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Photochemistry of *cis*-1-Phenylcyclohexene. Proof of Involvement of Trans Isomer in Reaction Processes

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Abstract: Kinetic studies showed that the formation of a [2 + 2] dimer in the direct irradiation of *cis*-1-phenylcyclohexene in methanol proceeds in the singlet manifold, possibly involving an excimer. The generation of a Markownikoff-type ether results from a common intermediate in the direct and the sensitized irradiation. Low-temperature studies indicate that *trans*-1-phenylcyclohexene is this intermediate. Evidence for the existence of a free *trans*-1-phenylcyclohexene is found in the structure of a [4 + 2] dimer formed in irradiations of *cis*-1-phenylcyclohexene in methanol at −75 °C.

Introduction

In the past decade much interest has been shown in the photoinduced addition of protic solvents to cyclic olefins.[2-4,6] In most such studies, compounds with simple ethylenic double bonds were employed and, thus, an aromatic hydrocarbon sensitizer had to be used for activation of the unsaturated linkage. The protic solvent addition reaction appeared to be acid catalyzed and the product formation was dependent upon the ring size of the cycloalkene.[3] Generally, the results have been interpreted in terms of the photoinduced formation of a strained ground state trans double bond which reacts readily with a proton to yield a carbocation, followed by the addition of a nucleophilic species. Indeed, Marshall has shown that the
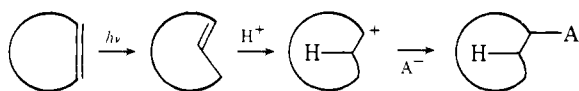

stereochemistry of the protonation is in agreement with the suggestion of a trans olefin as an intermediate.[4] However, in all the cases studied, the reaction of a triplet state (possibly

orthogonal) with protic solvents cannot be ruled out on the basis of the existing data.

In order to obtain a better evaluation of the nature of this photochemical solvent addition, a study using 1-phenylcyclohexene was initiated. With this substituted olefin it would be possible to apply direct as well as sensitized irradiation conditions. Furthermore, the presence of the benzene ring would permit the introduction of substituents on the ring and in this manner the importance of meta vs. para substitution could be evaluated, an approach used so successfully in interpreting the mechanism of aromatic photosubstitution and photosolvolysis.[5]

The photoaddition of methanol to *cis*-1-phenylcyclohexene (**1**) has been reported by Kropp, using a 0.13 M solution of **1**
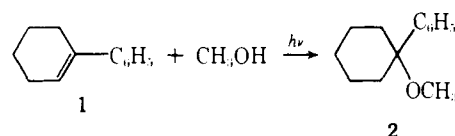
in methanol; a 13% formation of the Markownikoff ether **2** at

78% conversion was found.[3] In acidic methanol (1% H_2SO_4) the yield of ether **2** was 80% at 100% conversion of **1**. Under sensitized reaction conditions, acetophenone (0.17 M) in acidic methanol, 95% of ether **2** was formed at 97% conversion of **1**. From these results it was not possible to distinguish between a singlet or a triplet mechanism in the direct irradiation, but in all cases a ground-state trans olefin was proposed as an intermediate.

The photochemistry of *cis*-1-phenylcyclohexene in methanol also has been studied, in detail, by Rosenberg and Servé.[6] It
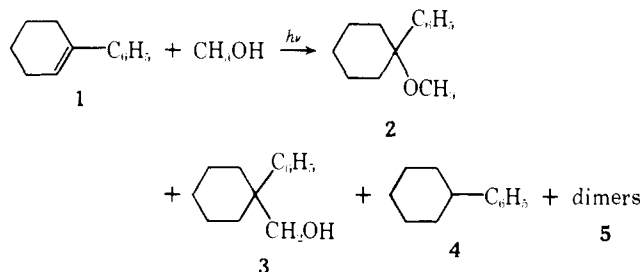
was reported that upon direct irradiation of a 0.2 M solution of **1** in methanol (no added acid) there was formed 26% of ether **2**, 7% of alcohol **3**, 13% of reduction product **4**, and 46% of dimers **5**, based upon the amount of reacted **1**. In a sensitized reaction in methanol (3-methoxyacetophenone as sensitizer) the same relative amounts of **2**, **3**, and **4** were formed but only trace quantities of dimers **5** could be detected. It was also reported that, upon the direct irradiation of **1** in the presence of 1,3-cyclohexadiene, the formation of **2**, **3**, and **4** was quenched but not the formation of the dimers **5**. From these results, it was concluded that **2**, **3**, and **4** were formed via the triplet state and that the formation of dimers **5** arose from the singlet state. The involvement of the ground-state trans olefin in one and/or the other of the processes was not excluded. These workers also reported a quantum yield of $\Phi = 0.12$ for the disappearance of *cis*-1-phenylcyclohexene. More recently, Zimmerman[7] has found that the quantum yield for intersystem crossing of *cis*-1-phenylcyclohexene is only $\Phi = 8 \times 10^{-4}$. Thus, the involvement of a triplet mechanism in the direct irradiation, as suggested by Rosenberg and Servé,[6] is highly unlikely.

Until recently, there existed no unequivocal evidence for the intermediacy of a trans olefin in the reaction processes. However, it was recently reported in a flash photolysis study of *cis*-1-phenylcyclohexene in methanol that a transient was observed to which was assigned the structure of *trans*-1-phenylcyclohexene.[8] The structural assignment was based upon the insensitivity of the lifetime of the intermediate to the polar nature of the solvent. The lifetime of this species in methanol at room temperature is 9 μs. The detection of the trans olefin does not necessarily imply that it also is involved in the photoreactions of *cis*-1-phenylcyclohexene in methanol. Indeed, the results of Rosenberg and Servé indicate that there is no common intermediate for the dimer and the ether formed in the singlet manifold.

To obtain more evidence for the involvement of the strained *trans*-1-phenylcyclohexene in the photoreactions of the cis isomer, the mechanisms leading to ether formation and dimer formation under various conditions have been investigated. Three reactive intermediates which can lead to these two products have to be taken into account. These intermediates are (1) the lowest excited singlet state, (2) the lowest triplet state, and (3) a ground-state trans olefin. This last intermediate could be formed via the singlet route or via the triplet route, or via both routes.

Results

Concentration and Multiplicity Dependence. It is well known that, upon direct irradiation of *cis*-1-phenylcyclohexene in

Scheme I
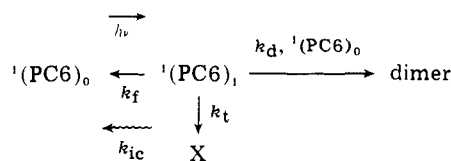
methanol, the amount of ether formed is very sensitive to the acidity of the system.[3] Reported yields of ether formation in neutral methanol, however, ranged from 13 to 26%.[3,6] In order to be sure that there was no acid present in the methanol used in the present study, the methanol was distilled from $Mg(OCH_3)_2$ just prior to utilization. Following such a reaction procedure, it was found that direct irradiation (λ 300 nm) of a 0.2 M solution of *cis*-1-phenylcyclohexene in freshly distilled methanol (approximately the same concentration as reported[3,6]) yielded only 3% of the ether at 68% conversion, the major product being the dimers (see Table I). This result shows that the photoreaction of the phenylcyclohexene with methanol is very inefficient.[9]

However, when a similar solution of the olefin was sensitized (*m*-methoxyacetophenone, λ 350 nm, Pyrex filter), the yield of the ether was markedly increased. At 72% conversion of *cis*-1-phenylcyclohexene it was possible to isolate the ether in 57% yield (see Table I). Such a result suggests that an entirely different reaction mechanism is operating from the triplet manifold, or that the increased yield of ether is caused by the lack of competing reactions, like dimer formation, brought on by the difference in the reaction conditions (singlet vs. triplet).

To investigate these possibilities, irradiations were carried out with lower concentrations of *cis*-1-phenylcyclohexene, in order to decrease its influence on the ether formation. Side-by-side irradiations (λ 300 nm) of *cis*-1-phenylcyclohexene (0.02 M) in neutral methanol were performed using direct irradiation and using a sensitizer (*m* = methoxyacetophenone, 0.19 M). The results are given in Table I and show that under identical reaction conditions[11] only 1% of the dimers **5** was formed under sensitized conditions as compared to 14% in the direct irradiation. The amounts of ether formed under the two conditions were much closer than those observed previously. Such results suggest a singlet pathway for the dimer formation and the possibility of a common reactive intermediate in the direct and in the sensitized reaction leading to the ether. Both of these concepts have been evaluated by kinetic studies.

Dimer Formation. If the dimers are formed in a singlet mechanism (possibly via an excimer), there has to be a kinetic relationship between dimer formation and fluorescence self-quenching with varying concentrations of *cis*-1-phenylcyclohexene. Scheme I describes this relationship, where $^1(PC6)_0$ and $^1(PC6)_1$ are the ground state and first excited singlet state of *cis*-1-phenylcyclohexene, respectively; k_f, k_{ic}, and k_d are the rate constants for fluorescence, internal conversion, and dimerization; k_t is the rate constant of other possible ways of deactivation. The quantum yield of dimerization (Φ_d) can be written as

$$\Phi_d = \frac{k_d[^1(PC6)_0]}{k_d[^1(PC6)_0] + k_f + k_{ic} + k_t}$$

and

$$1/\Phi_d = 1 + \frac{k_f + k_{ic} + k_t}{k_d} \frac{1}{[^1(PC6)_0]}$$

$$= 1 + \frac{1}{k_d\tau_f} \frac{1}{[^1(PC6)_0]}$$

The quantum yield of the fluorescence (Φ_f) can be written as

Table I. Irradiations of cis-1-Phenylcyclohexene in Methanol at Room Temperature[a]

[1]	sens	[sens]	filter	mL	t, h	% 1	% 2	% 5	ref
0.20			quartz	100	102	32	3	54	b, e
0.09	m-methoxyacetophenone	0.34	Pyrex	100	105	28	57		c, d, e
0.02			Vycor	2.0	5	50	5	14	b, f
0.02	m-methoxyacetophenone	0.19	Vycor	2.0	5	51	19	1	b, f

[a] The irradiations were carried out as described in the Experimental Section using a Rayonet photochemical reactor. [b] 3000-Å lamps used. [c] 3500-Å lamps used. [d] Dimer yield not determined. [e] Yields after isolation by column chromatography. [f] Yields determined by gas-phase chromatography.

$$\Phi_f = \frac{k_f}{k_f + k_{ic} + k_t + k_d[^1(PC6)_0]}$$

and

$$1/\Phi_f = \frac{k_f + k_{ic} + k_t}{k_f} + \frac{k_d}{k_f}[^1(PC6)_0] \qquad (1)$$

In eq 1 the slope divided by the intercept is equal to $k_d\tau_f$; from fluorescence studies at 35 °C,[12] it was found that $k_d\tau_f$ has a value of 4.75. From a study of the concentration dependence of the dimer formation at room temperature (~30 °C), it was found that $k_d\tau_f$ has a value of 4.8.

This is very strong kinetic evidence that both the dimer formation and the fluorescence are occurring from the same intermediate species, the lowest excited singlet state. In the case of the dimer formation, possibly an excimer is involved in the total mechanism.

The dimer mixture obtained upon direct irradiation was separated by silica gel chromatography and was found to contain 55% of dimer **5a**, 40% of dimer **5b**, and 5% of dimer **5c**;
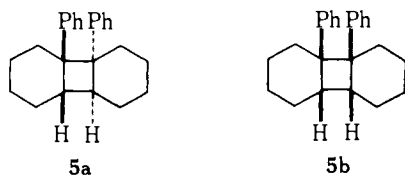
the last very minor dimer was never isolated in pure form. The structure of dimer **5a** was proved by independent synthesis (see Experimental Section) to have a head-to-head structure with cis-anti-cis stereochemistry. The ^{13}C NMR spectrum of **5a** contained only ten lines, four of which were due to the aromatic carbons. Such a spectrum indicates that the compound has a high degree of symmetry and the two phenyl rings have free rotation.[13] The ^{13}C NMR spectrum of dimer **5b** contained 12 lines, a result again indicative of a structure with a high degree of symmetry, but the presence of six lines for the aromatic ring shows that the two phenyl rings are *not* freely rotating. There are four head-to-tail dimers as well as the head-to-head cys-syn-cis structure which have the required symmetry. However, minimal energy conformations were calculated (PRXBLD program) and from the space-filling model drawings generated by this program it would appear that only structure **5b** showed substantial hindrance to the free rotation of the phenyl rings.[14] These data strongly suggest that the second dimer does possess the structure **5b**. Furthermore, the head-to-head orientation in both dimers strongly indicates the involvement of an excimer.[15]

Ether Formation, Fluorescence Quenching. In the direct irradiation of cis-1-phenylcyclohexene, the photoreaction leading to ether formation is not believed to proceed via the same reactive intermediate as involved in the dimer formation, i.e., the lowest excited singlet state.[6] Again, this postulate can be checked by a fluorescence study of cis-1-phenylcyclohexene under acidic conditions. If the lowest excited singlet state is involved in the photoprotonation reaction, there must be a kinetic relationship between the acid dependencies of the ether

Scheme II
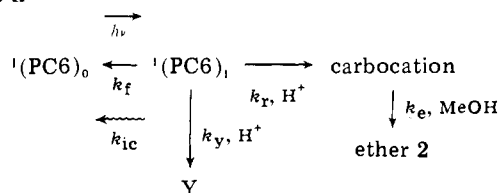
formation and the fluorescence intensity of cis-1-phenylcyclohexene. Scheme II describes, in simplified form, this relationship, where, again, $^1(PC6)_0$ and $^1(PC6)_1$ are the ground state and the first excited singlet state of cis-1-phenylcyclohexene, respectively; k_f, k_{ic}, k_y, k_r, and k_e are the rate constants for fluorescence, internal conversion, quenching by acid, protonation, and ether formation; Y is a possible other product formed by the acid quenching. The quantum yield of ether formation (Φ_e) can be written as[16]

$$\Phi_e = \frac{ak_r[H^+]}{k_f + k_{ic} + k_y[H^+] + k_r[H^+]}$$

and

$$1/\Phi_e = \frac{k_y + k_r}{ak_r} + \frac{k_f + k_{ic}}{ak_r}\frac{1}{[H^+]} \qquad (2)$$

The quantum yield of the fluorescence (Φ_f) can be written as

$$\Phi_f = \frac{k_f}{k_f + k_{ic} + k_y[H^+] + k_r[H^+]} \qquad (3)$$

When $[H^+] = 0$, this equation reduces to

$$(\Phi_f)_0 = \frac{k_f}{k_f + k_{ic}} \qquad (4)$$

From eq 3 and 4, the following relationship can be derived:

$$\frac{(\Phi_f)_0}{\Phi_f} = 1 + \frac{k_y + k_r}{k_f + k_{ic}}[H^+] \qquad (5)$$

If Scheme II adequately describes the photoreaction process leading to the formation of the ether **2**, then the intercept of eq 2 divided by the slope of eq 2 must have the same value as the slope of eq 5.

A methanolic solution of cis-1-phenylcyclohexene (0.02 M) was irradiated at 300 nm and the ether formation at various acid concentrations (0.0019–0.089 M) was determined. The data obtained were plotted via eq 2 and it was found that the intercept of the plot divided by the slope of the plot had a value of 45.

The relative fluorescence intensities of cis-1-phenylcyclohexene in methanol also were measured at various acid concentrations (0.00–0.46 M). The data obtained were plotted via eq 5 and it was found that the slope of the plot had a value of 0.3. Thus, these two kinetic analyses are not related to each other and it is indicative that the first excited singlet state is not the reactive intermediate in the acid-catalyzed ether formation.

Ether Formation, Common Intermediate. The occurrence of a common intermediate leading to the ether in a direct and

Table II. Irradiations of *cis*-1-Phenylcyclohexene in Methanol at Low Temperatures[a]

no.	[1]	sensitizer[b]	[sens]	[H₂SO₄]	t, h	T, °C	% 1	% 2	% 5	% 6
3a	0.02				5	+30	65	7	13	0
3b	0.02				5	−75	6	43	6	24
4a	0.02	acetophenone	0.20		2.5	+30	71	17	0.3	0
4b	0.02	acetophenone	0.20		2.5	−75	2	29	2	16
5a	0.02			0.018	2.5	+30	15	58	3	0
5b	0.02			0.018	2.5	−75	22	51	3	0

[a] The irradiations were conducted as described in the Experimental Section, using a Rayonet photochemical reactor equipped with 300-nm lamps. [b] No sensitizer was consumed upon irradiation.

Scheme III
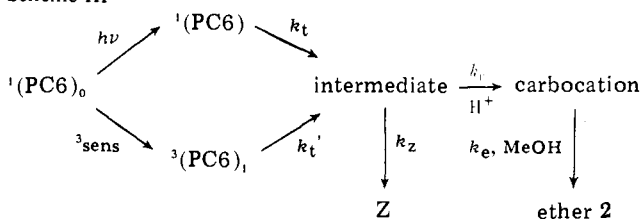
a sensitized irradiation can be investigated by studying the acid catalysis under both reaction conditions. Scheme III describes the reaction sequence, where k_t and k_t' are the rate constants for the formation of the intermediate from the singlet and the triplet state, respectively, and k_z is the combined rate constant for reactions to all other products. The actual quantum yields of the ether formation for both pathways depend on the other ways of deactivation (reaction) of the lowest excited singlet state, lowest triplet state, the common intermediate, and the carbocation.

Thus, in the singlet mechanism the quantum yield of ether formation can be written as[17]

$$\Phi_e^s = b\,\frac{k_r[H^+]}{k_r[H^+] + k_z} \text{ and } 1/\Phi_e^s = \frac{1}{b}\left(1 + \frac{k_z}{k_r}\frac{1}{[H^+]}\right) \quad (6)$$

In the triplet mechanism the quantum yield of the ether formation can be written as

$$\Phi_e^t = c\,\frac{k_r[H^+]}{k_r[H^+] + k_z} \text{ and } 1/\Phi_e^t = \frac{1}{c}\left(1 + \frac{k_z}{k_r}\frac{1}{[H^+]}\right) \quad (7)$$

If, indeed, a common intermediate is involved, the ratio of the intercept and the slope in eq 6 and in eq 7 have to be the same. Knowing the value of k_r/k_z permits calculation of the lifetime of the intermediate since k_r/k_z equals $k_r\tau$.

A direct irradiation (λ 300 nm) of *cis*-1-phenylcyclohexene (0.02 M) in methanol gave $k_r\tau = 45$. A sensitized irradiation (acetophenone, λ 300 nm) of *cis*-1-phenylcyclohexene (0.02 M) in methanol gave $k_r\tau = 47$. These data clearly indicate a common intermediate in each of these pathways for ether formation. Now, the possibility can be considered that this intermediate is the transient observed earlier in flash photolysis studies.[8] The rate constant for the reaction of the transient with acidic methanol was reported to be $7.6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. At 30 °C, the lifetime of this transient is 6.5 μs;[8] this leads to $k_r\tau_{trans} = 49$, suggesting that the *trans*-1-phenylcyclohexene, indeed, is the common intermediate.

trans-1-Phenylcyclohexene. The previous experiments have indicated that *trans*-1-phenylcyclohexene probably is the intermediate in the ether formation. In flash photolysis studies it has been observed that the lifetime of the trans olefin is very much affected by the temperature. In methanol, the lifetime of this species increased from 9 μs at room temperature to 500 μs at −70 °C.[18] This increased lifetime has been attributed to a decrease in the rate of the trans–cis isomerization. With such a change in rate in what had been the dominant reactive process for the intermediate, now other slow reaction processes can efficiently compete for reaction with the intermediate.

Scheme IV
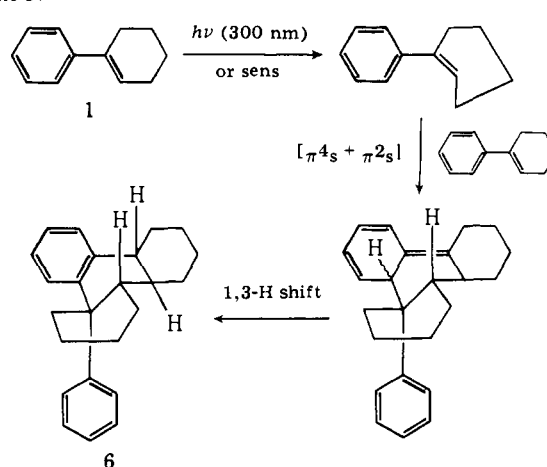
Irradiation of *cis*-1-phenylcyclohexene in neutral methanol at room temperature and at −75 °C, indeed, produced entirely different ratios of products (see Table II). Direct irradiation of *cis*-1-phenylcyclohexene in neutral methanol (0.023 M, λ 300 nm) at −75 °C gave a new dimer (6) in 24% yield at 95% conversion. Under these same reaction conditions the yield of the earlier discussed [2 + 2] dimers **5a, 5b,** and **5c** decreased and the yield of ether **2** increased with respect to the values found at room temperature. When the direct irradiation was carried out in acidic methanol (0.018 M H₂SO₄), the change in temperature had little effect upon the course of the reaction.
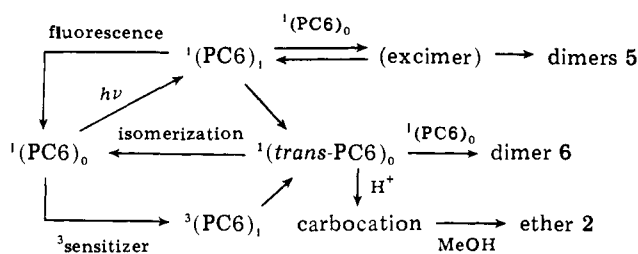
Sensitized irradiation (acetophenone, 0.2 M) of *cis*-1-phenylcyclohexene under the same neutral, low-temperature reaction conditions also afforded the new dimer **6**; the yield was 16% at 98% conversion of the starting material. It was also found that, under these sensitized conditions, the yield of the methyl ether **2** increased with respect to that found in the room temperature reaction.

The new dimeric product formed at −75 °C was purified by gas-phase chromatography and by crystallization from acetone (mp 198–201 °C) and its structure was established by X-ray crystallographic analysis.[19] The structure of dimer **6,** shown in Scheme IV, is the result of a [4 + 2] cycloaddition reaction. This new reaction process, occurring only after stabilization of the transient, is believed to be the Woodward–Hoffmann allowed concerted $[_\pi 4_s + _\pi 2_s]$ addition of *cis*-1-phenylcyclohexene to the endocyclic trans double bond of *trans*-1-phenylcyclohexene in the ground state, followed by a 1,3-hydrogen shift to yield the product. Thus, the changes in the product formation at −75 °C along with the trans ring juncture in dimer **6** prove the intermediacy of *trans*-1-phenylcyclohexene in the photoreactions of *cis*-1-phenylcyclohexene.

Discussion

The results reported in this study lead to a better understanding of those processes occurring upon irradiation of *cis*-

Scheme V

$$\text{fluorescence} \qquad {}^1(PC6)_0$$

$${}^1(PC6)_1 \rightleftarrows (\text{excimer}) \longrightarrow \text{dimers } 5$$

$$h\nu \qquad \text{isomerization}$$

$${}^1(PC6)_0 \longleftarrow {}^1(trans\text{-}PC6)_0 \xrightarrow{\ {}^1(PC6)_0\ } \text{dimer } 6$$

$$\downarrow H^+$$

$${}^3(PC6)_1 \quad \text{carbocation} \xrightarrow{\ \text{MeOH}\ } \text{ether } 2$$

$${}^3\text{sensitizer}$$

1-phenylcyclohexene in methanol in which 1-methoxy-1-phenylcyclohexane and dimers **5** and **6** are formed. These photoreactions are represented in Scheme V.

After direct excitation (or sensitization of *cis*-1-phenylcyclohexene ($^1(PC6)_0$) the resulting excited state ($^1(PC6)_1$ or $^3(PC6)_1$) is believed to twist around the endocyclic double bond to give the more relaxed twisted singlet or triplet state. These twisted excited states will yield the ground-state twisted *trans*-1-phenylcyclohexene ($^1(trans\text{-}PC6)_0$). The stability of this species toward trans–cis isomerization is the controlling feature in the product distribution in the photoreaction. Only at low temperature is dimer **6** formed. This dimeric structure still retains a trans ring juncture and this result is the first stereochemical evidence for the existence of a free *trans*-cyclohexene. This *trans*-1-phenylcyclohexene must be a very reactive dienophile in view of its reaction with a styrene type of molecule, even at −75 °C.[20,21]

Reactions of the more stable endocyclic trans double bonds in seven- and eight-membered rings have been reported to give [2 + 2] as well as [4 + 2] cycloadducts.[22] In a six-membered ring, although a new photocycloaddition product was reported from 1,3-cyclopentadiene and 1-acetylcyclohexene, the exact structure of the adduct has never been published.[23] However, the results from this present study would support the involvement of a trans intermediate in the reaction. Also, in the irradiation of cyclohexene in the presence of Cu(I), trans stereochemistry has been observed in the [2 + 2] dimer[24] and in a [4 + 2] adduct with butadiene.[25]

Also, the changes in the amounts of dimer **5a** and ether **2** formed upon lowering the temperature can be explained by the stabilization of the trans intermediate. Decreasing the rate of trans–cis isomerization, for instance, in the direct irradiation will decrease the yield of dimer **5a** since the number of times the cis isomer will be excited will be diminished. Since the dimer **5a** formation has been shown to stem directly from the singlet state, the dimer yield in the triplet reaction would not be expected to show a strong temperature dependency and, indeed, the yield varied only slightly, from 0.3 to 2%.[26] This change in dimer formation is reflected in the manner in which the ether **2** formation changes using neutral methanol in the singlet and in the triplet manifold; it is seen (Table II) that the ether yield increases sixfold in the singlet reaction as the temperature is lowered but the increase is less than twofold in the triplet process.

Preliminary studies have been conducted using compounds in which the benzene ring of *cis*-1-phenylcyclohexene has been substituted. Introduction of electron-donating substituents might lead to an increased polarity of the trans double bond and this result might lead to an increased ether formation. It is, however, also possible that such a substitution might damage the product distribution by affecting the lifetime of the trans intermediate or by making the first excited singlet state more reactive toward addition of methanol. Several photoadditions of methanol to double bonds have been reported to proceed by reaction of the first excited singlet state.[27,28] An indication for such a reaction course in the 1-phenylcyclohexene series was found in the fluorescence quenching of 1-(*p*-methoxyphenyl)-cyclohexene by methanol, the fluorescence intensity being quenched to 5% of its original intensity in hexane. This result indicates a strong interaction of the first excited singlet state with methanol, possibly this being a reaction leading to the formation of the observed ether, 1-methoxy-1-(*p*-methoxyphenyl)cyclohexane, in 43% yield. Also, the fluorescence intensity of 1-(*p*-methylphenyl)cyclohexene was quenched by methanol to 24% of its value in hexane. However, more fundamental kinetic studies are required to determine the photochemical mechanisms in these cases in a conclusive way.

Another effect of the introduction of substituents is the possible change in reaction products. In the irradiation of 1-(*p*-cyanophenyl)cyclohexene in acidic methanol, for instance, also the anti-Markownikoff ether was detected along with the Markownikoff type ether similar to those obtained with other compounds. Formation of an anti-Markownikoff ether has been reported to arise from an excited singlet state,[28] but it is also possible that a polarity change in the endocyclic trans double bond is responsible for this different product.

Experimental Section

General. Melting points were determined on a Mel-Temp laboratory device and are uncorrected. Ultraviolet spectra were obtained with a Perkin-Elmer Model 202 UV–visible spectrometer. ^1H magnetic resonance spectra were recorded on a Varian T-60 or Perkin-Elmer R-24A instrument. ^{13}C magnetic resonance spectra (25.144 kHz) were recorded on a Nicolet Technology Corp. TT-23 spectrometer. Infrared spectra were determined with a Perkin-Elmer 137, 237, and 71A spectrometer. Combustion analyses were determined by the Microanalytical Laboratory, College of Chemistry, University of California, Berkeley.

Analyses of Reaction Mixtures. The irradiation mixtures were analyzed by gas chromatography unless otherwise indicated. Aliquots (90 μL) were taken from the reaction solution and were extracted with 1.0 mL of a saturated solution of sodium bicarbonate in water and 1.0 mL of chloroform. The chloroform layer was analyzed on a Hewlett-Packard 402-high efficiency gas chromatograph, equipped with a 6 ft × 1/8 in. glass column (3% OV-225, Chromosorb W AW DCMS, 100–120 M), at temperatures ranging from 100 to 200 °C using a flame ionization detector. An internal standard (tetradecane, hexadecane, or triglyme) was used to calculate the composition of the reaction mixture.

On a preparative scale, the reaction mixture was concentrated and chromatographed on silica gel and the products were eluted with hexane and 2% ethyl acetate in hexane. The order of elution was phenylcyclohexene, phenylcyclohexane, dimer **5a**, dimer **5b**, and 1-methoxy-1-phenylcyclohexane.

Irradiation Procedures. All irradiations were conducted in a Rayonet photochemical reactor equipped with 300-nm lamps, unless otherwise indicated. Experimental designs included irradiations of 100-mL solutions in quartz or Pyrex vessels and irradiations of 2.0-mL solutions in Vycor vessels, the latter sometimes performed in a merry-go-round apparatus. In a typical experiment, the appropriate quantities of *cis*-1-phenylcyclohexene, sulfuric acid, and an internal standard were dissolved in methanol (Mallinckrodt analytical reagent) which had been freshly distilled from Mg(OMe)$_2$. Before the irradiation was started, a stream of dry nitrogen was passed through the reaction solution for a period of at least 30 min.

In sensitized irradiations, acetophenone was found to be a superior sensitizer to the earlier utilized *m*-methoxyacetophenone[6] since the latter compound is not stable upon irradiation under acidic conditions.

Synthesis and Identification of Materials. A. *cis*-1-Phenylcyclohexene. This material was prepared from cyclohexanone by reaction with phenylmagnesium bromide followed by treatment with *p*-toluenesulfonic acid in benzene: bp 80–82 °C (2.5 Torr); UV max (MeOH) 248 nm (ε 12 000); IR (CHCl$_3$) 2900, 1620, 1470, 730 cm^{-1}; NMR (CCl$_4$) δ 1.67 (m, 4), 2.12 (m, 4), 6.0 (br s, 1), 7.22 (br s, 5).

For fluorescence measurements, the 5.0 g of olefin was washed through a short silica gel column (2.5 × 9 cm) with 150 mL of pentane. The solvent was evaporated and the residue recrystallized three times from spectrophotometric-grade methylcyclohexane from −35 to −50 °C. The crystals were recrystallized twice from spectrophotometric-grade methanol at −40 °C. The recrystallized material was Kugelrohr

Table III. Acid Dependence of Ether Formation in a Direct and Sensitized Irradiation

[H$^+$], mol/L	direct irradiation % 2	sensitized irradiation % 2
0	3	6
0.0037	14	37
0.0092	31	75
0.037	64	94
0.092	78	92
0.179	81	85

Table IV. Acid Dependence of Relative Intensities of Fluorescence

[H$^+$], mol/L	$(I_f)_0/I_f$	[H$^+$], mol/L	$(I_f)_0/I_f$
0.00	1.00	0.24	1.05
0.06	1.01	0.46	1.14
0.13	1.04		

distilled (65 °C, 0.2 Torr) in an all-glass apparatus (no greased joints) to give 1.2 g of colorless oil, mp 3–5 °C. Fluorescence measurements were made on the same day as the purification.

B. 1-Methoxy-1-phenylcyclohexane. The ether isolated by chromatography was Kugelrohr distilled (bp 70 °C at 0.3 Torr) and was compared (NMR, TLC) with an authentic sample.[3,6]

C. Dimer 5a. The compound was recrystallized from 95% ethanol–chloroform to give colorless needles: mp 172–176 °C (phase change at 147–148 °C); UV max (hexane) 220 nm (sh, ε 13 000), 260 (460); IR (CHCl$_3$) 1590, 1490 cm^{-1}; ^{1}H NMR (CCl$_4$) δ 0.4–1.9 (m, 16), 2.86 (br s, 2), 7.1–7.6 (m, 10); ^{13}C NMR (CDCl$_3$) δ 21.3, 22.1, 23.6, 33.2, 35.0, 51.1, 125.7, 127.9, 128.0. 147.0; MS (70 eV) *m/e* (rel abundance) 159 (18), 158 (100), 141 (12), 129 (40), 117 (5), 115 (7), 91 (9). Anal. Calcd for C$_{24}$H$_{28}$: C, 91.08; H, 8.92. Found: C, 91.26; H, 8.93.

An authentic sample was prepared from the known *cis-anti-cis*-7,8-diphenyltricyclo[6.4.0.0^{2,7}]dodeca-3,12-dione.[29] A solution of 172 mg (0.5 mmol) of the dione, 0.41 g (73 mmol) of potassium hydroxide, and 0.85 mL of 85% hydrazine hydrate (0.72 g, 150 mmol) in 3.4 mL of triethylene glycol was heated at reflux (bath 145 °C) for 1.5 h. The bath temperature was raised slowly to 205 °C and liquid allowed to distill. The remaining solution was heated at 205 °C for 1.0 h, and the mixture processed in the usual manner. The residue was recrystallized from 95% ethanol–chloroform to give 71 mg (45%) of colorless needles, mp 167–171 °C (phase change at 146 °C). The material was identical with dimer **5a**: IR, ^{1}H NMR, ^{13}C NMR, and coinjection on μ-Porasil LC column.

D. Dimer 5b. The compound was recrystallized from ethanol to give colorless needles: mp 93–96 °C; IR (CCl$_4$) 1600, 1515, 703 cm^{-1}; ^{1}H NMR (CCl$_4$) δ 0.8–3.3 (m, 18), 6.8–7.6 (m, 10); ^{13}C NMR (CDCl$_3$) δ 19.7, 21.1, 21.9, 29.4, 37.5, 52.8, 124.7, 127.0, 127.7, 128.5, 128.9, 147.0; MS (70 eV) *m/e* (rel abundance) 316 (2), 159 (26), 158 (100), 143 (29), 130 (58), 129 (29), 128 (13), 117 (12), 115 (21), 91 (30). Anal. Calcd for C$_{24}$H$_{28}$: C, 91.08; H, 8.92. Found: C, 90.33; H, 8.79.

Dimer Formation, Concentration Dependence. Irradiations (see Table I) of 100-mL solutions of *cis*-1-phenylcyclohexene (0.2, 0.02 M) and sulfuric acid (0.0 or 0.019 M) in methanol were analyzed both by column chromatography and vapor phase chromatography. In kinetic runs, aliquots were taken at appropriate time intervals and the quantum yields for dimer formation were calculated using the isomerization of *exo*-tricyclo[6.2.1.0^{2,7}]undeca-3,5-diene as an actinometer.[30] The quantum yields for dimer formation (Φ_d) at concentrations of *cis*-1-phenylcyclohexene of 0.02 and 0.2 M are 0.008 and 0.31, respectively. The dependency of this quantum yield, Φ_d, on the initial concentration of the olefin PC$_6$ can be written as $1/\Phi_d = 2.0 + 0.21(1/[PC_6])$.

Ether Formation, Acid Dependencies. Direct irradiations (λ 300 nm, 2.5 h) of 2.0 mL of 0.02 M solutions of *cis*-1-phenylcyclohexene and sulfuric acid (0.0019–0.089 M) were carried out, side by side, in Vycor tubes. Sensitized irradiations (*t* = 1 h) were performed in a similar manner but with the addition of acetophenone (0.2 M). The reaction mixtures were analyzed by gas-phase chromatography. Table III lists the percentage of ether formation. These data lead to the following expressions: $1/(\% 2) = 0.01 + 0.00022(1/[H^+])$, direct and $1/(\% 2) = 0.004 + 0.000085(1/[H^+])$, sensitized.

Fluorescence Quenching by Acid. The intensity of the fluorescence of *cis*-1-phenylcyclohexene in methanol at various concentrations of sulfuric acid (0.00–0.23 M) was determined on an Aminco fluorimeter. The relationship between the relative fluorescence intensity [$(I_f)_0/I_f$] and acid concentration is given in Table IV. This dependency can be written as $(I_f)_0/I_f = 1.0 + 0.3[H^+]$.

Irradiations at Low Temperature. Vycor tubes, containing 2.0 mL of solution to be irradiated, were immersed in a cold mixture of methanol (Mallinckrodt, analytical reagent grade) and dry ice in a quartz Dewar flask. At all times, the reaction mixture was surrounded by methanol at a temperature of −75 °C. The analyses of the reaction mixture were performed by gas-phase chromatography, using triglyme as an internal standard.

For comparison, irradiations at room temperature (~30 °C) were carried out as described above, only omitting the dry ice. The results obtained in both of these series of irradiations are reported in Table II.

For isolation of the new dimer **6**, a 10-mL solution of 0.02 M *cis*-1-phenylcyclohexene in methanol was irradiated for 15 h at −75 °C, at which time gas-phase chromatographic analysis indicated a 24% formation of dimer **6** and little starting material. The reaction solution was processed in the standard manner and the dimer **6** collected from the analytical GPC column using 25-μL injections of the concentrated reaction mixture. The material was collected by placing a glass tube over the FID jet while the hydrogen flame was turned off. The collected material was crystallized first from methanol and then from acetone: mp 198–201 °C; MS (70 eV) *m/e* (rel abundance) 316 (22), 259 (27), 239 (26), 238 (78), 217 (10), 180 (11), 159 (15), 158 (16), 143 (6), 129 (20), 128 (12), 117 (11), 115 (16), 91 (70).

References and Notes

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(12) We wish to thank Professor N. C. Yang, University of Chicago, for supplying the data with respect to the concentration dependency and the temperature dependency of the fluorescence of *cis*-1-phenylcyclohexene. The values were determined by the least-squares analysis of I_0/I of *cis*-1-phenylcyclohexene fluorescence at 0.05, 0.1, and 0.2 M. The value of τ_f was obtained assuming that τ is proportional to Φ_f; the value of τ used was that reported by Zimmerman in ref 7.

(13) The high degree of symmetry strongly indicates that there were no stereochemical changes induced during the Wolff–Kishner reaction used to prepare **5a** since epimerization at two ring junctures would have to occur to give another symmetric product.

(14) A similar conclusion can be reached using Dreiding models. In all but the

head-to-head cis-syn-cis isomer, the maximum distance between ortho positions on the two phenyl rings is 3–4 Å; in the H–H, cis-syn-cis isomer the maximum separation is ~1.5 Å.

(15) Yang[12] found that the rate of self-quenching did not vary with temperature in the same manner as does the calculated diffusion control rates, a result indicating an excimer. Davidson and Whalen [R. S. Davidson and T. D. Whalen, *J. Chem. Soc., Chem. Commun.* **1977**, 361] have reported studies which indicate that fluorescence self-quenching occurs only when an excimer is formed and that dimerization only occurs when an excimer is present (not all excimers photodimerize).

(16) The constant *a* is the quantum yield for the formation of ether from the carbocation.

(17) The constant *b* is the product of the quantum yield for the formation of the intermediate and for the formation of the ether from the carbocation. The constant *c* incorporates the analogous quantum yields as well as the efficiency of sensitization in the triplet manifold.

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(21) The quenching of photoreactions of *cis*-1-phenylcyclohexene by 1,3-cyclohexadiene as observed by Rosenberg and Servé[8] can also be attributed to such a [4 + 2] cycloaddition reaction involving the trans olefin. Indeed, irradiation (λ 300 nm, Pyrex filter) of a solution of *cis*-1-phenyl-

cyclohexene (0.06 M) and 1,3-cyclohexadiene (0.12 M) in methanol yielded 22% of a 1:1 adduct (Dauben, W. G.; Robbins, J. D., unpublished results).

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(31) The data for high acid concentrations in the sensitized irradiations were not used to derive this expression because in these cases the reaction had already progressed too far.

Organic Photochemistry with 6.7-eV Photons: Irradiation of Molecular Oxygen in Hydrocarbon Solution

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Abstract: Irradiation of a solution of oxygen gas in cyclohexane with 185-nm light from a mercury resonance lamp leads to cyclohexyl hydroperoxide as the principal product. Control experiments show that (i) the radiation is absorbed by oxygen to give the observed product, (ii) there is no impurity in the solvent that is responsible for either the initiation or propagation of the process, (iii) a chain reaction is not involved, (iv) the reaction is distinct from thermal autoxidation, and (v) ozone is not an intermediate in the process. It is mostly likely that, on absorption of a photon, oxygen is excited to the $^3\Sigma_u^-$ state and reacts directly with the solvent. Irradiation of oxygen in methylcyclohexane under identical conditions leads to mixtures of nearly all possible methyl cyclohexyl hydroperoxides. The product composition changes very little over the temperature range −10 to +41 °C. The lack of selectivity in the formation of these products also supports the intermediacy of an energy-rich species. Photolyses of these solutions with the unfiltered light from a mercury resonance lamp lead not only to hydroperoxides but also to the corresponding alcohols and ketones. The latter are mostly, if not exclusively, formed by the secondary photolysis of the hydroperoxides at long wavelength.

Introduction

The intense absorption of oxygen gas which lies in the wavelength range 176–195 nm (Schumann-Runge bands) has been extensively studied by both spectroscopists[1] and photochemists.[2] The reactions which take place in this region will be mentioned later. The photochemistry of solutions of oxygen in the same wavelength region in solvents which are transparent to the light has attracted little attention. In this investigation, we demonstrate that, in such a system, a photochemical reaction takes place which can be attributed to the electronic excitation of the oxygen and its subsequent reaction with the solvent. Although the process gives rise to product(s) which are common to both the thermal autoxidation of the solvent[3-5] and the reaction of the solvent with ozonized oxygen,[6,7] we show that the process at 185 nm is distinctly different.

Interest in the concurrent action of light and air (oxygen) on organic compounds has attracted attention for nearly 100 years. Very early work using ultraviolet light in which the systems were not clearly defined has been summarized elsewhere.[8] More recent work which has concentrated on the O_2 ($^1\Delta_g$) state has given rise to a vast literature which has been reviewed.[9-11] It is only necessary to mention that O_2 ($^1\Delta_g$) is inert with respect to saturated hydrocarbons such as cyclohexane.

Results

Products. Irradiation of cyclohexane saturated with oxygen at 185 nm led to the rapid formation of cyclohexyl hydroperoxide (**1**) and lesser amounts of cyclohexanol and cyclohexanone. The yields of these products at conversions of the order