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PUTATIVE ELECTROCYCLIC REACTION OF CYCLOBUTENE RADICAL CATION

1,2-DIPHENYL-3,3,4,4-TETRAMETHYLCYCLOBUTENE

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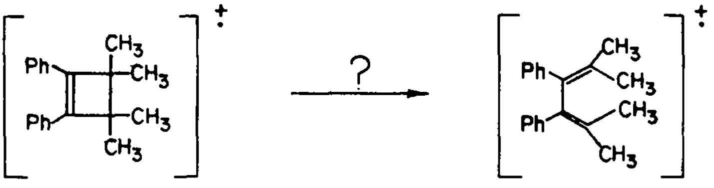
Abstract—The thermal and photochemical reactions of 1,2-diphenyl-3,3,4,4-tetramethylcyclobutene were investigated. Direct irradiation of this hydrocarbon leads to inefficient cyclization to a dehydrophenanthrene. Irradiation in the presence of diethyl terephthalate gives the cyclobutane radical cation and the ester radical anion. These intermediates were observed by laser flash photolysis. The cyclobutene radical cation does not rearrange rapidly to the radical cation of 3,4-diphenyl-2,5-dimethyl-2,4-hexadiene. This conclusion is supported by analysis of the flash photolysis results, examination of cyclic voltammetric behavior, and by observation of the EPR spectra of these radical cations formed by radiolysis of frozen Freon solutions of the neutral hydrocarbons.

Electrocyclic reactions of ground and excited state hydrocarbons are well known. These transformations form the basis upon which much of modern organic chemistry is built.[1] The corresponding reactions of radical ions are much less thoroughy understood. Indeed, it is not entirely certain that there will be broad generalizations coming from theory or experiment that will codify the reactions of these odd-electron intermediates. Herein we describe the results of our investigation of the properties of a substituted cyclobutene radical cation ($CB^{\dot{+}}$). In particular, we have examined the questions concerning its putative electrocyclic rearrangement to a butadiene radical cation ($BD^{\dot{+}}$) in fluid solution (Eq. 1).



(1)

$CB^{\dot{+}}$

Theory offers some advice on the expected reactions of cyclobutene radical cations. Haselbach *et al.* [2] clearly codified the general considerations that apply to analysis of the electrocyclic rearrangements of radical ions. They identified three groups of reactions differentiated by the type of correspondence between orbital and state symmetries for the reactant and product ions. Application of these concepts led to the general conclusion that there will be a barrier for the conversion of a cyclobutene radical cation in its electronic ground state to the isomeric 1,3-butadiene radical cation. However, the analysis showed that this barrier might be considerably smaller than for the corresponding neutral species. Similar conclusions have been described more recently by Dunkin and Andrews[3] who also analyzed the consequences of symmetry constraints on these reactions. Bauld and coworkers suggest that the barrier for direct rearrangement of cyclobutene radical cation is so high (>30 kcal mol^{-1}) that a two-stage process passing through a cyclopropylcarbinyl radical cation is the preferred path.[4] It is of relevance to results discussed later to note here that rearrangement of an excited state of the cyclobutene radical cation to the ground state of the butadiene radical cation is predicted by both Haselbach and Dunkin to occur with little or no barrier.

There has been experimental investigation of the reaction of cyclobutene radical cations. Much of this work has been done in the gas phase using mass spectrometric techniques. Comparison of the experimental findings with the theoretical predictions leads to some informative contrasts.

The initial studies of the cyclobutene radical cations in the gas phase centered on dicarboxylic acid derivatives and led to contradictory conclusions.[5] More recent efforts have focused on the parent system and several of its simpler derivatives. Using ion cyclotron resonance (ICR) techniques to examine cyclobutene radical cation, Gross and Russel conclude that this species rearranges efficiently to the 1,3-butadiene radical cation.[6] Various procedures were used to demonstrate that this reaction originates with the electronic ground state of the ion. Calculations from the ion transport time of the spectrometer lead to a conservative estimate of the activation energy for ring opening of cyclobutene radical cation of less than 7 kcal mol^{-1}.

Similarly, using collisionally activated dissociation (CAD) to examine the behavior of 1-phenylcyclobutene and 3-phenylcyclobutene, Dass and Gross conclude that the radical cation of the former rearranges to 1-phenyl-1,3-butadiene and the latter, perhaps, to 2-phenyl-1,3-butadiene radical cations.[7] The energy barrier for these reactions was estimated to be between 7 and 14 kcal mol^{-1} for the 1-substituted isomer and too small to detect for the 3-phenylcyclobutene radical cation. An essentially identical conclusion is obtained from the Fourier transform mass spectrometric (FTMS) study of 1-methyl- and 3-methylcyclobutene radical cations.[8] That is, the ion from the 1-methyl substituted example rearranges with an activation barrier of less than 14 kcal mol^{-1}, and the corresponding value for the 3-methyl case is claimed to be less than 4 kcal mol^{-1}. These studies seem to indicate that the position of substitution has a remarkable effect on the rearrangement of a cyclobutene radical cation to the isomeric butadiene derivative. Also, in the unsubstituted and 3-substituted examples, the barrier for isomerization appears to be much smaller than that predicted from applications of theory.

The rearrangement of the cyclobutene radical cation to butadiene has also been probed using radiolysis techniques in frozen media.[9] Under these conditions, no rearrangement could be observed at temperatures up to 90 K where the ions were irreversibly consumed. This finding can be viewed as consistent with the ICR measurements that give an activation energy for this reaction of less than 7 kcal mol^{-1}. With this barrier, the cyclobutene radical cation would have a half-life of *ca* 1 h at 90 K. However, the low-temperature experiments are equally consistent with a barrier much greater than 7 kcal mol^{-1}.

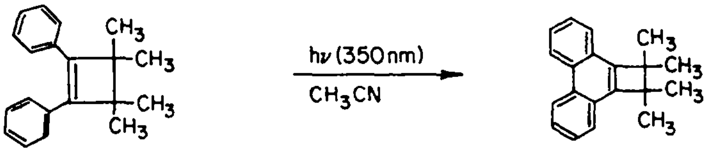
Kirschenheuter and Griffin[10] have studied the chemistry of $\mathrm{CB}^{\dot{+}}$ (Eq. 1) at room temperature in fluid solution. In these experiments $\mathrm{CB}^{\dot{+}}$ was generated by photostimulated electron transfer to an optically excited acceptor. When this reaction is carried out in the presence of dissolved O_2, the products obtained are indicative of trapping of the $\mathrm{CB}^{\dot{+}}$ before it has rearranged. The mass spectroscopic results seem to indicate that the alkyl substituents on CB should greatly lower the barrier to rearrangement. Yet, the product studies indicate that the electrocyclic rearrangement is a relatively slow process (if it exists at all). We undertook the study of $\mathrm{CB}^{\dot{+}}$ by laser spectrophotometric techniques, among others, to gain additional insight into the chemical properties of this radical cation.

RESULTS AND DISCUSSION

Thermal and photochemical reactions of CB

Thermolysis of CB leads cleanly to BD. This reaction has a half-life of *ca* 30 min at 170° which corresponds to a barrier for reaction ($\Delta G^{\neq}$) of *ca* 25 kcal mol^{-1}. This value is consistent with predictions made from application of substituent factors to the reaction of related systems.[11]

Photolysis of CB in deoxygenated acetonitrile leads to the phenanthrene (PHEN) derivative expected based on analogy with *cis*-stilbene photochemistry[12] in nearly quantitative yield (Eq. 2). The quantum yield for this reaction, however, is very low ($6.8 \pm 1.5 \times 10^{-5}$). This indicates that most of the excited states of CB return to the ground state with no net chemical change.



CB PHEN (2)

One of the processes that regenerates CB is fluorescence. The emission spectrum of CB is shown in Fig. 1. The fluorescence of CB is quenched by diethylterephthalate (DET). A Stern–Volmer plot of this reaction in acetonitrile gives a slope 54 M^{-1} which indicates that DET is an effective quencher of CB^{*1}. We anticipated this finding since the reduction potential of DET is *ca* −1.1 V vs SCE (irreversible) and calculations using the Weller equation indicate a free energy of electron transfer for this reaction (ΔG_{ET}) of −31 kcal mol^{-1}.[13] This finding predicts a diffusion limited rate constant for electron transfer quenching (*ca* 2×10^{10} M^{-1} s^{-1}) and thus the singlet lifetime for CB of 2.7 ns is estimated from the Stern–Volmer slope.

Irradiation of CB in oxygen-free acetonitrile solution containing 1.0 M DET (98% quenching of CB^{*1}) leads to its very slow consumption ($\Phi = 1.7 \pm 0.4 \times 10^{-4}$) and the formation of a low yield of the phenanthrene after prolonged irradiation. It is likely that the phenanthrene formed in this reaction arises exclusively from the 2% of the CB^{*1} that is not quenched by DET.

Photolysis of CB in oxygen-free methanol containing 6.7×10^{-2} M DET (80% quenching of CB^{*1})

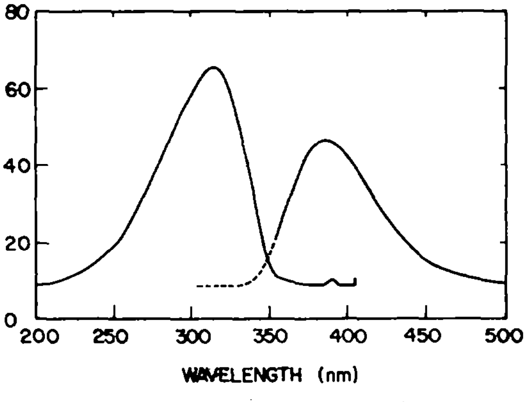
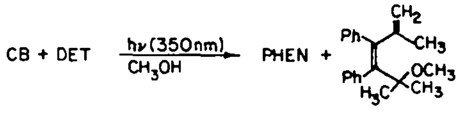


Fig. 1. Fluorescence emission (right) and fluorescence excitation spectrum (left) of CB (5.7×10^{-5} M) in CH_3CN.

leads to the phenanthrene and to some methanol incorporation products one of which we identify as a ring-opened product (Eq. 3). It is important to note that this product is not obtained when BD is used to quench the excited singlet state of 9,10-dicyanoanthracene in methanol. This result indicateds that the ring-opened product is not formed from $BD^{+\cdot}$. This conclusion is strongly supported by the results of some nanosecond laser spectroscopic experiments.



(3)

Pulsed laser spectroscopy

Irradiation of CB with the output of a nitrogen laser (337 nm, 13 ns, 7.0 mJ)[14] in acetonitrile containing 1.0 M DET gives the transient spectrum shown in Fig. 2. There are several features of this spectrum that can be easily recognized. First, the bands at 370 and 535 nm are associated with $DET^{-\cdot}$. The spectrum of the dimethylterephthalate radical anion is well known and quite similar to that assigned to $DET^{-\cdot}$.[15] Moreover, as expected, these bands are quenched very rapidly when the irradiation is performed in oxygenated solutions. The other feature in the transient spectrum has an apparent maximum at 490 nm. We assign this band to the $CB^{+\cdot}$. This assignment rests on three observations. First, although electron transfer quenching is *ca* 98% efficient under these conditions, only about one CB of every 5000 excited is converted to a product. Thus, most of the $CB^{+\cdot}$ formed must receive an electron and return to CB before any net irreversible chemistry occurs. Second, the chemical reactions observed in the presence of O_2 are those of $CB^{+\cdot}$.[10] Third, the spectrum resembles closely that reported for *cis*-stilbene radical cation,[16] a structure obviously related to $CB^{+\cdot}$. These results are summarized in Eq. 4.

$$CB + DET \longrightarrow CB^{+\cdot} + DET^{-\cdot} \qquad (4)$$

Assignment of structures based mainly on absorption spectroscopy is never unequivocal. For example, in the present case, the absorption maximum at 490 nm could be due to a product formed reversibly from $CB^{+\cdot}$. One candidate for such a species would be the dihydrophenanthrene radical cation formed from cyclization of $CB^{+\cdot}$. To test this possibility we carried out the photolysis of CB and BD in an acetonitrile solution containing both 9,10-dicyanoanthracene (DCA) and $CuSO_4 \cdot 5H_2O$. Cupric ions are known to intercept intermediate radical cations[17] and DCA^{*1} can oxidize CB to its radical cation. If $CB^{+\cdot}$ rearranges rapidly to the dihydrophenanthrene radical cation, then its reaction with cupric ion should lead to isolation of the phenanthrene in high yield. This is not the case, the phenanthrene remains a minor product under these conditions. Moreover, it is significant that reaction of BD under these conditions gives entirely different products than does CB. This indicates that no common intermediates are formed by oxidation of these hydrocarbons.

We generated $BD^{+\cdot}$ by irradiation of 1-cyanopyrene (CPY) in the presence of BD for comparison with the spectrum of $CB^{+\cdot}$. As expected, BD is an efficient quencher of CPY^{*1} in acetonitrile. The transient spectrum obtained by irradiation with the nitrogen laser is shown in Fig. 3. The species absorbing at 495 nm is assigned to $CPY^{-\cdot}$ by comparison with the spectrum of this ion that has been reported previously.[18] We assign the band at 410 nm to the $BD^{+\cdot}$ or to some product resulting from the intramolecular rearrangement of $BD^{+\cdot}$. An important point is that this band is totally absent from the spectra generated by oxidation of CB. Thus, under these conditions, rearrangement of $CB^{+\cdot}$ to $BD^{+\cdot}$ does not compete with the other reactions of $CB^{+\cdot}$ (mainly back electron transfer to generate CB).

In an attempt to increase the rate of rearrangement of $CB^{+\cdot}$ to $BD^{+\cdot}$, the temperature of the reaction was raised from room temperature to 180°. Even at this temperature, there is no evidence for the electrocyclic rearrangement of $CB^{+\cdot}$ to $BD^{+\cdot}$. These results allow us to estimate a lower limit to the activation barrier ($\Delta G^{\neq}$) for this rearrangement of *ca* 16.5 kcal mol^{-1}.

Sweep-rate-dependent cyclic voltammetry of CB *and* BD

CB exhibits a one-electron oxidation wave at *ca* 1.59 V vs SCE in acetonitrile solution containing $(n\text{-}Bu)_4NClO_4$ as supporting electrolyte. The shape of this wave is sweep rate dependent (Fig. 4). At fast scan rates, 50 V s^{-1}, the highest cathodic peak current ($i_{pa} = 3.2 \times 10^{-4}$ A, $i_{pc} = 2.2 \times 10^{-4}$ A) is

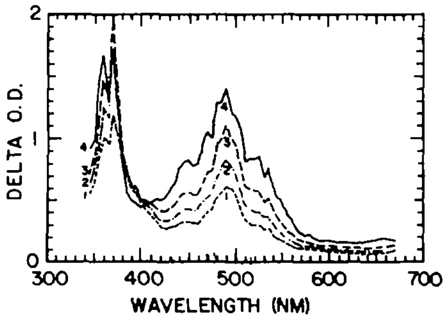


Fig. 2. Transient spectra obtained from pulse irradiation of CB in acetonitrile containing 1.0 M DET: (1) 1400 ns after the laser flash; (2) 900 ns after the laser flash; (3) 500 ns after the laser flash; (4) 100 ns after the laser flash.

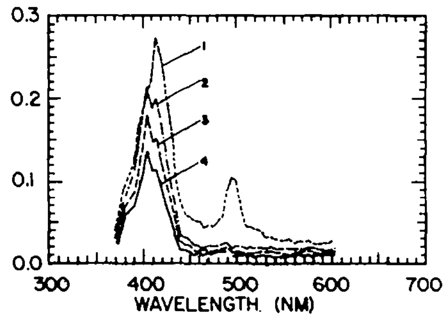


Fig. 3. Transient spectra obtained from pulse irradiation of CPY in acetonitrile containing 0.042 M BD: (1) 190 ns after the laser flash; (2) 600 ns after the laser flash; (3) 900 ns after the laser flash; (4) 1600 ns after the laser flash.

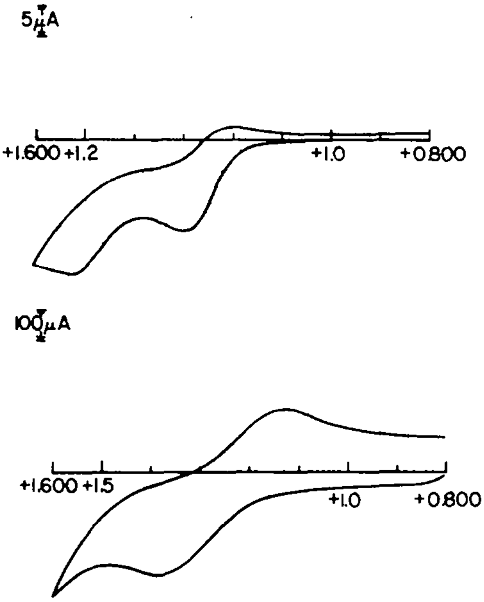


Fig. 4. Cyclic voltammogram of CB (0.01) in CH_3CN (0.1 M tetrabutylammonium perchlorate as supporting electrolyte) and Ag/0.01 M $AgNO_3$ in CH_3CN as reference electrode: upper trace, 100 mV s^{-1} scan rate; lower trace, 5 V s^{-1} scan rate.

observed. Under comparable conditions, BD exhibits an irreversible oxidation wave at *ca* 1.7 V that shows no signs of reversible behavior even at the highest sweep rates.

These electrochemical findings are exactly consistent with the chemical and spectroscopic results described above. The CB$^{\dot{+}}$ is reasonably stable even on a cyclic voltammetric time scale. There is no indication that it is converted to BD$^{\dot{+}}$.

It is not possible to identify the nature of the chemical process that consumes CB$^{\dot{+}}$ in the electrochemical experiments we have done. However, the dependence of i_{pc} on sweep rate does allow an estimate of the rate of the processes that compete with the hoped for electrocyclic reaction.[19] This permits calculation of the minimum activation barrier for the conversion of CB$^{\dot{+}}$ to BD$^{\dot{+}}$ of 15.9 kcal mol^{-1}. This estimate is in close agreement with that obtained from the laser spectroscopic measurements.

Radiolysis of BD *and* CB

γ-Radiolysis of $CFCl_3$ solutions of CB or BD at 77 K generates species that are easily detected by EPR spectroscopy at temperatures ranging from 7 to about 145 K. It has been demonstrated that γ-irradiation of frozen Freon solutions is an efficient method for generation of cation radicals of solute molecules.[20,21]

The EPR spectra observed at 118–145 K from the irradiated BD solutions are indicative of a paramagnetic species with hyperfine coupling to 12 protons. The corresponding spectra from the CB solutions are more complex. However, it is clear simply from inspection of the spectra that the species generated by radiolysis of CB solutions in $CFCl_3$ are not transformed to the one generated from radiolysis of BD in $CFCl_3$ or to any other common intermediate. Further work is underway to investigate a possible influence of the matrix on this transformation.

CONCLUSIONS

The properties of CB$^{\dot{+}}$, in particular its tendency toward rearrangement to BD$^{\dot{+}}$, are revealed in each of the four groups of experiments we carried out. These experiments, product studies, laser spectroscopy, cyclic voltammetry and radiolysis all lead to the same conclusion. That is, there is a large barrier, more than 16 kcal mol^{-1}, for the electrocyclic rearrangement of CB$^{\dot{+}}$ to BD$^{\dot{+}}$.

This finding has significance in several regards. First, theory readily anticipates the existence of the barrier. Our results confirm this prediction. The analysis of state symmetry correlation diagrams indicates that the barrier for the neutral species should be greater than for the radical cation. Our findings are also consistent with this forecast. But, for CB, the barrier reduction can be no more than *ca* 10 kcal mol^{-1}.

It is instructive to compare our results with those obtained in the gas phase using mass spectrometric techniques. We chose to study CB$^{\dot{+}}$ in part because the gas phase measurements seemed to indicate that its rearrangement to BD$^{\dot{+}}$ should be fast and uncomplicated. In particular, the permethylation of the 3- and 4-carbons of CB should eliminate deprotonation as a competing reaction path and should have facilitated the desired rearrangement both on electronic and steric grounds. The results indicate that despite these advantages, CB$^{\dot{+}}$ does not rearrange rapidly to BD$^{\dot{+}}$.

There are several possible explanations for the different behavior of cyclobutene radical cations in gas and solution phases. An obvious choice is that the structures that have been investigated are not identical. In particular, the example we studied is substituted with two phenyl groups on the double bond. The cyclobutenes examined mass spectrometrically have at most one of these groups. Two phenyl groups can provide resonance stabilization of both the "radical" and "cation" portions of CB$^{\dot{+}}$. A second difference, of course, is the phase. It seems reasonable that CB$^{\dot{+}}$ will be stabilized by solvation. Acetonitrile may be particularly beneficial in this regard. Finally, the different behavior may be associated with the different internal energies the ions have when they are created. The photostimulated electron transfer in solution probably leads to CB$^{\dot{+}}$ in its electronic and vibrational ground state. It is possible that the ions in the gas phase have some excess energy. With the results currently in hand, these explanations cannot be distinguished. We plan additional experiments to expand the understanding of electrocyclic reactions of radical cations.

EXPERIMENTAL

General. ^{1}H-NMR spectra were recorded on a Varian Associates EM-390 spectrometer or XL-200 Fourier transform spectrometer in $CDCl_3$ with TMS as internal standard. IR absorption spectra were recorded on a Perkin–Elmer model 1320 or 237 B IR spectrophotometer. Low-resolution electron-impact MS were obtained on a Varian MAT CH-5 and GCMS on a VG 7070E mass spectrometer. Analytical and prep GC were performed on a Varian Associates Model 3700 gas chromatograph equipped with a linear temperature programmer, flame ionization detector, and Hewlett–Packard 3390 A integrator. Analyses were carried out on a 3 ft glass column containing 5% OV-101 on Chromosorb W-H.P (100–120 mesh) and prep experiments were carried out on a 6 ft glass column containing 5% SE-30 on GasChrom Q (100–120 mesh). Temperature programs were run with initial temp at 120° for 9 min, then increasing to 220° at 7°C min^{-1} for analytical experiments. Photolyses were carried out in Pyrex vessels in a Rayonet photoreactor equipped with Hanovia 350 nm lamps. Oxygen was removed by purging the soln with argon for 10 min at 0°. The solns were continuously stirred during the photolysis.

For the low temp EPR experiments, solns of BD and CB (5×10^{-3} M in $CFCl_3$) were sealed on a vacuum line in Suprasil tubes (2.4 mm i.d.). The samples were irradiated at 77 K in a ^{60}CO γ-source with doses of about 0.45 Mrad. The frozen, irradiated samples were quickly transferred without thawing to a variable temp cryostat (Air Products Helitran model CTR-110) mounted in the EPR cavity. The EPR spectra were recorded on a Varian E9 spectrometer.

Materials. Acetonitrile (Aldrich Gold Label) was refluxed for 4 h over CaH_2 and distilled under N_2. Spectral grade MeOH (Fischer Scientific) was used as received. 9,10-Dicyanoanthracene (Eastman) was recrystallized from EtOH. Diethyl terephthalate (Tokyo Kasei) was recrystallized twice from n-hexane. Anhyd diethyl ether (Mallinckrodt) was used as received. Benzonitrile (Eastman) was washed with conc HCl and predried over K_2CO_3 and distilled from P_2O_5 at reduced pressure.

Methods. Fluorescence quenching data were obtained from argon-purged solns of 1,2-diphenyl-3,3,4,4-tetramethylcyclobutene (5.7×10^{-5} M) and diethylterephthalate (0–0.3 M), and 9,10-dicyanoanthracene (5.6×10^{-5} M) and 3,4-diphenyl-2,5-dimethyl-2,4-hexadiene ($0–7.2 \times 10^{-3}$ M) by using a Farrand Mark I spectrofluorometer. Quantum yields for the formation of phenanthrene derivative and the disappearance of starting cyclobutene derivative were determined for argon- or oxygen-purged solns of DET (1.0 M) and CB (2.1×10^{-3} M) irradiated with an Oriel 200 W Xe–Hg lamp through Corning 7–60 glass filter and 7.5 cm path length soln filter of K_2CrO_4 aq (306–358 nm). Light intensities were determined by Aberchrom 540 actinometry.[23] Solutions were analyzed for product formation at low (< 10%) conversion of CB to phenanthrene derivative by using GC described above with n-pentadecane as internal standard. Cyclic voltammetric measurement of redox potentials were done in acetonitrile soln, with 0.1 M tetrabutylammonium perchlorate as supporting electrolyte and Ag/0.01 M $AgNO_3$ in acetonitrile as reference electrode. Solutions were purged with dry N_2 for several minutes prior to measurement.

Preparation of 1,2-*diphenyl*-3,3,4,4-*tetramethylcyclobutene* (CB). Diphenylacetylene 2.00 g (11.3 mmol), tetramethylethylene 10.0 ml (84.1 mmol) and 150 ml of anhyd ether were placed in a Pyrex vessel. After purging with N_2 for 0.5 h, the mixture was irradiated with a Hanovia 450 W medium-pressure Hg lamp for 5 h. The soln was concentrated *in vacuo* to give 2.80 g of a dark yellow solid. The residue was dissolved in n-hexane and chromatographed on 50 g of silica gel (Brinkmann). Elution with n-hexane gave CB which was recystallized from MeOH (1.50 g, 51%, m.p. 81.5–92°) lit.[22] m.p. 92–98° as colorless needles.

Preparation of 3,4-*diphenyl*-2,5-*dimethyl*-2,4-*hexadiene* (BD). 1,2-Diphenyl-3,3,4,4-tetramethylcyclobutene (CB) (1.09 g, 4.2 mmol) was thermolyzed at 170° under argon for 3.5 h to give a light yellow oil. The oil was dissolved in 10 ml of MeOH and cooled in an ice bath. Recrystallization of the deposited solid from MeOH gave 375 mg (35%) of a BD derivative as colorless needles: m.p. 39.5–40°; ^{1}H-NMR ($CDCl_3$): δ 1.73 (6H, s), 1.92 (6H, s), 6.8–7.3 (10H, m); IR (oil): 3077, 3051, 3027, 3018, 2992, 2907, 2851, 1597, 1489, 1440, 1369, 1067, 1009 cm^{-1}; MS (70 eV) *m/e* (rel. intensity): 262 (100), 247 (42), 232 (23), 219 (98), 204 (21); UV (CH_3CN): λ 295 nm (end absorption). (Found: C, 91.57; H, 8.65%. Calc for $C_{20}H_{22}$: C, 91.57; H, 8.45%.)

Photolysis of 1,2-*diphenyl*-3,3,4,4-*tetramethylcyclobutene*. CB (26 mg, 0.10 mmol) was dissolved in 3 ml of acetonitrile and then irradiated with a Rayonet photoreactor equipped with 350 nm lamps for 12 h. Evaporation of the solvent *in vacuo* gave a light yellow solid. The solid was dissolved in n-hexane and chromatographed on silica gel (Brinkmann). Elution with n-hexane gave 19 mg (73%) of starting material and 6 mg (23%) of 3,3,4,4-tetramethylcyclobuta[1.2-*l*]phenanthrene which was recrystallized from MeOH as colorless needles: m.p. 177.5–178°; ^{1}H-NMR ($CDCl_3$: δ 1.52 (12H, s), 7.45–7.81 (6H, m), 8.63–8.82 (2H, m); IR ($CHCl_3$): 2979, 1044 cm^{-1}; MS (10 eV) *m/e* (rel. intensity): 260 (43), 245 (14), 230 (9), 218 (18), 217 (100), 203 (19); UV λ (ε): 210 (28,000), 221 (19,000), 246 (sh, 43,000), 254 (51,000), 270 (14,000), 278 (9200), 289 (8900), 302 (12,000), 324 (630), 339 (960), 356 (1200). (Found: C, 92.59; H, 7.8%. Calc for $C_{20}H_{20}$: C, 92.26; H, 7.98%.)

Photolysis of 1,2-*diphenyl*-3,3,4,4-*tetramethylcyclobutene in the presence of DET in methanol solution*. A 150 ml methanolic soln containing 101 mg (0.38 mmol) of CB and 2.22 g (9.99 mmol) of diethyl terephthalate was irradiated with a Hanovia 450 W medium-pressure Hg lamp through a uranium glass filter sleeve (> 330 nm) for 15 h under argon. After evaporation of the solvent *in vacuo*, the residue was dissolved in n-hexane and chromatographed on silica gel (Woelm 32–63). Elution with n-hexane gave the phenanthrene derivative (13 mg, 13%), recovered DET (1.94 g), and 3,4-diphenyl-2,5-dimethyl-5-methoxy-1,4-hexadiene (7 mg, 6%) as a colorless oil: ^{1}H-NMR ($CDCl_3$): δ 1.19 (6H, s), 1.19 (3H, d of d, J = 1, ~0.3 Hz), 3.22 (3H, s), 4.82 (1H, d of d, J = 1.0, 1.0 Hz), 4.95 (1H, d of d, J = 1.7, ~0.3 Hz), 6.95–7.18 (10H, m); MS found *m/e* 292.1806 (calc $C_{21}H_{24}$ 292.1821).

Photolysis of 1,2-*diphenyl*-3,3,4,4-*tetramethylcyclobutene in the presence of DCA and cupric ion*. CB (247 mg, 0.94 mmol) and DCA (2 mg, 9×10^{-3} mmol) and 467 mg (1.9 mmol) of cupric sulfate pentahydrate were dissolved in 150 ml of acetonitrile–MeOH (2 : 1) mixture. After purging with Ar for 0.5 h, the mixture was irradiated with a Hanovia 450 W medium-pressure Hg lamp through a uranium glass filter sleeve (> 330 nm) for 60 h under argon. Evaporation of solvent gave an orange semisolid. The solid was added to 30 ml of water and then extracted with ether (30 ml × 2). The combined organic layer was washed with water, brine, and dried over anhyd Na_2SO_4. After evaporation of solvent *in vacuo*, recrystallization from MeOH gave the phenanthrene derivative (58 mg, 24%).

Photolysis of 3,4-*diphenyl*-2,5-*dimethyl*-2,4-*hexadiene in the presence of DCA and cupric ion*. BD (6 mg, 0.02 mmol) and DCA (6 mg, 0.02 mmol) were dissolved in 50 ml of an acetonitrile–MeOH (2 : 1) mixture containing 10 mg (0.04 mmol) of cupric sulfate pentahydrate. After purging with argon for 10 min at 0°, the mixture was irradiated with a Hanovia 450 W medium-pressure Hg lamp through a uranium glass filter sleeve (> 330 nm) for 2.5 h under argon. After evaporation of the solvent *in vacuo*, water (10 ml) was added to the residue and the mixture was extracted with ether (10 ml × 2). The combined organic layers were washed with water, brine, and dried over anhyd $MgSO_4$. Evaporation of ether gave a light yellow oil (5 mg). ^{1}H-NMR showed that the oil contained BD and several other products, none of which correspond to those obtained from similar irradiations of CB.

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REFERENCES

[1] G. B. Gill and M. R. Willis, *Pericyclic Reactions*. Chapman & Hall, London (1974).

[2] E. Haselbach, T. Bally and Z. Lanyiova, *Helv. Chim. Acta.* **62**, 577 (1979).

[3] I. R. Dunkin and L. Andrews, *Tetrahedron* **41**, 145 (1985).

[4] D. J. Bellville, R. Chelsky and N. L. Bauld, *J. Comput. Chem.* 3, 548 (1982).

[5] M. K. Hoffman, M. M. Bursey and R. E. K. Winter, *J. Am. Chem. Soc.* **92**, 727 (1980); A. Mandelbaum, S. Weinstein, E. Gil-Av and J. H. Leffin, *Org. Mass Spec.* **10**, 842 (1975).

[6] M. L. Gross and D. H. Russel, *J. Am. Chem. Soc.* **101**, 2082 (1979).

[7] C. Dass and M. L. Gross, *J. Am. Chem. Soc.* **105**, 5724 (1983).

[8] C. Dass, T. M. Sack and M. L. Gross, *J. Am. Chem. Soc.* **106**, 5780 (1984).

[9] E. Haselbach, T. Bally, R. Gschwind, U. Hemm and Z. Lanyiova, *Chimia* **33**, 405 (1979).

[10] G. P. Kirschenheuter and G. W. Griffin, *J. Chem. Soc. Chem. Commun.* 596 (1983).

[11] C. F. Wilcox, Jr. and B. K. Carpenter, *J. Am. Chem. Soc.* **101**, 3879 (1979).

[12] W. H. Laarhoven, *Pure Appl. Chem.* **56**, 1225 (1984); K. A. Muszkat, *Top. Curr. Chem.* **88**, 89 (1980).

[13] D. Rehm and A. Weller, *Israel J. Chem.* **8**, 259 (1970).

[14] K. A. Horn and G. B. Schuster, *Tetrahedron* **38**, 1095 (1982).

[15] M. Yamamoto, M. Ohoka, K. Kitagawa, S. Nishimoto and Y. Nishijima, *Chem. Lett.* 745 (1973).

[16] R. Gooden and J. I. Brauman, *J. Am. Chem. Soc.* **104**, 1483 (1982).

[17] S. Murai and S. Tsutumi, *Bull. Chem. Soc. Japan* **39**, 198 (1966); K. Mizuno, J. Ogawa, H. Kagano and Y. Otsuji, *Chem. Lett.* 437 (1981); *Ibid.* 941 (1983); K. Mizuno, K. Yoshioka and Y. Otsuji, *J. Chem. Soc. Chem. Commun.* 1665 (1984); M. Kajima, H. Sakuragi and K. Tokumaru, *Bull. Chem. Soc. Japan* **58**, 521 (1985).

[18] N. J. Peacock and G. B. Schuster, *J. Am. Chem. Soc.* **105**, 3632 (1983); J. M. Panayotou and C. B. Tsuetanov, *Monat. Chem.* **101**, 1672 (1970).

[19] R. S. Nicholson and I. Shain, *Analyt. Chem.* **36**, 706 (1964).

[20] M. C. R. Symons, *Chem. Soc. Rev.* **103**, 393 (1984).

[21] T. Shida, E. Haselbach and T. Bally, *Accts Chem. Res.* **17**, 180 (1984).

[22] O. L. Chapman and W. R. Adams, *J. Am. Chem. Soc.* **90**, 2333 (1968).

[23] H. G. Heller and J. R. Langan, *J. Chem. Soc. Perkin Trans. II* 341 (1981).