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Photochemistry of 1,2-Diphenylcyclobutene in Protic Solvents. Addition of Alcohols, Acetic Acid, and Water

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Irradiation of 1,2-diphenylcyclobutene (**1**) in methanol affords the methyl ethers, 1,2-diphenyl-1-methoxycyclobutane (**2a**) and 1-(α-methoxybenzyl)-1-phenylcyclopropane (**3a**). In acetic acid and in a mixture of water and dioxane, the corresponding esters (**2b** and **3b**) and alcohols (**2c** and **3c**) are formed, respectively. Evidence supporting the involvement of a singlet species was obtained upon finding that the fluorescence of **1** is substantially quenched upon the addition of methanol or acetic acid to a solution of **1** in hexane.

One of the simplest organic chromophores is the carbon-carbon double bond. However, its photochemical behavior is not at all simple. This chromophore undergoes, on direct or sensitized irradiation, *cis-trans* isomerization, cycloaddition, reduction, and the addition of protic solvents depending on the nature of the double bond, the solvent, and the sensitizer.[1] Even for the photochemical behavior of cyclic olefins in protic solvents, no consistent explanation has been given. The behavior of six- and seven-membered cycloalkenes are the best documented and most studied.[2] Direct or sensitized irradiation of cyclohexenes and cycloheptenes in an (acidic) alcoholic solution affords ethers arising from the addition of the alcohol to the double bond.[2] In these cases, the orthogonal excited triplet olefin or a highly-strained ground state of *trans*-olefin is considered to be the reactive species.[2]

Eight-membered cycloalkenes, which easily isomerize through the triplet state upon irradiation, also undergo this polar addition, but less efficiently.[2b,2d,2j,3] Polar addition disappears on going to smaller ring sizes. Cyclopentenes undergo reduction of the double bond, but do not undergo the addition of protic solvents.[2d,2e,2j] However, bicyclic olefins containing a five-membered ring, such as 2-phenylbicyclo[2.2.1]hept-2-ene and its 1,7,7-trimethyl derivative, have been reported to undergo polar addition of methanol under illumination.[4] The reaction products are apparently similar to those from cyclohexenes, cycloheptenes, and cyclooctenes, but the reaction course is unequivocally different because the bicyclic olefins fail to transform to the orthogonal triplet states or to the *trans*-configurations. The polar addition of the bicyclic olefins as well as styrene derivatives has been interpreted in terms of a reactive singlet excited state displaying a charge-transfer character.[4]

In a previous communication,[5] the first example of the photochemical ionic addition to the rigid cyclobutene system was reported and evidence supporting the involvement of a singlet excited species in the addition was presented by showing that the irradiation of 1,2-diphenylcyclobutene (**1**) in methanol and acetic acid affords polar addition products, methyl ethers and acetates and that the fluorescence of **1** is quenched substantially by methanol. In the present paper, the details of these results will be described.

Results and Discussion

A solution of 1,2-diphenylcyclobutene (**1**, 5×10^{-5} M) in methanol, ethanol, acetic acid, or in a mixture of water and dioxane was irradiated with 330 nm light. The bands of **1** at 227 and 297 nm decreased in intensity during the irradiation. A typical example is shown for methanol in Fig. 1. Three isosbestic points maintained their positions during the reaction, suggesting that this reaction is straightforward. In order to obtain the reaction products, **1** in methanol (7×10^{-3} M) was irradiated by a 500 W xenon lamp through a filter (Corning glass filter 0—54, nominally wavelengths longer than 300 nm). The reaction mixture was separated by column chromatography on silica gel into two components in addition to the recovered starting material. One component was a colorless liquid which was identified as 1-(α-methoxybenzyl)-1-phenylcyclopropane (**3a**) by the presence in the NMR spectrum of a four-proton multiplet at δ 0.65—1.15 which is characteristic of methylene protons attached to a cyclopropane ring and by elemental analysis (*cf.* Experimental). The other component was a white crystalline solid which was characterized as 1,2-diphenyl-1-methoxycyclobutane (**2a**) from the spectral data and elemental analysis (*cf.* Experimental). Gas chromatographic analysis and the NMR spectrum show that **2a** consists of only one isomer.

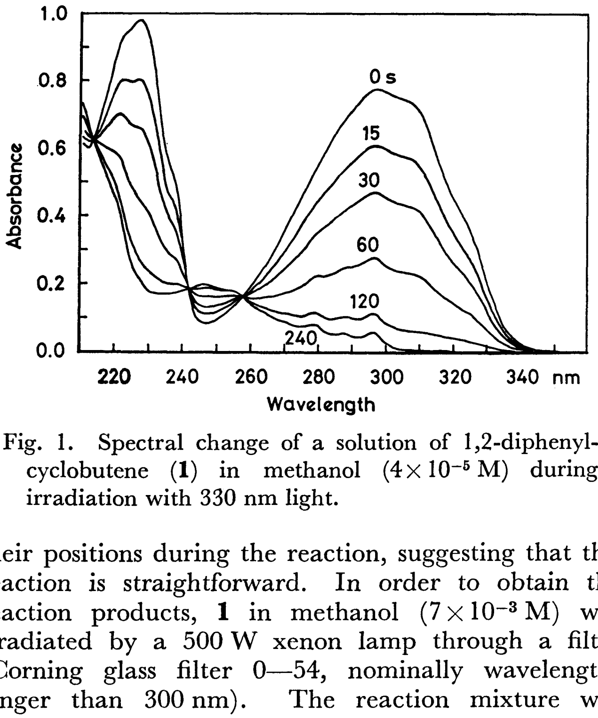
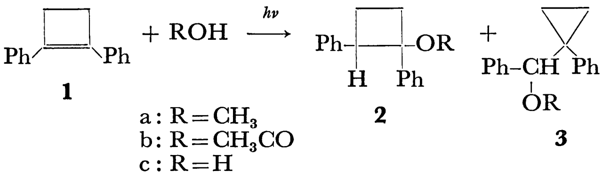


Fig. 1. Spectral change of a solution of 1,2-diphenylcyclobutene (**1**) in methanol (4×10^{-5} M) during irradiation with 330 nm light.



Similar irradiation of **1** in acetic acid afforded 1,2-diphenylcyclobutyl acetate (**2b**) and α-(1-phenylcyclopropyl)benzyl acetate (**3b**). Their structures were established from spectral data and elemental analysis (*cf.* Experimental). Compound **2b** was also found to consist of one isomer from gas chromatographic analysis and NMR data. The addition products, **2a** and **2b**, as well as *N*,*N*-disubstituted 1,2-diphenylcyclobutanamines, the adducts of **1** with *s*-amines, displayed a multiplet due to a methine proton at the same region (δ 3.7—4.2) as did *cis*-1,2-diphenylcyclobutane, while *trans*-1,2-diphenylcyclobutane exhibited a multiplet at a somewhat higher field (δ 3.2—3.6).[6] Taking into account the small effect of the β-substituents on the chemical shift of a methine proton,[7] **2a** and **2b** can safely be assigned to the *cis*-configuration. The results are summarized in Table 1.

Table 1. Products from the irradiation of 1,2-diphenylcyclobutene (**1**) in polar solvents

Solvent	Irradiation time (h)	Product yield (%)[a] 2	3
MeOH	18	25	43
AcOH	100	50	17
H_2O[b]	80	12	44
D_2O[b]	90	16	34

a) The yield based on the amount of **1** reacting.
b) In dioxane.

α,1-Diphenylcyclopropanemethanol (**3c**) and 1,2-diphenylcyclobutanol (**2c**)[8] were similarly obtained upon irradiation of **1** in a mixture of water and dioxane (1: 4 by volume), as is summarized in Table 1. These products, **2c** and **3c**, were characterized by their spectral data and by comparing the spectral data of their acetates with those of **2b** and **3b**.

The possibility that **2** and **3** could have arisen nonphotochemically from **1** was eliminated by leaving solutions of **1** in methanol, acetic acid, and water–dioxane in the dark for 3 days.

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

Although a protonated bicyclobutane has been proposed as an intermediate in the deamination of cyclobutanamine and cyclopropylmethanamine producing the same mixture of cyclobutanol and cyclopropanemethanol in each case,[9] there is no need to postulate a nonclassical cation in this photochemical process, and the product ratio is attributable to kinetic control in the nucleophilic capture by the solvent. This assumption is consistent with the sole formation of the *cis*-cyclobutane derivatives since the nucleophile would preferentially attack the 1,2-diphenylcyclobutyl cation from the less hindered side. The behavior of the diphenylcyclobutyl cation upon rearrangement to the cyclopropylmethyl cation is in remarkable contrast to that of the 1-phenylcyclobutyl cation, which shows no tendency to rearrange in superacid solutions.[10] For the photoreaction of 2,3-diphenyl-1,3-butadiene in methanol, Baldry[11] has isolated **2a** and **3a** together with **1** and other products, and postulated a mechanism for the ether formation involving a bicyclobutane intermediate.[12] However, the possibility that **2a** and **3a** arise from the photoprotonation of primarily formed **1** can not be ruled out completely in view of the photolability of **1**.

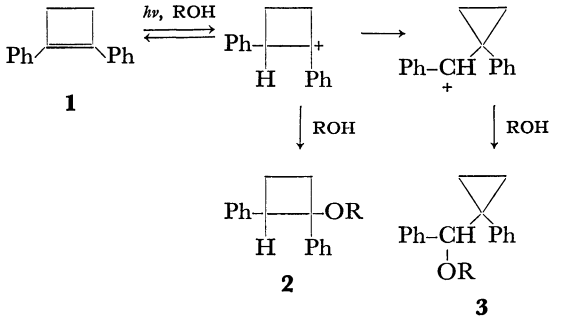
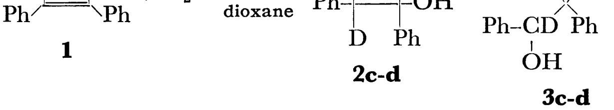


Table 2. Kinetic data for the photoprotonation of 1,2-diphenylcyclobutene (**1**) in hexane[a]

Quencher	$k_q\tau_0$ (M^{-1}) From fluorescence quenching experiment	From quantum-yield measurement	k_d/k_r
EtOH	0.36	0.41	12
AcOH	0.38	0.40	9

a) Conducted under aerated conditions.

In order to gain more insight into the mechanism for the polar addition, a labeling study using deuterated water as the additive was undertaken. 1,2-Diphenylcyclobutene (**1**) was irradiated in a mixture of deuterated water and dioxane (1: 4 by volume), and the products were isolated in a manner similar to that described above. The deuteration position for each product was determined by comparing its NMR spectrum with that of the non-deuterated product; 1,2-diphenylcyclobutanol (**2c-d**) undergoes deuteration at the 2-position and α,1-diphenylcyclopropanemethanol (**3c-d**) at the α-position. These results confirm the assumption that the addition proceeds from the initial photoprotonation of the cyclobutene (**1**).



Since the quantum yield for fluorescence of **1** is reported to be almost as high as unity in a diluted solution,[13)] photoprotonation is assumed to proceed from the excited singlet state of **1**. Evidence supporting the involvement of a singlet species was obtained from the finding that the fluorescence of **1** is substantially quenched upon the addition of methanol, ethanol, and acetic acid to the solution of **1** in hexane. Plots of the reciprocals of the relative fluorescence intensities against the quencher concentrations are linear and can be fitted to the Stern-Volmer equation,

$$I_0/I = 1 + k_q\tau_0[\mathrm{Q}],$$

where I_0 and I denote the intensities of the fluorescence of **1** in the absence of and in the presence of the quencher, respectively, in the concentration [Q], k_q is the rate constant of the bimolecular quenching process, and τ_0 denotes the average lifetime of the excited singlet state of **1** in the absence of the quencher. The quenching constants, $k_q\tau_0$, obtained from the slopes of these plots are 0.42, 0.36, and 0.38 M^{-1} for methanol, ethanol, and acetic acid, respectively. The singlet lifetime of **1** (τ_0) has been reported to be shorter than 5 ns,[13)] and thus the k_q values are estimated to be larger than 8×10^7 $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$, and are probably about 10^8 $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$, suggesting that the excited singlet state of **1** interacts with the ground state of the alcohols and acetic acid.

The quantum yield of the photochemical polar addition of ethanol and acetic acid to **1** was determined under aerated conditions in hexane by monitoring the decrease of **1** upon irradiation with 330 ± 7 nm light. A linear relationship is found between the reciprocal of the quantum yield (Φ) for the decrease of **1** and the reciprocal of the concentration of the additive. The intercepts and the slopes were estimated to be 13 and 32 for ethanol, and 10 and 25 for acetic acid, respectively.

The simplest mechanism which accounts for all the above results can be written as follows,

$$\mathbf{1} + h\nu \longrightarrow \mathbf{1}^*$$

$$\mathbf{1}^* \xrightarrow{k_f} \mathbf{1} + h\nu'$$

$$\mathbf{1}^* + \mathrm{O}_2 \xrightarrow{k_0} \mathbf{1} + \mathrm{O}_2$$

$$\mathbf{1}^* + \mathrm{HOR} \xrightarrow{k_q} [\mathbf{1}\cdots\mathrm{HOR}]^*$$

$$[\mathbf{1}\cdots\mathrm{HOR}]^* \xrightarrow{k_d} \mathbf{1} + \mathrm{HOR}$$

$$[\mathbf{1}\cdots\mathrm{HOR}]^* \xrightarrow{k_r} [\mathbf{1}\text{-H}^+ + {}^-\mathrm{OR}] \longrightarrow \text{products},$$

where **1*** denotes the excited singlet state of **1**. At infinite dilution under degassed conditions, the quantum yield for the fluorescence of **1** is unity,[13)] and therefore, intersystem crossing to the triplet state can be neglected. By making the usual steady-state assumption, the quantum yield for the decrease of **1** is written as follows;

$$1/\Phi = (1+k_d/k_r)(1+1/k_q\tau_0[\mathrm{Q}]).$$

The k_d/k_r values, *i.e.*, the ratio of rates for the decay process and the protonation in the interaction of excited **1** and the polar solvent, can be estimated to be 12 for ethanol and 9 for acetic acid, and the $k_q\tau_0$ values were found to be 0.41 M^{-1} for ethanol and 0.40 M^{-1} for acetic acid. These values are in good agreement with those obtained in the fluorescence quenching experiments: 0.36 M^{-1} for ethanol and 0.38 M^{-1} for acetic acid. These results substantiate the above mechanism.

When 1-phenylcyclobutene was irradiated in methanol no addition products resulted. This, combined with the results for 1,2-diphenylcyclobutene, suggests that substituents on the cyclobutene ring play important roles in the reactivity of cyclobutenes. These substituent effects upon the reactivity will be discussed in a future publication. 1,2-Diphenylcyclopentene was also irradiated in methanol giving no polar addition products but a phenanthrene derivative, the formation of which was so efficient that it was observed in the course of the fluorescence measurement.

The only previously observed ring system for photoprotonation from the excited singlet state is the case of 2-phenylbicyclo[2.2.1]hept-2-ene derivatives,[4)] and thus 1,2-diphenylcyclobutene is the first example for a four-membered cycloalkene. For three-membered cycloalkenes, 1,2-diphenyl-3,3-dimethylcyclopropene has been reported to give open-ring products, 1,2-diphenyl-1-methoxy-3-methyl-2-butene and *cis*-1,2-diphenyl-3-methoxy-3-methyl-2-butene, upon irradiation in methanol, through a carbene intermediate arising from the excited singlet state with subsequent capture by methanol.[14)] It is interesting that the cyclobutene system has almost the same strain energy as the bicyclo[2.2.1]hept-2-ene system, the cyclopropene system having a much higher energy.[15)]

Recently, the reactive intermediate in the photoprotonation of 1-phenylcyclohexene was shown to be *trans*-phenylcyclohexene, which must be very twisted, by more than 90°.[16)] This is assumed to be the case for the phenylcycloheptene photoprotonation. These *trans*-cycloalkenes are singlet in nature and possess a partial singlet diradical character if the twist is not completed to 180°.[16)] This may be common to the excited singlet states of highly-strained cycloalkenes, such as the phenylbicyclo[2.2.1]heptenes and diphenylcyclobutene. Thus, protonation in the highly-strained *cis*-cycloalkenes, as well as in the highly-twisted *trans*-cycloalkenes, would be effected by the simultaneous release of strain in those intermediates.

Experimental

The IR and UV spectra were recorded on a Hitachi EPI-G3 grating infrared spectrophotometer and a Hitachi EPS-3 recording spectrophotometer, respectively. The NMR spectra were recorded on a JEOL C-60HL spectrometer. GLPC analysis was performed on a Hitachi 163 gas chromatograph equipped with a flame ionization detector.

Materials. 1,2-Diphenylcyclobutene,[17)] 1-phenylcyclobutene,[18)] and 1,2-diphenylcyclopentene[19)] were prepared according to reported methods. Solvents were purified by distillation.

Irradiation of 1,2-Diphenylcyclobutene (1) in Methanol. A solution of **1** (300 mg) in methanol (200 ml) was irradiated in a nitrogen atmosphere for 18 h using a 500-W xenon lamp and a Corning 0—54 filter. This procedure was repeated six times. The reaction mixtures were combined, and the solvent was removed by rotary evaporation. The residue was subjected to chromatography on silica gel using hexane–benzene eluants affording a colorless liquid (540 mg), a white crystalline solid (310 mg), and the starting olefin (720 mg).

The colorless liquid was identified to be 1-(α-methoxybenzyl)-1-phenylcyclopropane (**3a**) from the spectral data and elemental analysis. Bp *ca.* 270 °C. IR (liquid film) 1090 cm^{-1}. NMR δ 0.65—1.15 (m, 4H, cyclopropyl CH_2-CH_2), 3.22 (s, 3H, OCH_3), 4.02 (s, 1H, methine H), 6.8—7.4 (m, 10H, aromatic H). Found: C, 85.47; H, 7.44%. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61%.

The white solid was deduced to be 1,2-diphenyl-1-methoxycyclobutane (**2a**) from the spectral data and elemental analysis. The GLPC analysis and NMR data showed that **2a** consists of only one isomer. Mp 91.5—92.0 °C (from petroleum ether). IR (KBr) 1080 cm^{-1}. NMR ($CDCl_3$) δ 1.7—2.3 (m, 4H, CH_2CH_2), 2.93 (s, 3H, OCH_3), 3.7—4.1 (m, 1H, methine H), 6.6—7.3 (m, 10H, aromatic H). Found: C, 86.09; H, 7.54%. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61%.

Irradiation of 1,2-Diphenylcyclobutene (1) in Acetic Acid. A solution of **1** (2.0 g) in acetic acid (200 ml) was similarly irradiated for 100 h using a 500-W xenon lamp. The solvent was removed by rotary evaporation, and the residue was subjected to chromatography on silica gel with hexane–benzene eluants resulting in three components: the first white solid (640 mg) was found to be the starting olefin, and the second colorless liquid (300 mg) was identified as α-(1-phenylcyclopropyl)benzyl acetate (**3b**) from spectral data and elemental analysis. Bp *ca.* 300 °C. IR (liquid film) 1740, 1240 cm^{-1}. NMR (CCl_4) δ 0.6—1.4 (m, 4H, cyclopropyl CH_2CH_2), 1.95 (s, 3H, $OCOCH_3$), 5.40 (s, 1H, methine H), 6.6—7.2 (m, 10H, aromatic H). Found: C, 81.17; H, 6.74%. Calcd for $C_{18}H_{18}O$: C, 81.17; H, 6.81%.

The third colorless liquid (870 mg) was characterized as 1,2-diphenylcyclobutyl acetate (**2b**) from spectral data and elemental analysis. The GLPC analysis and NMR data showed that **2b** consists of only one isomer. Bp *ca.* 235 °C. IR (liquid film) 1745, 1240 cm^{-1}. NMR (CCl_4) δ 1.90 (s, 3H, $OCOCH_3$), 1.7—3.35 (m, 4H, CH_2CH_2), 3.7—4.1 (m, 1H, methine H), 6.4—7.2 (m, 10H, aromatic H). Found: C, 81.01; H, 6.90%. Calcd for $C_{18}H_{18}O$: C, 81.17; H, 6.81%.

Irradiation of 1,2-Diphenylcyclobutene (1) in a Mixture of Water and Dioxane. A solution of **1** (300 mg) in a mixture of water (40 ml) and dioxane (160 ml) was similarly irradiated by a 500-W xenon lamp for 80 h. This procedure was repeated twice. The reaction mixtures were combined, and the solvent was removed by rotary evaporation. The residue was subjected to chromatography on silica gel. The products obtained were diphenylacetylene$^{20)}$ (20 mg), α,1-diphenylcyclopropanemethanol (**3c**, 235 mg), 1,2-diphenylcyclobutanol (**2c**, 65 mg), and 1,2-dibenzoylethane$^{21)}$ (40 mg). The starting olefin (10 mg) was recovered. **3c** and **2c** were identified upon esterification with acetic anhydride to the corresponding acetates, **3b** and **2b**, respectively.

α,1-Diphenylcyclopropanemethanol (**3c**). NMR (CD_3-$COCD_3$) δ 0.6—1.4 (m, 4H, cyclopropyl CH_2CH_2), 4.45 (s, 1H, OH, exchanged with D_2O), 4.75 (s, 1H, methine H), 7.2—7.7 (m, 10H, aromatic H).

1,2-Diphenylcyclobutanol (**2c**).$^{8)}$ NMR (CD_3COCD_3) δ 2.0—3.0 (m, 4H, CH_2CH_2), 3.9—4.4 (m, 1H, methine H), 5.15 (s, 1H, OH, exchanged with D_2O), 6.9—7.9 (m, 10H, aromatic H).

Irradiation of 1,2-Diphenylcyclobutene (1) in a Mixture of Deuterated Water and Dioxane. The irradiation of **1** (500 mg) in a mixture of deuterated water (40 ml) and dioxane (160 ml) was performed under otherwise similar conditions. Deuterated products, α,1-diphenylcyclopropanemethanol-α-*d* (**3c-d**, 140 mg) and 1,2-diphenylcyclobutanol-2-*d* (**2c-d**, 70 mg), were isolated in a similar manner together with 1,2,5,6-tetraphenyltricyclo[4.2.0.0^{2,5}]octane$^{13,20)}$ (35 mg), 1,2,5,6-tetraphenylcycloocta-1,5-diene$^{13,20)}$ (10 mg), and the recovered starting olefin (120 mg). The position of deuteration in the products, **2c-d** and **3c-d**, was determined by comparing their NMR spectra with those for non-deuterated products, **2c** and **3c**, respectively.

Quenching of the Fluorescence of 1,2-Diphenylcyclobutene (1). The fluorescence of **1** (4×10^{-4} M) in hexane containing various concentrations of alcohols or acetic acid (0—0.8 M) was determined using a Hitachi MPF-2A fluorescence spectrophotometer.

Quantum-yield Measurements. The exciting light for the quantum-yield measurements was furnished by a JASCO CRM-FA spectroirradiator. Hexane solutions of **1** (10^{-3} M) and ethanol or acetic acid (0—1 M) were irradiarted with 330±7 nm light for 3 min. The reaction mixture was diluted twenty times with the same solvent and its UV spectrum was measured. The light intensity was measured by potassium ferrioxalate actinometry.

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