

1, 1'-디시클로알케닐 화합물에 대한 광화학적 연구*

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Photochemistry of Some 1, 1'-Dicycloalkenyls. The Mechanism of Sensitized Photocyclization*

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요 약. 1, 1'-디시클로알케닐의 광고리화 반응을 형광 쉐킹, 증감제등을 써서 연구하였다. 증감제를 쓰는 경우 이 디엔의 광고리화 반응은 비틀린 삼중상태나 평면구조의 트란스 삼중상태 보다 높은 에너지 준위에 있는 평면구조의 *s*-시스 삼중상태에서 일어남을 알았다.

ABSTRACT. The photocyclization of 1, 1'-dicycloalkenyls (1, 1'-dicyclohexenyl, 1, 1'-dicyclopentenyl, 1, 1'-dicycloheptenyl and 1, 1'-dicyclooctenyl) is studied. Irradiation at liquid nitrogen temperature does not show *trans* double bond band in IR spectra. Even though naphthalene and pyrene fluorescence are quenched very efficiently by 1, 1'-dicycloalkenyls, no or trace amount of cyclobutenes are accompanied. When acetophenone or benzophenone is used, cyclobutene is obtained only from 1, 1'-dicyclohexenyls, 1, 1'-dicycloheptenyl giving some adducts. Naphthalene and pyrene sensitizes adduct formation but not cyclization. From above observations, it is concluded that photocyclization occurs from the planar *s-cis* triplet state rather than twisted triplet, singlet excited state or vibrationally excited ground state in sensitized photocyclization of 1, 1'-dicycloalkenyls.

INTRODUCTION

Some cyclic homodienes and 1, 1'-dicycloalkenyls undergo electrocyclic reactions to give cyclobutene derivatives either by direct or sensitized excitation¹ but linear conjugated dienes give cyclization products on direct excitation^{1, 2} and dimerize on

sensitized excitation³. The effects of structural changes on the nature of excited states of dienes and the resultant control of the course of diene photochemistry have potential mechanistic and synthetic importance. For instance, the reactive *s-cis* triplet state in cyclic dienes or in 1, 1'-dicycloalkenyls cannot assume the preferred non-spectroscopic twisted geometry. It is considered that the unavailability of the twisted geometry which leads to *cis-trans* isomerization in linear olefins causes the 1, 1'-dicycloalkenyls to cyclize

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instead. Alternatively the triplet state of both linear dienes and 1,1'-dicycloalkenyls could undergo normal *cis-trans* isomerization and the highly strained *trans* olefinic bond in 1,1'-dicycloalkenyls could then cause thermal cyclization to cyclobutenes. A remote possibility is that sensitized excitation induces the reactive singlet state rather than the triplet state in 1,1'-dicycloalkenyls and cyclization occurs from this state. A course of study designed to distinguish among these possibilities is pursued.

EXPERIMENTAL

Materials. Acetophenone and benzophenone used in sensitization and quantum yield measurements were zone refined by James Hinton, Newport News, Virginia (99.8 % of stated purity) and were used as received.

Benzene (Reagent Grade) was purified by sulfuric acid treatment. 1,1'-dicyclopentenyl, 1,1'-dicyclohexenyl, and 1,1'-dicycloheptenyl were prepared by dehydration⁴, under acidic conditions, of pinacols resulting from pinacol-reduction of their respective cycloalkanones. In all cases, dienes were found to be 95 % pure as analyzed by gas-liquid phase chromatography. Infrared and NMR spectra for each compound were obtained and found to be comparable to reported data.

Cyclohexane, spectroquality, Matheson, Coleman & Bell, hexadecane, spectroquality, Matheson, Coleman & Bell, and hexane, Fischer spectroquality reagent were used as received.

Naphthalene of stated purity 99 % was zone refined by James Hinton, Newport News, Virginia: used in fluorescence studies and sensitized irradiations as received.

GENERAL IRRADIATION PROCEDURE

The preparative irradiations were conducted using the Rayonet photochemical Reactor housed

with 16 RPR-300 lamps. The irradiation flask, made of Pyrex, was of 150 ml volume and had a center opening, two side arms and a delivery tube. The irradiations were also performed using a 450-W Hanovia mercury lamp (Type 679A 36) and a quartz immersion well with water condenser. All reaction mixtures were degassed by flushing thoroughly with nitrogen stream for 15 minutes prior to irradiation.

QUANTUM YIELD

Sample irradiation was carried out in a "merry-go-round"⁵ unit. Various filter systems⁶ were used to get 313.0 and 366.0 nm monochromatic light beams. All samples were degassed by three freeze-pump-thaw cycles with cooling in liquid nitrogen and then sealed. The outsides of the sealed cells were cleansed with spectroquality methanol prior to irradiation. The light intensity was measured by benzophenone-benzhydrol actinometry⁷.

DIRECT IRRADIATIONS

1,1'-Dicyclopentenyl. A sample irradiation of a solution of 0.2 ml of 1,1'-dicyclopentenyl and 0.1 ml of hexadecane in 5 ml of hexane was conducted in a quartz tube attached to the quartz immersion probe. The irradiation was interrupted periodically to remove aliquots. A resinous deposit was formed inside the quartz tube. The solution was irradiated for a maximum of 10 hours, after which time no evidence of the photocyclization of the diene was observed.

1,1'-Dicyclohexenyl. A solution of 1 ml of 1,1'-dicyclohexenyl and 0.5 ml of hexadecane (monitoring agent) in 100 ml of hexane was irradiated under standard conditions for a maximum of 24 hours, by which time 80 % of the starting diene was converted to photoproducts (as determined with Aerograph 1520 Gas Chro-

matograph by monitoring the ratio with hexadecane). The irradiation was interrupted periodically to remove aliquots. A resinous deposit formed on the probe. The solvent was removed by Flash-Büchi Evaporator. The residue was analyzed by gas chromatography (20% OV-1 on Chromosorb W-DHCS, 150 °C) and indicated the presence of a major photoproduct amounting to 29% of converted diene. The remaining 51% was a combination of minor products. The yields of these photoproducts were not determined.

Evidence of photoproduct formation was observed by g. c. after one hour of irradiation.

1,1'-Dicycloheptenyl A solution of 1 ml of 1,1'-dicycloheptenyl and 0.5 ml hexadecane in 100 ml of hexane was irradiated under standard conditions for a maximum of 50 hours. A resinous deposit was formed on the probe. Aliquots were removed periodically. Analysis of the irradiated mixture by gas chromatography (20% OV-1 on Chromosorb W-DHCS, 180 °C) showed no evidence of volatile photoproducts, although 85% of starting diene was consumed. After one hour of irradiation, 57% of starting diene was consumed while no photocyclization of the diene was apparent.

SENSITIZED IRRADIATION

1,1-Dicyclohexenyl-Acetophenone Sensitization. A solution of 1 ml of 1,1'-dicyclohexenyl, 1 ml of acetophenone and 0.5 ml hexadecane in 100 ml of benzene was irradiated under standard conditions using a Pyrex filter. The progress of the reaction was monitored by gas chromatography (20% OV-1 on Chromosorb W-DHCS, 185 °C). After five hours, 43% of starting diene had been consumed, of which 21.5% was the cyclobutene photoproduct. Further irradiation showed a pronounced decrease in the yield of the cyclobutene photoproduct. After fifteen hours of irradiation 82% of the

diene was consumed, while only 15% of the cyclobutene product remained. Upon continued irradiation of 25 hours, 93.5% of diene was consumed, 6.5% of cyclobutene photoproduct remained and an additional photo (dimer) product (least volatile) formed to the extent of 26%. A further irradiation of 50 hours showed 95% of diene was consumed, 1.8% of cyclobutene photoproduct remained, and dimer remained relatively unchanged.

On a large scale, 20 ml of 1,1'-dicyclohexenyl, 20 ml of acetophenone and 1 ml of hexadecane in 50 ml of benzene was irradiated for 50 hours, at which time the ratio of diene to photoproduct was approximately 1:1. The solvent was removed by Flash-Büchi Evaporator. The mixture was passed through 200 gr of alumina with pentane which removed the acetophenone. After the solvent was evaporated, the residue was vacuum distilled b. p. 32~34 °C (.03 mm). No fraction was greater than 90% pure.

Only the valence isomeric cyclobutene photoproduct was examined in detail. The pure photoproduct was isolated by gas chromatography (20% OV-1 on Chromosorb W-DHCS, 115 °C). The material had the following properties: molecular weight 162 (mass spectrum), it showed IR (1,700 cm^{-1}) indicative of a substituted non-conjugated double bond (literature value¹⁴ 1,703 cm^{-1}).

Analysis: Calculated for $\text{C}_{12}\text{H}_{18}$: 162.26; C, 88.82; H, 11.18. Found C, 88.72; H, 11.11. Reported data⁹ C, 88.58; H, 11.14.

1,1'-Dicyclohexenyl-Pyrene Sensitization. A solution of 2 gr of pyrene, 2 ml 1,1'-dicyclohexenyl and 0.5 ml hexadecane in 100 ml of benzene was irradiated under standard conditions using a Pyrex filter. Analysis of irradiated solution after 24 hours indicated that 1% of starting diene was consumed and no photoproducts were apparent. Further irradiation of 70 hours

showed at 25 % consumption of starting diene, however, no evidence of the photocyclization was uncovered. The 25 % diene consumption is attributed to dimer as previously indicated.

1,1'-Dicyclohexenyl-Naphthalene Sensitization. A solution of 1 ml of 1,1'-dicyclohexenyl, 1 gr of naphthalene and 0.1 ml hexadecane in 100ml was irradiated under standard conditions using a Pyrex filter. Aliquots were removed periodically. Analysis of the solution by gas chromatography after 16 hours of irradiation indicated that 65 % diene was consumed and 5.4 % of a volatile product formed. Initial photoproduct formation was observed after 6 hours.

1,1'-Dicycloheptenyl-Acetophenone Sensitization. A solution of 0.1 ml 1,1'-dicycloheptenyl, 0.1 ml acetophenone, and 0.05 ml hexadecane in 10 ml of benzene was irradiated under standard conditions in a Pyrex test tube using a Pyrex filter. The solution was monitored by gas chromatography during the irradiation. After 10 hours, gas chromatography indicated a 95% consumption of diene with no evidence of volatile photoproducts.

1,1'-Dicycloheptenyl-Naphthalene Sensitization. A solution of 1 ml of 1,1'-dicycloheptenyl, 1gr of naphthalene and 0.1ml of hexadecane in 100 ml of benzene was irradiated under standard conditions using a Pyrex filter. Monitoring of solution after 10 hours by gas chromatography indicated 42.5 % of starting diene was consumed, and no evidence of volatile photoproduct was uncovered.

1,1'-Dicyclopentenyl-Acetophenone Sensitization A solution of 0.1 ml 1,1'-dicyclopentenyl, 0.1 ml acetophenone and 0.05 ml hexadecane in 5 ml of benzene was irradiated in a Pyrex test tube using a Pyrex filter. The solution was monitored by gas chromatography during the irradiation, and after 8 hours, 70 % of diene was consumed and no evidence of photocyclization

of the diene observed.

Fluorescence. All measurements were carried out in a Hellma Cell on Hitachi Fluorescence Spectrophotometer.

UV spectra were recorded with Cary 14 spectrophotometer.

RESULTS and DISCUSSIONS

The singlet mechanism was tested by the quenching of fluorescence of aromatic sensitizers 1,1'-dicycloalkenyls. The intensity of naphthalene fluorescence is proportionally reduced upon concentration of the dienes as shown in Fig. 1. The results are interpreted in terms of the following kinetic scheme:

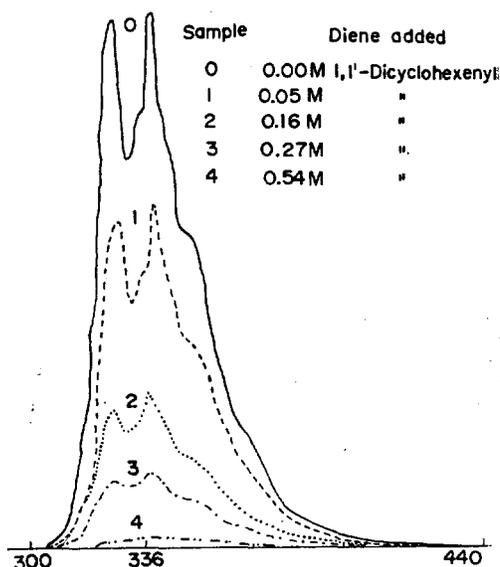
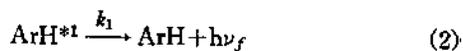
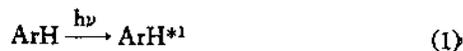


Fig. 1 Fluorescence quenching of naphthalene with 1,1'-dicyclohexenyl.

The quantum yield of fluorescence in the absence of (F_0) and in the presence of (F) diene are given by

$$F_0 = k_1 / (k_1 + k_2 + k_3)$$

$$F = k_1 / (k_1 + k_2 + k_3 + k_4[O])$$

and

$$F_0/F = I_0/I = 1 + \frac{k_4}{k_1 + k_2 + k_3} [O]$$

$$= 1 + k_4 \tau_s [O]$$

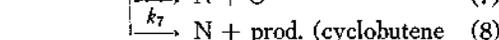
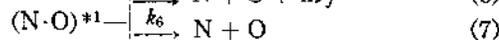
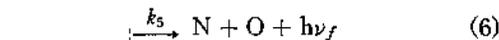
where τ_s = singlet lifetime of naphthalene and $[O]$ = concentration of the diene used.

The fluorescence of aromatic hydrocarbons are quenched very efficiently, even though it is energetically unfavorable. Hammond *et al.*⁸ have reported that dienes quench the fluorescence by accelerating nonradiative decay of the excited aromatic singlet, and obtained straight lines of slope $\tau_s k_4$ in the plot of F_0/F vs. $[O]$.

Plots of I_0/I versus diene concentration for 1,1'-dicyclohexenyl and 1,1'-dicycloheptenyl are shown in Fig. 2 and 3. A straight line of slope $\tau_s k_4$ is expected if the above mechanism is operating. However, non-linear plots were obtained probably due to static quenching or a ground state complex formation between the naphthalene and 1,1'-dicycloalkenyls.

The possible singlet mechanism for fluorescence quenching of naphthalene by 1,1'-dicyclo-

alkenyls include the following:



$$\phi_p = k_4 [O] / (k_1 + k_2 + k_3 + k_4 [O]) \cdot (k_7 / (k_5 + k_6 + k_7))$$

where ϕ_p = Quantum yields of product formation by singlet and since $k_7 / (k_5 + k_6 + k_7)$ is a constant,

$$1/\phi_p = [1 + k_4 [O]] C \text{ or } 1/\phi_p \propto 1/[O]$$

Therefore, we expect a parallel relationship between the fluorescence quenching of naphthalene by 1,1'-dicycloalkenyls and cyclobutene derivative formation.

We have observed no new emission, so route (6) is either unimportant or emission from the complex matches that of the aromatic singlet exactly. Representative solutions of each diene with varying concentrations of naphthalene were examined with the Cary 14 spectrophotometer, where no evidence was obtained to suggest ground state complex formations. It has been noted that new chemical compounds were formed, and reactions represented by equation (8) do occur, although inefficiently. The details of these

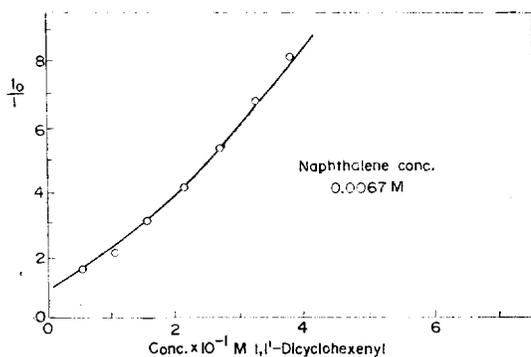


Fig. 2. Quenching of naphthalene fluorescence by 1,1'-Dicyclohexenyl.

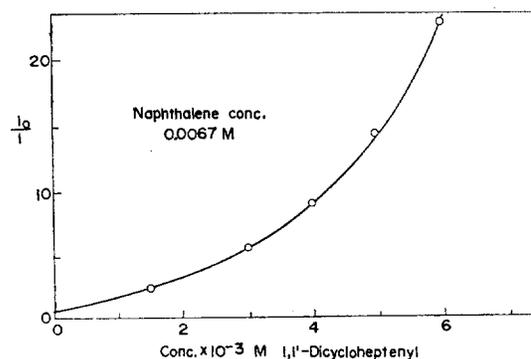


Fig. 3. Quenching of naphthalene fluorescence by 1,1'-Dicycloheptenyl.

photochemical reactions will be reported later. Therefore, static quenching is the most important process responsible for non-linearity in the plot F_0/F vs. $[O]$. Also, no cyclobutene derivative, the reaction product of the excited singlet of 1, 1'-dicyclohexenyl, was detected in a cyclohexane solution of naphthalene and sufficient 1, 1'-dicyclohexenyl (0.54 M) to quench nearly all of the naphthalene fluorescence. The results provide strong evidence that the singlet mechanism is not operating in the cyclobutene formation by sensitization.

The fluorescence quenching of acetophenone was not recorded due to the low fluorescence quantum efficiency of acetophenone. Additional fluorescence studies using pyrene produced no

quenching of its fluorescence by 1, 1'-dicyclohexenyl, probably due to the structural characteristics of pyrene.

Results for the direct and sensitized reactions are summarized in Tables 1~4. In most cases photolysis was carried out under conditions such that 50 % of the diene was consumed. Photolysis of 1, 1'-dicyclohexenyl by both direct and acetophenone sensitized irradiation yielded the valence isomeric cyclobutene as reported by Crowley^{1d} and Dauben *et al.*^{1a, b} Comparison of the direct irradiation and acetophenone sensitization of 1, 1'-dicyclohexenyl clearly indicated the higher efficiency of photocyclization in sensitized reactions. After 5 hours of irradiation, the latter produced 21.5 % of cyclobutene pho-

Table 1. Photolysis of dienes by direct irradiation at 253.7 nm.

| Diene* | Irradiation time | % Conversion | % Photoproduct cyclobutene |
|-------------------------|------------------|--------------|----------------------------|
| Dicyclopentenyl 0.28 M | 10 hrs | 51.0 | none observed |
| Dicyclohexenyl 0.06 M | 1 hrs | 34.0 | 7.9 |
| Dicyclohexenyl 0.06 M | 3 hrs | 54.6 | 13.6 |
| Dicyclohexenyl 0.06 M | 5 hrs | 65.2 | 18.2 |
| Dicyclohexenyl 0.06 M | 10 hrs | 75.7 | 23.2 |
| Dicyclohexenyl 0.06 M | 24 hrs | 84.6 | 29.5 |
| Dicycloheptenyl 0.052 M | 1 hrs | 57.1 | none observed |
| Dicycloheptenyl 0.052 M | 10 hrs | 78.5 | none observed |
| Dicycloheptenyl 0.052 M | 50 hrs | 84.1 | none observed |

* Molarity values are approximate.

Table 2. Photolysis of dienes by naphthalene sensitized irradiation at 313.0 nm.

| Diene* | Irradiation time | % Conversion | % Photoproduct cyclobutene |
|-------------------------|----------------------|--------------|----------------------------|
| Dicyclopentenyl | no data was recorded | | |
| Dicyclohexenyl 0.06 M | 2 hrs | 14.7 | none observed |
| Dicyclohexenyl 0.06 M | 4 hrs | 24.4 | none observed |
| Dicyclohexenyl 0.06 M | 6 hrs | 31.0 | 0.45 |
| Dicyclohexenyl 0.06 M | 8 hrs | 39.5 | 1.02 |
| Dicyclohexenyl 0.06 M | 16 hrs | 64.5 | 5.43 |
| Dicyclohexenyl 0.06 M | 20 hrs | 74.0 | unchanged |
| Dicycloheptenyl 0.052 M | 5 hrs. | 30.5 | none observed |
| Dicycloheptenyl 0.052 M | 10 hrs | 42.5 | none observed |
| Dicycloheptenyl 0.052 M | 57 hrs | 79.5 | none observed |

* Molarity values are approximate.

Table 3. Photolysis of dienes by acetophenone sensitized irradiation at 313.0 nm.

| Diene* | Irradiation time | % Conversion | % photoproduct cyclobutene | Adduct |
|-------------------------|------------------|--------------|----------------------------|--------|
| Dicyclopentenyl 0.04 M | 2 hrs | 25.5 | none observed | — |
| Dicyclopentenyl 0.04 M | 5 hrs | 61.8 | none observed | — |
| Dicyclopentenyl 0.04 M | 8 hrs | 69.1 | none observed | — |
| Dicyclohexenyl 0.06 M | 1 hrs | 10.7 | 6.4 | — |
| Dicyclohexenyl 0.06 M | 5 hrs | 42.8 | 21.5 | — |
| Dicyclohexenyl 0.06 M | 10 hrs | 63.7 | 19.35 | — |
| Dicyclohexenyl 0.06 M | 15 hrs | 81.8 | 15.0 | — |
| Dicyclohexenyl 0.06 M | 25 hrs | 93.5 | 6.5 | 26.0 |
| Dicyclohexenyl 0.06 M | 50 hrs | 95.0 | 1.8 | 27.6 |
| Dicycloheptenyl 0.052 M | 1 hrs | 68.1 | none observed | — |
| Dicycloheptenyl 0.052 M | 3 hrs | 89.1 | none observed | — |
| Dicycloheptenyl 0.052 M | 5 hrs | 96.0 | none observed | — |

Table 4. Photolysis of dienes by pyrene sensitized irradiation at 313.0 nm.

| Diene* | Irradiation time | % conversion | % Pyrene converted |
|-----------------------|------------------|--------------|--------------------|
| Dicyclohexenyl 0.12 M | 24 hrs | <1 | <1 |
| Dicyclohexenyl 0.12 M | 70 hrs | 24 | 40 |

*Molarity Values are Approximate

toproduct, whereas the former, after the same irradiation period, yielded 13.6 % of photoproduct. Although upon continued direct irradiation the amount of photoproduct increased, some secondary side reactions were initiated. It should also be noted that after 25 hours of the sensitized irradiation, the acetophenone was gradually consumed in the reaction and a high molecular weight compound, probably oxetane was formed between cyclobutene derivative and acetophenone sensitization can be attributed to efficient triplet energy transfer to the 1,1'-dicyclohexenyl molecule.

The valence isomeric cyclobutene was obtained in about 90 % purity by careful fractional distillation of the acetophenone sensitization irradiation mixture. In order to obtain pure material, the distillate had to be purified by tedious preparative gas chromatography. Its physical and chemical properties agreed with data reported by Dauben^{6b}.

Additional sensitized photolysis of 1,1'-dicyclohexenyl by naphthalene and pyrene presented surprising results. The latter (Table 4) failed to form the cyclobutene photoproduct, and more surprisingly, no reaction occurred and the starting material remained unchanged after an irradiation time of 24 hours. Continued irradiation for a maximum of 70 hours resulted in consumption of both diene and sensitizer indicative of adduct formation. No volatile photoproducts were observed. The former (Table 2) provided a volatile photoproduct, apparently the cyclobutene derivative, although inefficiently. Irradiation after 6 hours indicated presence of 0.45 % photoproduct. Conversely, the acetophenone sensitization after 1/6 of the time afforded 6.4 %. The inefficient cyclobutene formation by naphthalene sensitization of 1,1'-dicyclohexenyl is consistent with previously reported data on fluorescence quenching, and indicates that triplet energy transfer is not involved in photocyclization. In

addition, failure of triplet sensitization by naphthalene is derived from the triplet-state energy of sensitizer employed. The triplet-state energy of naphthalene is only 60.9 kcal/mole, pyrene is 48.7 kcal/mole, whereas acetophenone and benzophenone are 74 kcal/mole and 68.5 kcal/mole respectively. Preliminary sensitization of 1,1'-dicyclohexenyl using benzophenone yielded the cyclobutene photoproduct after 1 hour irradiation.

In contrast to the direct and sensitized irradiation of 1,1'-dicyclohexenyl, no volatile products indicative of photocyclization were obtained from 1,1'-dicyclopentenyl, and 1,1'-dicycloheptenyl although the efficient diene consumption was observed in each case. Similar results were obtained in the photolysis of 1,1'-dicycloöctenyl⁹. Crowley^{1d} reported no cyclobutene formation in the irradiation of 1,1'-dicyclopentenyl which is consistent with our data.

The failure of the direct and sensitized reaction in the attempted valence isomerization of 1,1'-dicyclopentenyl could be attributed to severe strain associated with a five-membered ring closure. In seven and eight membered rings, the twisted triplet may be quite stable and easily formed, followed by *cis-trans* isomerization or by dimerization without giving cyclobutene derivatives.

Results for benzophenone sensitization of 1,1'-

dicyclohexenyl are reported in Table 5. There is a significant variation in the quantum yields with concentration. In general, no variation is observed, but if the product comes from exciplex between benzophenone triplet and 1,1'-dicyclohexenyl, then a linear relationship is expected in the plot of $1/\phi$ vs. $1/[O]$. Fig. 4 shows a plot of $1/\phi$ vs. $1/[O]$.

The non-linearity indicates that no excited triplet complex is formed in the sensitization of 1,1'-dicyclohexenyl.

Low temperature infrared spectroscopy failed to uncover presence of the *trans* double bond in 1,1'-dicyclohexenyl.

Cyclobutene formation by sensitized photolysis is not singlet state directed but occurring from higher energy states, probably a triplet state. It is suggested from the above results that higher energy triplet state, probably planar *s-cis* triplet state rather than twisted triplet state, is responsible for the cyclobutene formation in sensitized reactions of 1,1'-dicyclohexenyl.

Other photocyclization routes for cyclobutene derivative formation including twisted triplet state and thermal reaction from *trans* double bond formed from triplet state are repudiated based on experiments of seven and eight-membered rings as well as naphthalene sensi-

Table 5. Quantum Yields for Benzophenone Sensitization of 1,1'-Dicyclohexenyl at 313.0 nm.

| [O] Concn., <i>M</i> | 1/[O], <i>M</i> | [O] Conversion, <i>M</i> | Photocyclization | 1/ ϕ |
|----------------------|-----------------|--------------------------|------------------|-----------|
| 0.1 | 10.1 | 0.0063 | 0.0018 | 847.0 |
| 0.09 | 11.1 | 0.00914 | 0.00172 | 582.0 |
| 0.08 | 12.5 | 0.0071 | 0.00134 | 746.0 |
| 0.06 | 16.7 | 0.0116 | 0.002185 | 458.0 |
| 0.05 | 23.7 | 0.01095 | 0.00206 | 485.0 |
| 0.03 | 33.3 | 0.01083 | 0.00204 | 490.0 |
| 0.01 | 100.0 | 0.0079 | 0.00150 | 668.0 |

i) $I=8.847 \times 10^{-6}$ Einsteins/min.
 ii) Irradiations were conducted in benzene solution
 iii) Benzophenone-benzhydrol used as actinometer

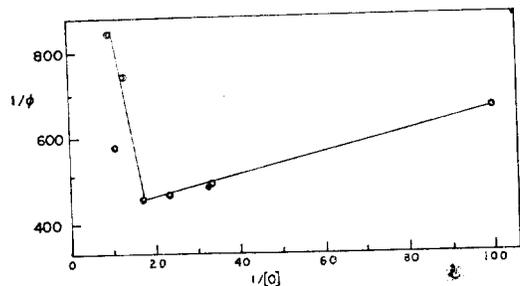


Fig. 4. Plot of $1/(\text{quantum yield})$ vs. $1/(\text{diene conc.})$ for the benzophenone sensitization of 1,1'-dicyclohexenyl at 313 nm.

zation and infrared results.

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