to be α-(1-phenylcyclopropyl)benzyl methyl ether and 1,2-diphenylcyclobutyl methyl ether from satisfactory elemental analyses and spectral data, respectively.[3] Similarly irradiation of 1 (2.0 g) in acetic acid (200 ml) afforded α-(1-phenylcyclopropyl)benzyl acetate (2b, bp ca. 300°, 12%) and 1,2-diphenylcyclobutyl acetate (3b, bp ca. 235°, 34%). The structure of 2b and 3b was established by satisfactory elemental analyses and spectral data.[4)] The possibility that 2 and 3 could have arisen from 1 nonphotochemically was eliminated by standing a solution of 1 in methanol or acetic acid in the dark for 3 days.



The formation of 2 as well as 3 from 1 suggests that these products arise from an initial photoprotonation of 1 to form the cyclobutyl cation which in turn undergoes three competing reactions: (a) nucleophilic capture by solvent to afford 3, (b) skeletal rearrangement to the cyclopropylmethyl cation, which is captured by solvent to afford 2, (c) deprotonation to regenerate the starting olefin 1.



A bicyclobutonium cation is proposed as an intermediate in the deamination of cyclobutylamine and cyclopropanemethylamine giving rise to the same mixture of cyclobutanol and cyclopropanemethanol in each case, but in the photochemical addition to the cyclobutene there is no need to postulate the nonclassical cation.

It has been suggested that photosensitized ionic additions to cycloolefins proceed through the cycloolefin triplet or a highly strained trans-cycloolefin derived from it.[1)] However, the fluorescence quantum yield of 1 has been reported to be as high as about unity,[2b)] suggesting that the initial protonation arises from the excited singlet state of 1. Evidence supporting the involvement of a singlet species was obtained by the finding that the fluorescence of 1 is substantially quenched on addition of methanol to the solution of 1 in *n*-hexane. Thus, the fluorescence intensity of 1 (5×10^{-5} M) was measured in the presence of various concentrations of methanol (0.0 - 0.76 M) in *n*-hexane solution using a Hitachi MPF-2A fluorescence spectrophotometer. There is no change in the emission maximum or in the shape of the emission curve, thus ruling out the possibility of exciplex fluorescence.

Plots of the ratio I_0/I against methanol concentration $[Q]$ fit the Stern-Volmer equation (1), where I_0 and I mean the fluorescence intensity of 1 in the absence and

$$I_0/I = 1 + k_q\tau_0[Q] \qquad (1)$$

in the presence of methanol in concentration of $[Q]$, respectively; k_q is the rate constant for the quenching by methanol; τ_0 is the fluorescence lifetime of 1 in the absence of methanol. The $k_q\tau_0$ value obtained from the slope of these plots is 0.43. τ_0 has been reported to be shorter than 5 nsec,2b) therefore, k_q value is larger than 8×10^7 $M^{-1}sec^{-1}$, probably about 10^8 $M^{-1}sec^{-1}$.

As far as we are aware, this presents the first example of photochemical ionic addition to the rigid cyclobutene system, which occurs exclusively by way of the singlet state. It has been recently reported that 2-phenyl-2-norbornene and 2-phenyl-2-bornene undergo photoprotonation on irradiation in methanol, further the photoreaction appears to occur *via* a singlet.5) The photochemical ionic addition to these rigid norbornenes bears a strong resemblance to that to 1,2-diphenylcyclobutene.

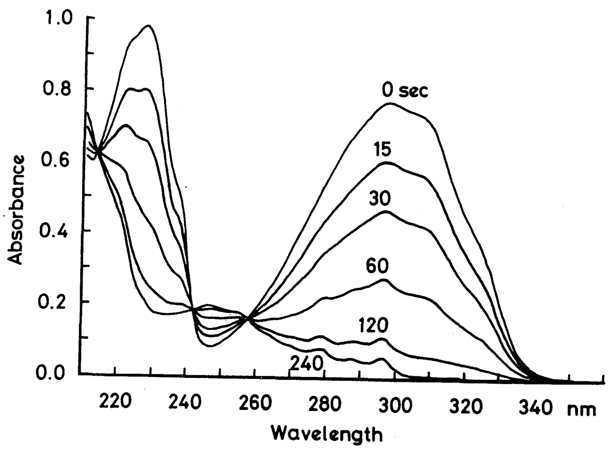


Figure 1. Spectral change of a solution of 1,2-diphenylcyclobutene in methanol (4×10^{-5} M) during irradiation with 330 nm light.

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2) In nonpolar solvents 1,2-diphenylcyclobutene is known to dimerize by way of the singlet state upon irradiation: a) E. H. White and J. P. Anhalt, Tetrahedron Lett., 3937 (1965); b) C. D. DeBoer and R. H. Schlessinger, J. Amer. Chem. Soc., 90, 803 (1968).

3) 2a. Elemental analysis: C, 85.47%; H, 7.44% (calcd. for $C_{17}H_{18}O$: C, 85.67%; H, 7.61%). Infrared: 1090 cm^{-1}. Nmr ($CDCl_3$): τ 2.6 - 3.2 (m, 10H, aromatic), τ 5.98 (s, 1H, $\text{H-}\overset{|}{\underset{|}{\text{C}}}\text{-}$), τ 6.78 (s, 3H, $-OCH_3$), τ 8.85 - 9.35 (m, 4H, $\overset{\wedge}{CH_2CH_2}$).

3a. Gas chromatographic and nmr data show that 3a consists of only one isomer, but the configuration of 3a has not been established. Elemental analysis: C, 86.09%; H, 7.54% (calcd. for $C_{17}H_{18}O$: C, 85.67%; H, 7.61%). Infrared: 1080 cm^{-1}. Nmr ($CDCl_3$): τ 2.7 - 3.4 (m, 10H, aromatic), τ 5.95 - 6.35 (m, 1H, $\text{H-}\overset{|}{\underset{|}{\text{C}}}\text{-}$), τ 7.07 (s, 3H, $-OCH_3$), τ 7.2 - 8.3 (m, 4H, $-CH_2CH_2-$).

4) 2b. Elemental analysis: C, 81.17% H, 6.74% (calcd. for $C_{18}H_{18}O_2$: C, 81.17%; H, 6.81%). Infrared: 1740, 1240 cm^{-1}. Nmr (CCl_4): τ 2.8 - 3.4 (m, 10H, aromatic), τ 4.60 (s, 1H, $\text{H-}\overset{|}{\underset{|}{\text{C}}}\text{-}$), τ 8.05 (s, 3H, $-OCOCH_3$), τ 8.6 - 9.4 (m, 4H, $\overset{\wedge}{CH_2CH_2}$).

3b. Gas chromatographic and nmr data show that 3b consists of only one isomer, but the configuration of 3b has not been established. Elemental analysis: C, 80.55%; H, 6.66% (calcd. for $C_{18}H_{18}O_2$: C, 81.17%· H, 6.81%). Infrared: 1745, 1240 cm^{-1}. Nmr (CCl_4): τ 2.8 - 3.6 (m, 10H, aromatic), τ 5.9 - 6.3 (m, 1H, $\text{H-}\overset{|}{\underset{|}{\text{C}}}\text{-}$), τ 6.65- 8.3 (m, 4H, $-CH_2CH_2-$), τ 8.1 (s, 3H, $-OCOCH_3$).

5) P. J. Kropp, J. Amer. Chem. Soc., 95, 4611 (1973).

(Received October 26, 1973)