can be rationalized if $E_2^\circ - E_1^\circ = 30–50$ mV (i.e., E_2°, $C^{\bullet +} \rightarrow C^{2+} + e^- > E_1^\circ$, $C \rightarrow C^{\bullet +} + e^-$). This indicates that for reaction 3 $\Delta E^\circ < 0$, which implies that $\Delta G^\circ > 0$, and the forward reaction of 3 is not spontaneous. However, these values are based on theory and do not take into consideration such important experimental effects as solvation, which may cause a small, but sufficient, change in the ΔE° to produce a spontaneous reaction.

We therefore conclude that compounds II and III directly generate radical cations upon electrochemical oxidation in CH_2Cl_2 and $C_2H_4Cl_2$ solvents through a one-electron process. On the other hand, the two-electron oxidation of β-carotene results in the primary production of dications, which undergo further reaction with the neutral β-carotene molecule to form the radical cation species. This result might seem surprising, since II and III are carbonyl compounds and would be expected to stabilize anion radical, but perhaps not cation radical, formation. Similarly, β-carotene does not contain carbonyl groups and might be expected to generate the radical cation, rather than the dication species. However, this argument does not consider the fact that compounds II and III have long conjugated chains (canthaxanthin has 11 double bonds and β-apo-8′-carotenal has 9 double bonds) attached to the carbonyl group(s). Thus, in the case of β-apo-8′-carotenal, the cation radical may be stabilized at the end of the chain away from the C=O group, while for canthaxanthin, the radical could be stabilized along the chain, somewhere between the two carbonyl end groups. This suggests that β-carotene, which has no C=O substituents and 11 double bonds, might readily accommodate the dication species.

Conclusions

The results of CV measurements of β-carotene in THF, CH_2Cl_2, and $C_2H_4Cl_2$ indicate that the oxidation process occurs via a two-electron-transfer mechanism. In contrast, CV measurements of II and III showed that the oxidation in THF involves two-electrons, while in CH_2Cl_2 and $C_2H_4Cl_2$ the process occurs via the transfer of only one electron. Absorption measurements of β-carotene in all three solvents showed that new bands are formed in the near-IR following controlled potential oxidation at the first anodic peak potential. Absorption measurements of II and III showed new bands were formed only in the chlorinated solvents. Previous literature reports indicated that these bands could be due to either cations or radical cations. EPR measurements showed definitely that the electrochemically generated oxidation products in CH_2Cl_2 and $C_2H_4Cl_2$ are carotenoid cation radicals. In THF solution, however, β-carotene oxidation gives rise to a cation that is not a radical. The half-lives of all radical species are on the order of several minutes in CH_2Cl_2 but are considerably shorter in $C_2H_4Cl_2$. For the carotenoid radicals the order of solvent stability is therefore $CH_2Cl_2 > C_2H_4Cl_2 >$ THF.

We have thus shown that carotenoid cation radicals can be formed electrochemically in nonaqueous solvent systems, and furthermore, these radicals can be stabilized for several minutes in the solvent CH_2Cl_2.

Acknowledgment. This work was supported by the Division of Chemical Sciences, Office of Basic Energy Science, Dept. of Energy under Grant DE-FG05-86ER13465. We thank M. Wasielewski for many useful discussions, and A. J. Bard, B. P. Sullivan, and L. O. Spreer for helpful hints on electrochemical techniques. We also thank Professor L. Bottomley for use of the IBM instrument at Georgia Institute of Technology, Atlanta, and Grant Holder and John Helfrick, Jr., for assistance with those experiments, Professor M. Cava for loan of the BAS equipment, and M. Kendrick for use of the Cary 14. V.J.K. thanks NSF for a Summer Undergraduate stipend as part of the 1987 REU Site at The University of Alabama.

Photochemical Generation of [4]Paracyclophanes from 1,4-Tetramethylene Dewar Benzenes: Their Electronic Absorption Spectra and Reactions with Alcohols

Takashi Tsuji* and Shinya Nishida

Contribution from the Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan. *Received August 31, 1987*

Abstract: Irradiation of 1,4-tetramethylene Dewar benzene (**1a**) in alcohols (methanol, ethanol, 2-propanol) affords 1-alkoxybicyclo[4.2.2]deca-7,9-dienes **3a–3c**, formal adducts of the alcohols to the central σ bond of **1a**. Photolyses of the 7-methoxymethyl and the 7-methoxycarbonyl derivatives **1b** and **1c** in ethanol produce mixtures of regioisomeric adducts, viz. 1- and 4-ethoxy derivatives **3** and **3′**. 2,5-Ethano bridging of **1a** leads to a complete loss of photochemical reactivity toward methanol. Thus, the compound **9**, the 2,5-ethano derivative of **1a**, gives merely benzobicyclo[2.2.2]oct-2-ene upon prolonged irradiation in methanol. Irradiation of **1a–1c** in rigid glass with a low-pressure Hg lamp at 77 K leads to development of absorptions in the UV–visible region that show systematic substituent-induced red shifts. The generated species, which are thermally extremely unstable, appear to revert to **1a–1c**, respectively, with 366-nm light irradiation. In contrast, no corresponding new absorption appears upon irradiation of **9** at 77 K. Evidence is presented to show that the irradiation of **1a–1c** leads to the formation of [4]paracyclophanes **2a–2c** from which the alcohol adducts **3** and **3′** are derived and that the electronic absorption spectra observed at 77 K are due to **2a–2c**. The contrasting behavior of **9** is accounted for in terms of still higher strain associated with the corresponding benzenoid derivative **10** than that in **2**.

Geometrically distorted unsaturated compounds have attracted considerable interest in recent years.[1] Paracyclophanes having a short bridge have presented a particular challenge in this field, and efforts to prepare paracyclophanes having very short bridges have led to a recent achievement of generating [5]paracyclophanes.[2] Despite severe bending of the benzene ring, it has been suggested that [5]paracyclophanes still retain aromatic character,[2,3] though they appear to lack thermal stability enough

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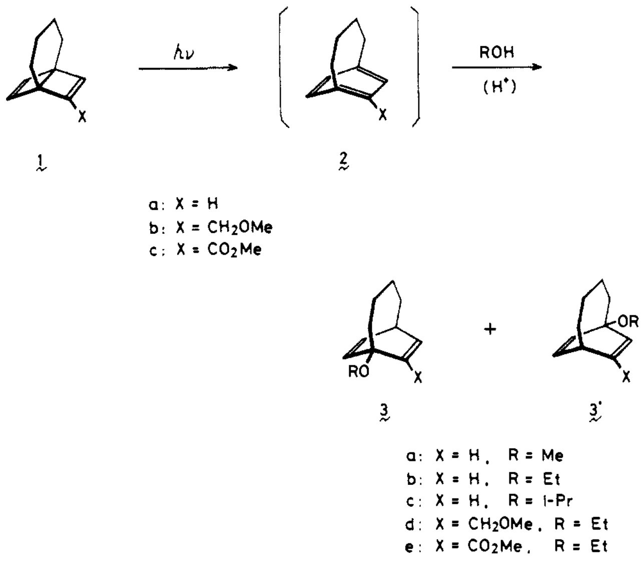
(1) (a) Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic: New York, 1978. (b) Shea, K. J. *Tetrahedron* **1980**, *36*, 1683. (c) Szeimies, G. *Reactive Intermediates*; Plenum: New York, 1983; Vol. 3, Chapter 5. (d) Keehn, P. M.; Rosenfeld, S. M. *Cyclophanes*; Academic: New York, 1983. (e) Wiberg, K. B. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 312.

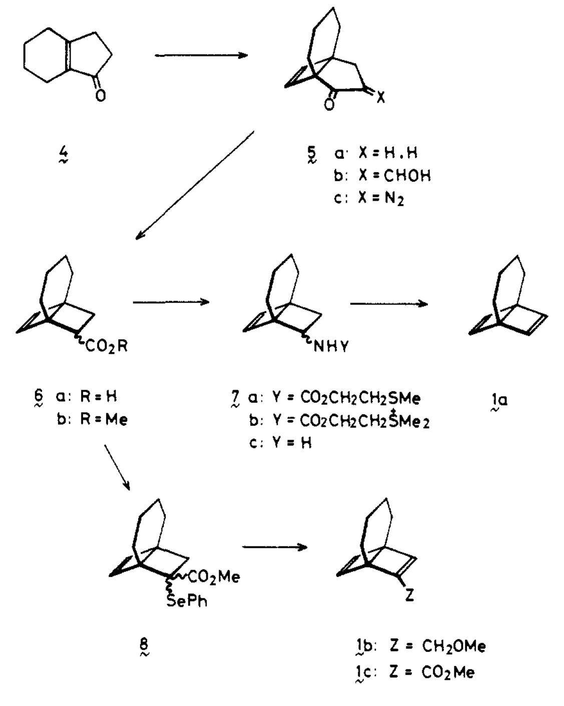
(2) (a) Jenneskens, L. W.; De Kanter, F. J. J.; Kraakman, P. A.; Turkenburg, L. A. M.; Koolhaas, W. E.; De Wolf, W. H.; Bickelhaupt, F.; Tobe, Y.; Kaneda, T.; Kakiuchi, K.; Odaira, Y. *J. Am. Chem. Soc.* **1985**, *107*, 3716. (b) Tobe, Y.; Kaneda, T.; Kakiuchi, K.; Odaira, Y. *Chem. Lett.* **1985**, 1301. (c) Kostermans, G. B. M.; DeWolf, W. H.; Bickelhaupt, F. *Tetrahedron Lett.* **1986**, *27*, 1095. (d) Kostermans, G. B. M.; DeWolf, W. H.; Bickelhaupt, F. *Tetrahedron*, **1987**, *43*, 2955.

0002-7863/88/1510-2157$01.50/0

Scheme I



Scheme II



to be isolated in a pure form at room temperature. The substantially reduced stability of [5]paracyclophanes compared with the [6] homologues[4] suggested that [4]paracyclophane **2** (Scheme I) would be extremely labile if it were generated. Recently, Bickelhaupt and co-workers reported that 1,4-tetramethylene Dewar benzene (**1a**) undergoes the photochemical addition of electrophiles at the central σ bond and interpreted the results by assuming the intermediate formation of **2a**, although **2a** has eluded direct observation in their hands.[5] We independently made an analogous observation, i.e., the photochemical addition of alcohols to **1a** giving **3a**–**3c**, in the course of studies on 1,4-bridged Dewar benzenes[6] and proposed the intermediacy of **2a**.[7] Subsequently, we observed that irradiation of **1a** with a low-pressure Hg lamp at liquid nitrogen temperature led to development of an electronic absorption ascribable to **2a**.[8] In this paper, we give full details of the evidence to support our conclusion that **2a**–**2c** were indeed directly observed by electronic absorption spectroscopy and that the photochemical addition of alcohols to **1** proceeded in fact by way of **2**, as shown in Scheme I. Those absorption spectra exhibited by **2a**–**2c** are particularly interesting, since they provide an insight into the bonding and electronic configuration of the extremely bent benzene ring of [4]paracyclophane.

Results and Discussion

Preparation of 1,4-Tetramethylene Dewar Benzenes 1a–1c. The parent compound **1a** was prepared by two independent routes. The first route was that developed by Bickelhaupt and co-workers.[9] The second preparation was accomplished following the procedure that we have developed for the preparation of the fully unsaturated derivatives of **1**.[6] The second route allowed the preparation of the 7-substituted derivatives **1b** and **1c** in addition to **1a** (Scheme II).

The tricyclic ketone **5a**, which was obtained by the photocycloaddition of acetylene[10] to readily accessible **4**,[11] was diazotized by a standard procedure.[12] The ring contraction via photo-Wolff rearrangement of the resultant **5c** in aqueous dioxane or in methanol afforded the carboxylic acid **6a** (66%) or the corresponding methyl ester **6b** (79%). Treatment of **6a** with diphenylphosphoryl azide[13] in boiling benzene followed by the addition of 2-(methylthio)ethanol gave the carbamate **7a** in 81% yield. The S-methylation of **7a** with dimethyl sulfate followed by hydrolysis–decarboxylation of the resultant **7b**[14] furnished the amine **7c** in 77% yield. The quaternization of **7c** with methyl iodide and the subsequent treatment with potassium *tert*-butoxide in dimethylformamide afforded **1a** in 66% yield. The samples of **1a** obtained via the two independent routes were identical in all respects, including the photochemical behavior. The α-phenylselenenylation of **6b**[15] followed by oxidation to the selenoxide and the subsequent fragmentation afforded the 7-methoxycarbonyl derivative **1c** in 40% yield. The ester was reduced with diisobutylalane to the allylic alcohol, which was methylated to give the 7-methoxymethyl derivative **1b**. The preparation of **9** has previously been reported.[16]

Photolysis of 1 and 9 in Alcohols. Product Study. Bickelhaupt and co-workers[5] reported that irradiation of **1a** in methanol in the presence of trifluoroacetic acid (TFA) produces an adduct **3a** in 97% yield. In our hands, **3a** was obtained as a single volatile product in 60% yield when a methanolic solution of **1a** was irradiated through a Pyrex filter with a high-pressure Hg lamp in the absence of TFA.[17] The same methanol adduct was also

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(3) According to the recent theoretical calculation, [5]paracyclophane is judged not to be aromatic: Rice, J. E.; Lee, T. J.; Remington, R. B.; Allen, W. D.; Clabo, D. A., Jr.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1987**, *109*, 2902.

(4) (a) Kane, V. V.; Wolf, A. D.; Jones, M., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 2643. (b) Kammula, S. L.; Iroff, L. D.; Jones, M., Jr.; Van Straten, J. W.; De Wolf, W. H.; Bickelhaupt, F. *Ibid.* **1977**, *99*, 5815. (c) Liebe, J.; Wolff, C.; Krieger, C.; Weiss, J.; Tochtermann, W. *Chem. Ber.* **1985**, *118*, 4144. (d) Tobe, Y.; Ueda, K.; Kaneda, T.; Kakiuchi, K.; Odaira, Y.; Kai, Y.; Kasai, N. *J. Am. Chem. Soc.* **1987**, *109*, 1136.

(5) Kostermans, G. B. M.; Bobeldijk, M.; De Wolf, W. H.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1987**, *109*, 2471.

(6) (a) Tsuji, T.; Komiya, Z.; Nishida, S. *Tetrahedron Lett.* **1980**, 3853. (b) Tsuji, T.; Nishida, S. *Ibid.* **1983**, *24*, 3361. (c) Tsuji, T.; Nishida, S. *Chem. Lett.* **1986**, 1389.

(7) Tsuji, T.; Nishida, S. 8th IUPAC Conference on Physical Organic Chemistry, Tokyo, Japan, Aug 1986.

(8) For a preliminary account of a portion of this work, see: Tsuji, T.; Nishida, S. *J. Chem. Soc., Chem. Commun.* **1987**, 1189.

(9) Landheer, I. J.; De Wolf, W. H.; Bickelhaupt, F. *Tetrahedron Lett.* **1974**, 2813.

(10) Cargill, R. L.; Bushey, D. F.; Dalton, J. R.; Prasad, R. S.; Dyer, R. D.; Bordner, J. J. *J. Org. Chem.* **1981**, *46*, 3389.

(11) Dev, S. *J. Indian Chem. Soc.* **1957**, *34*, 169.

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(13) Shioiri, T.; Ninomiya, K.; Yamada, S. *J. Am. Chem. Soc.* **1972**, *94*, 6203.

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(15) (a) Reich, H. J.; Reich, I. L.; Renga, J. M. *J. Am. Chem. Soc.* **1973**, *95*, 5813. (b) Sharpless, K. B.; Rauer, R. F.; Teranishi, A. Y. *Ibid.* **1973**, *95*, 6137. (c) Reich, H. J.; Renga, J. M.; Reich, I. L. *Ibid.* **1975**, *97*, 5430.

(16) Gleiter, R.; Krennich, G.; Bishop, P.; Tsuji, T.; Nishida, S. *Helv. Chim. Acta* **1986**, *69*, 962.

(17) Irradiation without the filter brought about much faster consumption of **1a** but resulted in the formation of amorphous precipitate and a decreased yield of **3a**.

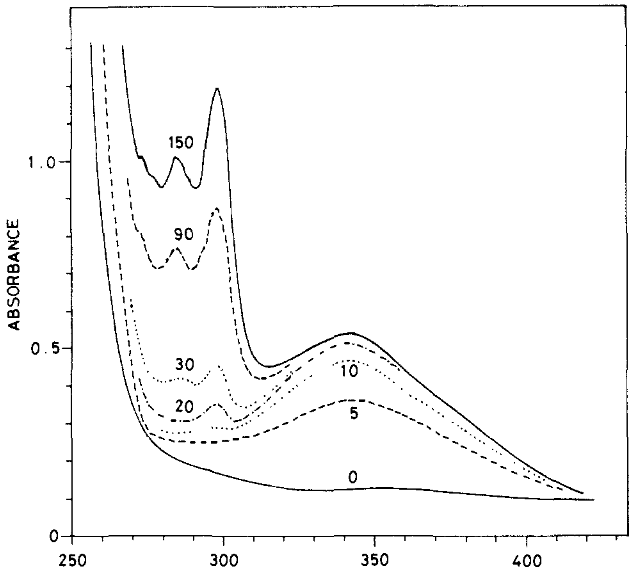
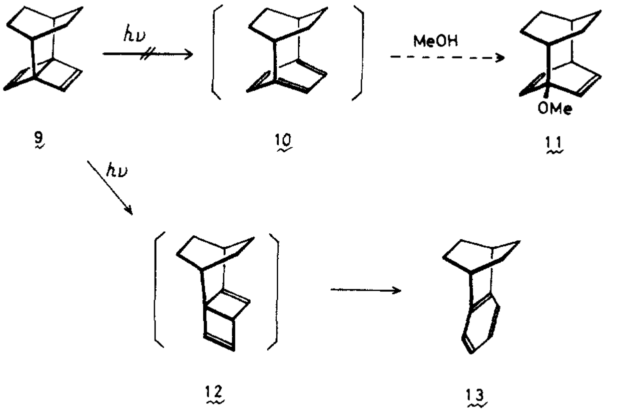


Figure 1. Electronic absorption spectra observed upon irradiation of **1a** in ethanol with a low-pressure Hg lamp at 77 K. Numerals by the absorption curves indicate irradiation times (min).

Scheme III



produced under the acetone-sensitized conditions, though in a much lower yield (14%). Irradiation of **1a** in ethanol analogously afforded **3b** in 47% yield, but the photoreaction in 2-propanol produced **3c** in mere 5% yield.[18] When the latter reaction was carried out in a 1% (v/v) solution of TFA, however, **3c** was obtained in 57% yield.

Photolysis of **1b** in ethanol afforded a mixture of two ethanol adducts, **3d** and **3d'**,[19] in 40% yield in total. In the presence of TFA (1% v/v), the yield was increased to 66%. The photoreaction of **1c** in ethanol produced the expected adducts only in the presence of TFA. Thus, photolysis of **1c** in a 1% (v/v) ethanolic solution of TFA afforded **3e** and **3e'** in 32% and 29% yields, respectively.

In striking contrast, the compound **9**, which differs from **1a** in structure only by the presence of an ethano bridge on the saturated side chain, did not undergo the photochemical addition of methanol to give **11**,[20] even in the presence of TFA. Under the photochemical conditions, **9** underwent slow isomerization to **13** (58%), probably via **12** (Scheme III).

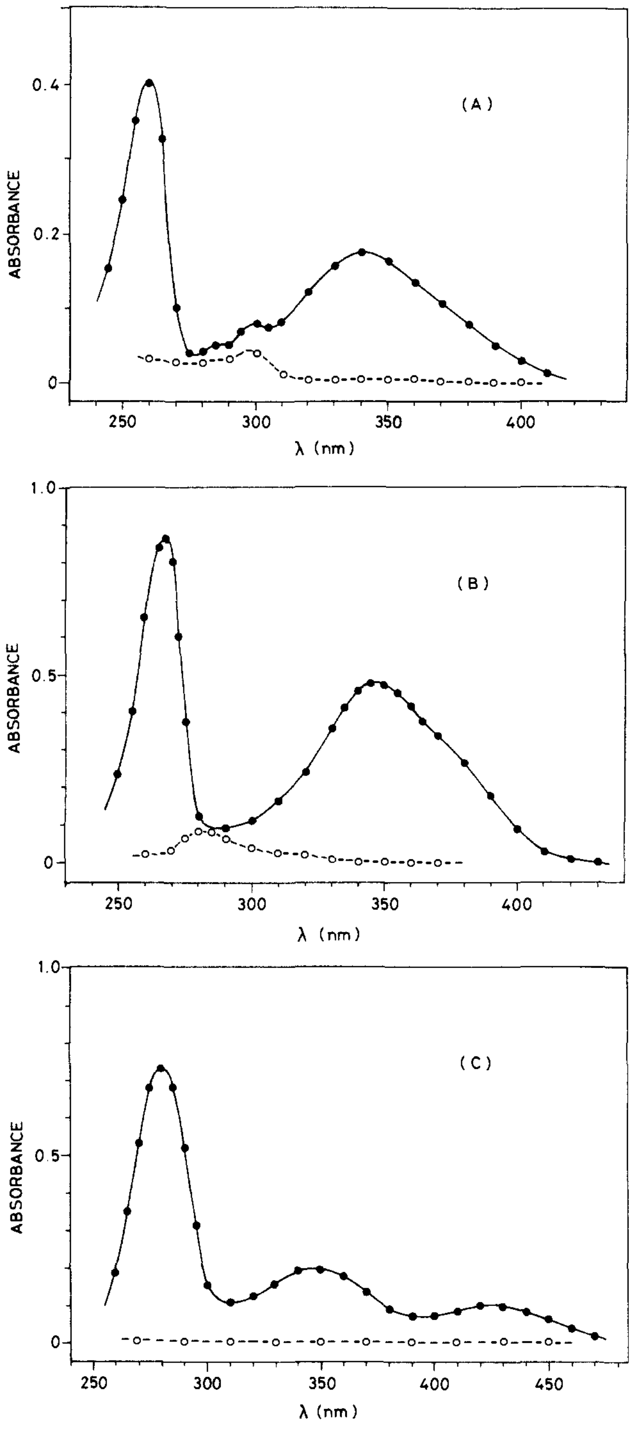


Figure 2. Difference spectra (ethanol, 77 K) obtained by subtracting the spectrum of nonirradiated sample from the spectrum exhibited after irradiation with a low-pressure Hg lamp (●) and from the spectrum shown after further irradiation with a high-pressure Hg lamp through a Corning 7-60 color filter (○): (A), **1a**; (B), **1b**; (C), **1c**.

Electronic Absorption Spectra Observed upon Irradiation of 1a–1c with 254-nm Light at 77 K. When a degassed ethanolic solution of **1a** in a quartz tube was irradiated with a low-pressure Hg lamp at liquid nitrogen temperature, development of an absorption having maxima at 260 ± 2 and 340 ± 2 nm (relative intensity, ca. 2:1) was observed. The growth of the absorption, however, tapered down to a halt after a short period of irradiation. A slight inflection of the absorption curve at ca. 360 nm suggested that the broad band at 340 nm might consist of two components, one with λ_{max} 330–340 nm and the other with λ_{max} 370–380 nm. Along with the above absorption, a second absorption having maxima at 285 and 300 nm appeared later and continued to grow, though at a considerably slower rate, even after the intensity of

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(18) Significant amounts of side products were produced.

(19) The structural assignments of the adducts **3** and **3'** were readily made by examining the coupling constants between the olefinic protons and the bridgehead proton in the ^{1}H NMR. In the reaction of **1b**, the major product was readily elucidated as **3d'**, but the minor product was difficult to obtain in a pure form. The assignment of **3d** was therefore made on the basis of partially resolved 500-MHz ^{1}H NMR and GLC–MS analysis of the mixture. The ratio of **3d** to **3d'** estimated from the GLC peak area was 2:9.

(20) The compound **11**, which we prepared previously,[7] was stable under the reaction conditions.

the first absorption reached a plateau, as shown in Figure 1.[21] The generated species exhibiting the first absorption remained unchanged for more than 1 h at 77 K but underwent complete decomposition when the rigid solution was thawed, warmed to −100 °C, and immediately refrozen at 77 K. If the irradiation of **1a** with 254-nm light was terminated before the development of the second absorption proceeded to a significant extent and the resultant rigid solution was irradiated with 366-nm light, the developed absorption, except for the weak second absorption, was efficiently bleached and the original spectrum was almost restored (Figure 2A), suggesting the efficient photochemical reversion of the generated intermediate to **1a**. This supposition explains why the first absorption ceased to grow after it reached a certain intensity. Presumably, a quasi-photoequilibrium would be attained under the conditions. The development of a similar absorption having maxima at 260 and 340 nm upon irradiation of **1a** with 254-nm light at 77 K and the bleaching of the absorption with 366-nm light were also observed in ether/isopentane/ethanol (5:5:2, EPA) or pentane/isopentane (1:1). Therefore, the protic solvent is not essential to the generation of the transient species. Moreover, it should be stressed here that the two samples of **1a** prepared by the independent pathways showed exactly the same photochemical behavior. Accordingly, the possibility that the observed absorptions derived from adventitious impurities in the sample of **1a** may be ruled out.

In a similar manner, irradiation of **1b** in ethanol with 254-nm light at 77 K led to development of an absorption having maxima at 267 ± 2 and 346 ± 2 nm (relative intensity, ca. 2:1). A clearly discernible inflection of the absorption curve at about 370 nm indicated that the band at 346 nm consisted of two components, one with λ_{max} at ca. 340 nm and the other with λ_{max} at ca. 380 nm. Thus, the absorption band at 340 nm observed upon irradiation of **1a** would indeed consist of the two components. Those bands ceased to grow after a short period of irradiation, and continued irradiation only induced the growth of a band in the 270–310-nm region. The former absorption bands were efficiently bleached with 366-nm light again, suggesting the ready photochemical reversion of the generated transient to **1b** (Figure 2B). Irradiation of **1c** in ethanol or pentane/isopentane (1:1) with 254-nm light at 77 K led to the generation of a yellow species. The electronic absorption spectra showed development of an absorption having three maxima at 280 ± 2, 348 ± 2, and 425 ± 3 nm (relative intensity, ca. 7:2:1) in ethanol and of a similar absorption slightly blue-shifted ($\sim$2 nm) in pentane/isopentane (1:1). These absorptions also ceased to grow after a short period of irradiation and were efficiently bleached with 366-nm light to cleanly restore the spectra before irradiation with 254-nm light (Figure 2C). The thermal stabilities of the intermediates generated from **1b** and **1c** with 254-nm light irradiation were comparable to that derived from **1a**, and they remained unchanged for more than 1 h at 77 K but underwent complete decomposition when the rigid solutions were thawed, warmed to −100 °C, and immediately refrozen in liquid nitrogen.

In contrast to the results mentioned so far, virtually no new absorption occurred in the 300–400-nm region upon irradiation of **9** with 254-nm light at 77 K.

Assignment of the Transient Species Produced in the 254-nm Light Photolysis of 1a–1c. What is most striking is the similarity in spectral pattern, besides the characteristic substituent-induced bathochromic shifts, of those three-component absorptions exhibited by the species photochemically generated from **1a–1c**. No less striking are the common features in their behavior upon irradiation with 366-nm light and of their extreme thermal instabilities. It seems certain, therefore, that the irradiation of **1a–1c** led to the production of the intermediates possessing a common basic structure. Their ready photochemical reversions to the Dewar benzene precursors strongly suggest that they may be [4]paracyclophanes **2**. Photocyclization of strained paracyclophanes to the corresponding 1,4-bridged Dewar benzenes has been established for [6]paracyclophane[4b] and suggested also for the [5] analogues.[2]

Table I. Electronic Absorption Spectra of Some Strained [*n*]Paracyclophanes

n	λ_{max}, nm (log ϵ)	ref
7	216 (4), 245 (4), 283 (3)	22c
6	212 (4.3), 253 (4.0), 296 (2.8)	4a
5	280, 330	2a
4	260, 330–340, 370–380	this work

Unfortunately, to the best of our knowledge, no theoretical study of probable electronic transitions in [4]paracyclophane has been conducted so far. However, the fact that increasing degree of bending of the benzene ring of paracyclophane brings about increasing bathochromic shift in the electronic absorption spectrum has been experimentally[2,4,22] and theoretically[23] well documented (Table I). If we accept the supposition that the correlation between the degree of aromatic ring bending and the magnitude of bathochromic shift is reasonably extended to [4]paracyclophane, the appearance of the three bands at 260, 330–340, and 370–380 nm upon irradiation of **1a** also seems consistent with the generation of **2a**.

We[8] and Bickelhaupt et al.[5] proposed that the photoaddition of methanol to **1a** to give **3a** would proceed via **2a**. If this is correct, there should be a correlation between the photoreactivity toward alcohols and the development of absorption in the UV–visible region upon irradiation at 77 K. This was indeed found to be true. Thus, the compounds **1a–1c**, irradiation of which led to the development of the absorptions in the UV–visible region, all gave the alcohol adducts, whereas **9**, from which no corresponding absorption was generated, was photochemically inert toward methanol. Taking all those observations together, it seems most probable that the characteristic absorption spectra observed at low temperature are due to **2a–2c**, to which the alcohols add to give **3** and **3′**, as depicted in Scheme I. More convincing evidence for this assignment was provided by the following experiment.

Irradiation of **1a** in ethanol containing 1% (v/v) of sulfuric acid with 254-nm light at 77 K apparently led to the development of the same absorption as observed in neutral ethanol. The photolysis was discontinued while the growth of the second absorption around 300 nm remained still insignificant, and the resultant rigid solution was warmed to room temperature to allow the generated intermediate to react with ethanol. After having repeated this freeze–irradiation (254 nm)–thaw cycle ten times, the photolysate was analyzed by GLC and GLC–MS spectrometry. The formation of the ethanol adduct **3b** under the above conditions was thus confirmed.[24] In the next experiment, the absorption generated with 254-nm light irradiation was bleached with 366-nm light each time before the rigid solution was thawed. After ten freeze–irradiation (254 nm)–irradiation (366 nm)–thaw cycles, the photolysate was analyzed as before. It was found that the amount of **3b** produced in the latter experiment was only one-tenth of that obtained in the former reaction. Because **3b** is transparent above 300 nm and stable toward 366-nm light, the greatly diminished yield of **3b** in the latter experiment unequivocally demonstrates that the major fraction, if not all, of **3b** obtained in the former experiment was produced during the thaw in the dark but not in the rigid glass during the irradiation and that the precursor of **3b** was quenched by 366-nm light. Thus, the species exhibiting the first absorption would certainly be the direct precursor of **3b**. [4]Paracyclophane **2a** seems to be the only conceivable species capable of accommodating all those observations. The possibility that **3b** was produced by the addition of ethanol to **1a** in the excited

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(21) Absorption below 270 nm could only be observed with the more dilute solution of **1a**, owing to the interference from the tail of the absorption due to **1a**.

(22) (a) Cram, D. J.; Knox, G. R. *J. Am. Chem. Soc.* **1961**, *83*, 2204. (b) Allinger, N. L.; Walter, T. L. *Ibid.* **1972**, *94*, 9267. (c) Wolff, A. D.; Kane, V. V.; Levin, R. H.; Jones, M., Jr. *Ibid.* **1973**, *95*, 1680.

(23) Allinger, N. L.; Sprague, J. T.; Liljefors, T. *J. Am. Chem. Soc.* **1974**, *96*, 5100.

(24) After ten cycles, the conversion of **1a** was still quite low.

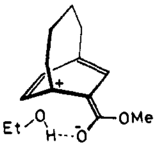


Figure 3. Presumed charge polarization in **2c** and association with ethanol, which would facilitate the formation of **3c**.

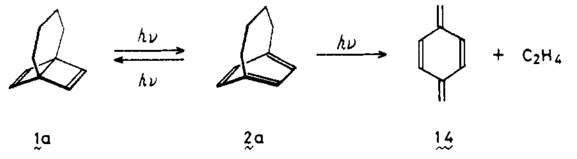
state or a prismane intermediate[25] is definitely ruled out. The compound **1a** was stable in this acidic ethanol, and the formation of **3b** was not detected in the dark. A small amount of **3b** produced in the latter experiment would probably result from the incomplete bleaching of **2a**.[26] Thus, it may be concluded that the electronic absorption spectra observed upon irradiation of **1a**–**1c** at 77 K are due to **2a**–**2c**, from which the alcohol adducts **3** and **3′** are derived.

The acid catalysis observed in the present photoaddition of the alcohols to **1** is also consistent with the intermediacy of **2**, since the reactions of alcohols with distorted double bonds such as anti-Bredt bridgehead alkenes are generally subject to acid catalysis.[1] Even in the 1% (v/v) ethanolic solution of sulfuric acid, however, the interception of **2a** with ethanol would be incomplete in the above-mentioned experiment. The photolysate was already cloudy after four freeze–irradiation (254 nm)–thaw cycles, and colorless precipitate had been formed after ten cycles. In the freeze–irradiation (254 nm)–irradiation (366 nm)–thaw experiment, however, the photolysate remained clear even after ten cycles. The results thus indicate that a substantial fraction of **2a** would polymerize rather than react with ethanol when the medium lost its rigidity.[27] Indeed, attempts to measure the electronic absorption spectra of **2** in fluid solution have been unsuccessful so far. Thus, irradiation of a magnetically stirred isopentane solution of **1a** with 254-nm light at −135 to −140 °C did not give the expected absorption in the 300–400-nm region, and if the irradiation was continued, the solution became cloudy and colorless precipitate was formed ultimately. In fluid solution in which species could freely diffuse, **2a** would polymerize even at the above low temperature. Since [5]paracyclophane is known to polymerize above 0 °C in dilute solution,[2a] the ready polymerization of far more strained **2a** is not unexpected.

The addition of the alcohols, 2-propanol in particular, to **2** in an ionic manner indicates that the ground state of **2** is singlet.[28] The formation of the same methanol adduct **3a** in the acetone-sensitized photolysis of **1a** in methanol implies that **1a** in the excited triplet state also undergoes the rearrangement to triplet **2a**, which is subsequently deactivated to **2a** in its ground state prior to the reaction with methanol.

The site-selective addition of the alcohols to the bridgehead carbons of **2** would be dictated by a steric factor. The effective release of strain in **2** is realized only by the addition to the bridgeheads. Otherwise, an anti-Bredt bridgehead olefin results. The preferred formation of **3d′** over **3d** in the reaction of **1b** would be due to steric repulsion between the substituent and an incoming ethanol molecule. In the case of **1c**, charge polarization in **2c** induced by the electron-withdrawing substituent and, possibly, the association of an ethanol molecule to the carbonyl oxygen by hydrogen bonding might counterbalance the steric effect (Figure 3).

Scheme IV



The contrasting results that **9** failed to give both transient absorption and the methanol adduct **11** would arise from the still higher strain associated with **10**. Owing to the additional ethano bridge, the saturated side chain in **9** is shorter than that in **1**.[29] The benzene ring in **10**, if it were formed therefore, would suffer more severe bending than that in **2**. Isomerization to **10** being sterically inhibited, **9** would undergo the relatively slow 1,3-shift of its double bond giving **12** and subsequent aromatization to **13** (Scheme III).[30]

Species Responsible for the Second Absorption Generated from 1a. As described above, the prolonged irradiation of **1a** with 254-nm light at 77 K led to the development of the second absorption with λ_{max} 285 and 300 nm (Figure 1). The relative intensity and wavelengths of these absorption maxima are in a good agreement with those reported for *p*-xylylene **14**.[31] The formation of **14** was in fact proved by trapping with bromine. Thus, **1a** was irradiated in pentane/isopentane (1:1) with 254-nm light at 77 K for a certain period of time, and the photolysate was treated with bromine at low temperature. The GLC-MS analysis of the product mixture clearly indicated the formation of *p*-xylylene dibromide. The seemingly delayed development of the absorption of *p*-xylylene compared with that of **2a** suggests that **14** was a secondary photoproduct presumably derived from **2a** (Scheme IV). The prolonged irradiation of **1b** at 77 K led to the development of a structureless band in the 270–310-nm region, besides the absorption ascribable to **2b**. The origin of this absorption, however, has not been analyzed yet. In the case of **1c**, virtually no second absorption appeared above 300 nm. The efficient reversion to **1c** upon the excitation of **2c** might overshadow the ring cleavage, giving the *p*-xylylene derivative and ethylene.

Conclusion. Aromatization of 1,4-bridged Dewar benzenes has provided a major means of access to paracyclophanes with short bridges. Thus, a variety of paracyclophanes bridged by more than four carbons have been prepared in this manner.[2,4] In this report we presented the evidence that [4]paracyclophanes could also be generated in the same manner. However, the compound **9**, which is 1,4-bridged by a four-carbon chain constricted by an ethano bridge, showed no sign of isomerization to **10** under the present conditions. The photochemical rearrangement of **1** to **2**, therefore, may represent a limiting case of this methodology.

Experimental Section

Unless otherwise specified, all ^{1}H and ^{13}C NMR spectra were recorded with a JEOL FX-100 spectrometer in $CDCl_3$ in the High-Resolution NMR Laboratory, Hokkaido University. IR spectra were taken on a Hitachi Model 215 grating spectrometer. Mass spectra were recorded on JEOL D-100 and DX-100 spectrometers at an ionizing voltage of 70 eV unless otherwise indicated. UV spectra were taken on a Cary Model 17 spectrophotometer. GLC work was done on Hitachi 063 and 163 gas chromatographs with He as a carrier gas. The following columns were used: A, 5% poly(ethylene glycol) (PEG) 20M, 1 m; B, 20% PEG 20M, 1 m; C, 20% PEG 20M, 2 m; D, 5% PEG 20M and 1% KOH, 1 m; E, 10% silicone SE-30, 0.5 m; F, 10% silicone SE-30, 1.5 m; G, 5% silicone DC-550, 1 m; H, 15% Apiezone Grease L, 2 m; I, 15% Apiezone Grease L, 4 m. Preparative chromatography was performed on Merck Kieselgel 60 (70–230 mesh). The light sources for photochemistry were Halos (Eiko-sha, Japan) 450-W high-pressure Hg and Halos 120-W low-pressure Hg lamps. The high-pressure Hg lamp fit with a Corning color filter 7-60 was employed as the 366-nm light source. Bicyclo[4.3.0]non-1(6)-en-7-one (**4**),[11] diphenylphosphoryl azide,[13] diphenyl di-

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(25) Prismanes, which could be derived from **1a**, should be transparent above 300 nm: (a) Wilzbach, K. E.; Kaplan, L. *J. Am. Chem. Soc.* **1965**, *87*, 4004. (b) Lemal, D. M.; Lokensgard, J. P. *Ibid.* **1966**, *88*, 5934. (c) Schäfer, W.; Criegee, W.; Askani, R.; Grüner, H. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 78. (d) Barlow, M. G.; Haszeldine, R. N.; Hubbard, R. *J. Chem. Soc. C* **1970**, 1232. (e) Katz, T. J.; Acton, N. *J. Am. Chem. Soc.* **1973**, *95*, 2738.

(26) The source of 366-nm light was more remote than that of 254-nm light from the window of Dewar through which the rigid solution of **1a** in a quartz tube was irradiated. Therefore, 366-nm light might not reach **2a** generated in the periphery of the region irradiated with 254-nm light.

(27) Attempts to determine the molar absorptivities of the absorption bands due to **2a** from the intensity of the absorption generated and the yield of **3b** were thwarted by the partial polymerization of **2a**.

(28) Cf.: Meisl, M.; Janoschek, R. *J. Chem. Soc., Chem. Commun.* **1986**, 1066.

(29) According to Greenberg and Liebman's logic, **10** may be viewed as [3.5]paracyclophane. See: Reference 1a, p 135.

(30) Photolysis of **1a** proceeded more than 6 times faster than that of **9** in methanol. Therefore, the inability of **9** to give **11** is not the result of a fast 1,3-shift giving **12**, which inhibits the isomerization of **9** to **10**.

(31) Kaupp, G. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 442.

selenide,[15] and tosyl azide[32] were prepared following the known procedures. Other reagents and solvents were obtained from commercial sources.

Tricyclo[4.3.2.0^{1,6}]undec-10-en-7-one (5a). The photoaddition of acetylene to **4** under the present conditions gave **5a** in a substantially improved yield compared with that previously reported.[10] A mixture of 22.0 g of **4** (0.16 mol) and 3 mL of triglyme as an internal standard in 900 mL of acetone was cooled in a dry ice/methanol bath, and acetylene was condensed in it until the volume of the solution became about 1400 mL. The mixture was photolyzed through Pyrex with a high-pressure Hg lamp, and the reaction was monitored by GLC (column B, 180 °C). After 9 h, the magnitude of the adduct peak reached maximum, and continued irradiation only induced secondary reactions. The cooling bath was removed, and boiling stones were added to allow excess acetylene to evaporate. After the evaporation of acetylene ceased, the slightly brown residue was concentrated in vacuo and subjected to chromatography on silica gel eluted with ether/hexane (1:9). The eluent was concentrated and distilled to give 7.53 g of **5a** (29%) bp 64–68 °C (1.8 Torr).

8-(Hydroxymethylene)tricyclo[4.3.2.0^{1,6}]undec-10-en-7-one (5b). To CH_3ONa prepared from 2.06 g of Na (90 mmol) and dried at 180 °C (2 Torr) were added successively 120 mL of benzene, 7.40 g of ethyl formate (0.10 mol), and 5.80 g of **5a** (36 mmol) in 70 mL of benzene. The mixture, which soon became thick, was stirred at room temperature. After 18 h, an aliquot was hydrolyzed and analyzed by GLC (column B, 180 °C), which showed that **5a** had already been consumed. The mixture was cooled in an ice bath and treated with 40 mL of water. The organic layer was separated from the aqueous layer and extracted with 20 mL of water and then 20 mL of 10% aqueous NaOH. The aqueous extracts and the aqueous layer were combined, washed with ether, and acidified with 12 mL of concentrated HCl. The liberated product was extracted with ether (3 × 100 mL), and the combined ethereal extracts were washed with water, dried with $MgSO_4$, concentrated, and distilled to give 5.54 g of **5b** (81%): bp 95–100 °C (3×10^{-3} Torr); ^1H NMR δ 1.4–1.9 (m, 8 H), 2.30 (dd, $J = 2, 15$ Hz, 1 H), 2.65 (dd, $J = 2, 15$ Hz, 1 H), 6.16 (d, $J = 3$ Hz, 1 H), 6.27 (d, $J = 3$ Hz, 1 H), 7.35 (m, 1 H), 7.7 (br s, 1 H); IR (film) 3500–2400 (br), 2930, 2860, 1690, 1610, 1450, 1395, 1205, 925, 775, 735 cm^{-1}.

8-Diazotricyclo[4.3.2.0^{1,6}]undec-10-en-7-one (5c). To a solution of 2.49 g of **5b** (13.1 mmol) in 50 mL of dichloromethane were added 2.30 g of tosyl azide (11.6 mmol) in 25 mL of dichloromethane and 3.26 mL of triethylamine (2.37 g, 23.4 mmol). The resultant bright yellow mixture was stirred at ca. 15 °C for 5 h and then cooled in an ice bath and treated with 12 mL of 7% aqueous KOH. The aqueous solution was extracted with dichloromethane, and the combined organic solutions were washed three times with water and dried with $MgSO_4$. The crude product, which was contaminated by unreacted tosyl azide, was purified by chromatography on silica gel. Elution with ether/hexane (1:4) afforded 2.00 g of **5c** (81%): ^1H NMR δ 1.3–2.0 (m, 8 H), 2.78 (d, $J = 14$ Hz, 1 H), 3.00 (d, $J = 14$ Hz, 1 H), 6.22 (d, $J = 2.5$ Hz, 1 H), 6.31 (d, $J = 2.5$ Hz, 1 H); ^{13}C NMR, δ 18.57, 24.42, 30.54, 31.44, 48.26, 58.74, 60.93, 140.43, 144.32, 200.81; IR (film) 3050, 2935, 2860, 2075, 1665, 1455, 1320, 1245, 930, 825, 775, 725 cm^{-1}; MS, *m/z* 188 (M^+, 25), 159 (20), 132 (16), 131 (45), 117 (40), 115 (22), 105 (19), 104 (95), 103 (35), 91 (100), 78 (39), 77 (26), 65 (22); HRMS calcd for $C_{11}H_{12}N_2O$ 188.0950, found 188.0952.

9-Tricyclo[4.2.2.0^{1,6}]dec-7-enecarboxylic acid (6a). A solution of 2.00 g of **5c** (10.6 mmol) and 1 mL of triethylamine (7.2 mmol) in 150 mL of 60% aqueous dioxane was irradiated through Pyrex until gas evolution ceased. The photolysate was treated with 0.5 g of K_2CO_3 and concentrated in vacuo. The residue was dissolved in 100 mL of water and washed with ether to remove nonacidic components. The aqueous solution was acidified with concentrated HCl, and the liberated product was extracted with ether (3 × 100 mL). The combined ethereal extracts were washed twice with water, dried with $MgSO_4$, concentrated, and distilled to give 1.25 g of **6a** (66%), bp 95–115 °C (7×10^{-3} Torr). The NMR spectrum indicated that the product was a ca. 1:4 mixture of geometrical isomers, which was used in the subsequent reaction without separating the isomers: IR (film) 3500–2400 (br), 1700, 1445, 1410, 1305, 1280, 1235, 945, 795, 780, 750 cm^{-1}. Major isomer: ^1H NMR δ 1.2–2.1 (m, 8 H), 2.06 (dd, $J = 10, 12$ Hz, 1 H), 2.25 (dd, $J = 6, 12$ Hz, 1 H), 3.05 (dd, $J = 6, 10$ Hz, 1 H), 6.18 (d, $J = 2$ Hz, 1 H), 6.30 (d, $J = 2$ Hz, 1 H), 11.0 (s, 1 H).

Preparation of 7a. A mixture of 1.35 g of **6a** (7.0 mmol), 2.30 g of diphenylphosphoryl azide (8.4 mmol), and 1.30 mL of triethylamine (9.3 mmol) in 50 mL of benzene was refluxed overnight. The GLC analysis (column E, 120–200 °C) of the reaction mixture showed almost complete consumption of **6a**. 2-(Methylthio)ethanol (4.0 mL, 46 mmol) was added, and refluxing was continued for 22 h. After workup in the usual manner, excess 2-(methylthio)ethanol was evaporated in vacuo, and the residue was chromatographed on silica gel. Elution with benzene/dichloromethane (1:1) afforded a mixture of the two geometrically isomeric **7a**'s (1.50 g, 81%): IR (film), 3340, 2930, 2850, 1710, 1520, 1245, 1060, 765 cm^{-1}; MS (23 eV) *m/z* 132 (14), 104 (13), 75 (100). Major isomer: ^1H NMR δ 1.2–2.0 (m, 8 H), 1.76 (dd, $J = 6, 13$ Hz, 1 H), 2.15 (s, 3 H), 2.35 (dd, $J = 10, 13$ Hz, 1 H), 2.71 (t, $J = 7$ Hz, 2 H), 4.0 (m, 1 H), 4.21 (t, $J = 7$ Hz, 2 H), 4.8 (br s, 1 H), 6.16 (d, $J = 2$ Hz, 1 H), 6.40 (d, $J = 2$ Hz, 1 H).

9-Tricyclo[4.2.2.0^{1,6}]dec-7-enamine (7c). A mixture of 1.50 g of **7a** (5.7 mmol), 2.0 mL of dimethyl sulfate (21 mmol), and 0.60 g of $NaHCO_3$ (7.1 mmol) in 30 mL of methanol was stirred at ca. 35 °C. After 10 h, an additional 1 mL of dimethyl sulfate (11 mmol) and 0.60 g of $NaHCO_3$ (7.1 mmol) were added, and stirring was continued for 30 h at the above temperature. A solution of 6.3 g of NaOH (0.16 mol) in 30 mL of 50% aqueous methanol was added to the resultant mixture, which was further stirred for 2.5 h at 35 °C, cooled in an ice bath, and then made acidic with concentrated HCl. After removal of the methanol, the residual aqueous solution was washed with ether, 15 g of NaOH was added, and the liberated amine was extracted with ether. The extract was dried with KOH, concentrated in vacuo, and distilled to give 0.70 g of **7c** (77%): bp 90–100 °C (30 Torr); MS, *m/z* 149 (M^+, 14), 148 (36), 120 (52), 107 (34), 106 (80), 105 (34), 91 (100), 79 (36), 78 (50); HRMS calcd for $C_{10}H_{15}N$ 149.1205, found 149.1213. Major isomer: ^1H NMR δ 1.2–2.0 (m, 10 H), 1.63 (dd, $J = 6, 12$ Hz, 1 H), 2.23 (dd, $J = 9, 12$ Hz, 1 H), 3.23 (dd, $J = 6, 9$ Hz, 1 H), 6.20 (d, $J = 2$ Hz, 1 H), 6.41 (d, $J = 2$ Hz, 1 H).

Tricyclo[4.2.2.0^{1,6}]deca-7,9-diene (1a). A mixture of 0.70 g of **7c** (4.7 mmol), 2.5 mL of methyl iodide (40 mmol), and 1.50 g of $NaHCO_3$ (18 mmol) in 50 mL of methanol was heated at 50 °C for 40 h. After removal of the volatile components in vacuo, the residue was extracted with warm chloroform (4 × 50 mL). The combined extracts were evaporated in vacuo to give 1.44 g of crude crystalline ammonium salt. To a mixture of the ammonium salt obtained above, 70 mL of dimethylformamide, and 100 mL of pentane was added 4.0 g of *t*-BuOK (36 mmol). After the resultant mixture was stirred overnight at room temperature, an additional 3.0 g of *t*-BuOK (27 mmol) was added, and stirring was continued for 2 d. The mixture was poured on ice and the aqueous layer, which separated from the organic layer, was extracted with pentane. The combined pentane solutions were washed well with water and dried with $MgSO_4$. After removal of the solvent through a short Vigreux column, the residue was distilled to give 410 mg of **1a** (66%), bp 70–72 °C (32 Torr). The physical property of **1a** obtained above was in good agreement with that of **1a** prepared following the procedure of Bickelhaupt et al.[9]

Methyl 9-Tricyclo[4.2.2.0^{1,6}]dec-7-enecarboxylate (6b). A soluton of 2.00 g of **5c** (10.6 mmol) and 1 mL of triethylamine (7.2 mmol) in 150 mL of methanol was irradiated through Pyrex with a high-pressure Hg lamp until gas evolution ceased. After removal of the methanol, the residue was distilled to give 1.60 g of a ca. 2:5 mixture of geometrically isomeric **6b** [79%; bp 80–90 °C (2 Torr)], which was used in the subsequent reaction without separating the isomers: IR (film), 3030, 2930, 2850, 1730, 1450, 1435, 1205, 1175 cm^{-1}; MS, *m/z* 192 (M^+, 8), 160 (16), 133 (35), 132 (20), 131 (18), 117 (20), 105 (36), 104 (17), 91 (100), 79 (18), 77 (19); HRMS calcd for $C_{12}H_{16}O_2$ 192.1150, found 192.1145. Major isomer: ^1H NMR δ 1.2–2.0 (m, 8 H), 2.06 (dd, $J = 10, 12$ Hz, 1 H), 2.25 (dd, $J = 6, 12$ Hz, 1 H), 3.00 (dd, $J = 6, 10$ Hz, 1 H), 3.65 (s, 3 H), 6.10 (d, $J = 2$ Hz, 1 H), 6.29 (d, $J = 2$ Hz, 1 H).

Methyl 7-Tricyclo[4.2.2.0^{1,6}]deca-7,9-dienecarboxylate (1c). Diisopropylamine (0.76 mL, 5.4 mmol) in 10 mL of THF was treated with 2.05 mL of 2.54 M butyllithium (5.2 mmol) in hexane at −78 °C to produce *i*-Pr_2NLi, to which a solution of 0.86 g of **6b** (4.5 mmol) in 15 mL of THF was added over a period of 15 min. After 30 min at −78 °C, a solution of 1.72 g of diphenyl diselenide (5.5 mmol) in 1 mL of HMPA and 9 mL of THF was added. The reaction was stirred at −78 °C for 30 min and then at −50 to −40 °C for 1 h and quenched with wet ether. The reaction mixture was washed successively with aqueous $NaHCO_3$, dilute HCl, water, and aqueous $NaHCO_3$ and dried with $MgSO_4$. The GLC analysis (column B, 120–200 °C) of the mixture showed that **6b** had completely been consumed.

After removal of the solvent, the crude product was dissolved in 50 mL of dichloromethane. To the solution cooled in an ice bath were added 6 mL of water, 1.1 mL of pyridine, and 6 mL of 30% aqueous H_2O_2. The reaction was stirred at 0 °C for 1 h and then at room temperature for 1 h. The organic solution was separated from the aqueous layer, washed successively with water, aqueous $NaHCO_3$, and water, dried with $MgSO_4$, and filtered. To the filtrate was added 2 mL of pyridine, and the mixture was refluxed for 2 h, cooled, and washed with dilute HCl, water, and aqueous $NaHCO_3$. After removal of the solvent, the residue was

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(32) Regitz, M.; Hocker, J.; Liedhegener, A. In *Organic Syntheses*; Wiley: New York, 1973; *Collect. Vol. V*, p 179.

subjected to chromatography on silica gel eluted with ether/hexane (1:19). The eluent containing the product was concentrated in vacuo and distilled to give 340 mg of **1c** (40%): bp 75–80 °C (1 Torr); ^{1}H NMR δ 1.25–1.55 (m, 4 H), 1.8–2.2 (m, 4 H), 3.74 (s, 3 H), 6.45 (d, J = 2 Hz, 1 H), 6.60 (d, J = 2 Hz, 1 H), 7.20 (s, 1 H); ^{13}C NMR δ 20.56, 21.03, 25.15, 25.62, 51.04, 53.00, 54.84, 143.89, 145.26, 147.07, 154.94, 163.16; IR (film) 3100, 3040, 2930, 2860, 1720, 1595, 1545, 1450, 1435, 1305, 1270, 1230, 1150, 1085, 785 cm^{-1}; UV λ_{max} (95% EtOH) 237 nm (ϵ 2400, sh); MS, m/z 190 (M^+, 4), 162 (100), 147 (49), 132 (30), 131 (46), 119 (41), 104 (50), 91 (50), 77 (33); Anal. ($C_{12}H_{14}O_2$) C, H.

7-(Methoxymethyl)tricyclo[4.2.2.0^{1,6}]deca-7,9-diene (1b). To a solution of 232 mg of **1c** (1.22 mmol) in 20 mL of benzene was added 1.15 mL of 50% i-Bu_2AlH (3.0 mmol) in hexane at 0 °C. The reaction was stirred at room temperature for 3 h, cooled to 0 °C, and quenched with 0.35 mL of methanol and then 0.20 mL of water. To dissolve the gelatinous precipitate, dilute HCl was added, and the aqueous solution separated from the organics was extracted twice with ether. The organics were combined with the ethereal extracts, washed with water and aqueous $NaHCO_3$, and dried with $MgSO_4$. The GLC analysis (column A, 140 °C) of the mixture showed the complete consumption of **1c** and the formation of a single major product. After removal of the solvent, the residue in 40 mL of DME was added to ca. 300 mg of NaH. After the resultant mixture was stirred for 20 min at room temperature, 0.70 mL of methyl iodide (11 mmol) was added. The etherification was complete within 5 h. The reaction mixture was cooled to 0 °C, treated with methanol to destroy excess NaH, and concentrated in vacuo. The crude product extracted from the residue with ether was purified by preparative GLC (column B, 120 °C) to give 160 mg of **1b** (75%): ^{1}H NMR δ 1.25–1.5 (m, 4 H), 1.8–2.0 (m, 4 H), 3.33 (s, 3 H), 3.94 (d, J = 1.5 Hz, 2 H), 6.29 (m, 1 H), 6.47 (d, J = 2 Hz, 1 H), 6.51 (d, J = 2 Hz, 1 H); IR (film) 3100, 3030, 2930, 2855, 2820, 1450, 1285, 1200, 1100, 1085, 840, 820, 755 cm^{-1}; MS, m/z 176 (M^+, 0.3), 131 (26), 118 (100), 117 (20), 105 (23), 103 (17), 91 (40), 77 (16); Anal. ($C_{12}H_{16}O$) C, H.

Irradiation of 1a in Methanol. A solution of 50 mg of **1a** (0.38 mmol) in 20 mL of methanol was placed in a Pyrex test tube (18 mm × 18 cm), bubbled with argon for 15 min at 0 °C, and irradiated with a high-pressure Hg lamp at 12 °C. The reaction was monitored by GLC (columns B and H, 150 °C), which showed the formation of a single volatile product. After 30 h (60% conversion), the irradiation was terminated, the mixture was poured into 30 mL of water, and the product was extracted with pentane (2 × 30 mL). The combined extracts were washed with water and dried with $MgSO_4$. After removal of the solvent through a short Vigreux column, the residue was subjected to preparative GLC (column G, 100 °C) to give 22 mg of **3a** (60%): ^{1}H NMR δ 1.3–1.8 (m, 8 H), 2.8–3.0 (m, 1 H), 3.24 (s, 3 H), 5.90 (d, J = 10 Hz, 2 H), 6.06 (dd, J = 5, 10 Hz, 2 H); ^{13}C NMR δ 24.69, 25.01, 34.17, 35.63, 41.39, 52.01, 77.49, 132.01, 133.85; IR (film) 3030, 2920, 2850, 2820, 1390, 1110, 1090, 1025, 920, 805, 710 cm^{-1}; MS, m/z 164 (M^+, 11), 122 (17), 121 (100), 91 (18); Anal. ($C_{11}H_{16}O$) C, H.

Acetone-Sensitized Photolysis of 1a in Methanol. A solution of 3 mg of **1a** (23 μmol) and 80 μL of acetone (1.1 mmol) in 2 mL of methanol was placed in a Pyrex test tube (12 mm × 8 cm), bubbled with argon for 5 min at 0 °C, and irradiated with a 100-W high-pressure Hg lamp. The solution soon became cloudy, and colorless precipitate was observed at the end of the photolysis (30 min). The GLC analysis (columns D and F, 100–160 °C) of the photolysate showed the formation of a single major product and a few minor products. The retention times on the GLC and the fragmentation pattern in the MS spectrum of the major product agreed with those of **3a**. The yield of **3a** determined by GLC was 14%. A control experiment showed that **1a** was not photolyzed appreciably in the absence of acetone under the otherwise comparable conditions.

Irradiation of 1a in Ethanol. Photolysis of **1a** (35 mg, 0.27 mmol) in ethanol (20 mL) was carried out as described for the reaction in methanol. After 40 h, the conversion of **1a** was 91%, and the formation of a single volatile product was observed. Preparative GLC (column D, 125 °C) of the photolysate produced 19 mg of **3b** (42%): ^{1}H NMR δ 1.19 (t, J = 7 Hz, 3 H), 1.3–1.8 (m, 8 H), 2.8–3.0 (m, 1 H), 3.43 (q, J = 7 Hz, 2 H), 5.90 (d, J = 10 Hz, 2 H), 6.02 (dd, J = 5, 10 Hz, 2 H); ^{13}C NMR δ 16.17, 24.52, 24.92, 34.08, 35.51, 41.39, 58.58, 131.16, 134.50; IR (film) 3040, 2950, 2920, 1390, 1100, 1075, 805 cm^{-1}; MS, m/z 178 (M^+, 22), 136 (15), 135 (100), 108 (14), 107 (92), 94 (19), 91 (27), 77 (10); Anal. ($C_{12}H_{18}O$) C, H. In the ^{13}C NMR, the signal of C-1 was not found. Presumably, it would accidentally overlap with one of the three lines of the $CDCl_3$ signal.

Irradiation of 1a in 1% (v/v) CF_3CO_2H/2-Propanol. Photolysis of **1a** (35 mg, 0.27 mmol) in a mixture of 0.2 mL of CF_3CO_2H and 20 mL of 2-propanol was carried out as described for the reaction in methanol and monitored by GLC (columns D and F, 100–200 °C), which showed the formation of a major product and a few minor products. After 40 h (82% conversion), the irradiation was terminated, and the photolyzed mixture was neutralized with aqueous $NaHCO_3$, concentrated in vacuo, and extracted with ether. The ethereal extract was washed with water, dried with $MgSO_4$, concentrated, and subjected to preparative GLC (column A, 120–220 °C) to give 14 mg of **3c** (34%, 58% by GLC): ^{1}H NMR δ 1.15 (d, J = 6 Hz, 6 H), 1.3–1.8 (m, 8 H), 2.8–3.0 (m, 1 H), 3.77 (hept, J = 6 Hz, 1 H), 5.8–6.1 (m, 4 H); ^{13}C NMR δ 24.60, 24.86, 25.13, 34.22, 35.42, 41.77, 66.49, 77.80, 130.43, 134.94; IR (film) 3040, 2950, 2920, 2850, 1390, 1380, 1070, 990, 810 cm^{-1}; MS, m/z 192 (M^+, 0.5), 150 (30), 108 (19), 107 (100), 91 (17); Anal. ($C_{13}H_{20}O$) C, H.

Irradiation of 1b in 1% (v/v) CF_3CO_2H/Ethanol. Photolysis of **1b** (48 mg, 0.27 mmol) in a mixture of 0.2 mL of CF_3CO_2H and 20 mL of ethanol was carried out as described for the reaction of **1a** in methanol. The GLC analysis (column I, 180 °C) of the photolysate showed the formation of two products in a ratio of 2:9. This ratio remained almost constant throughout the irradiation. After 94 h (50% conversion), the irradiation was terminated, and the photolysate was worked up as described for the reaction of **1a** in CF_3CO_2H/2-propanol. The preparative GLC (column A, 100–200 °C) of the product mixture gave 20 mg of ethanol adducts (66%) as a mixture. Pure **3d′** (the major adduct) was obtained by repeating the preparative GLC (column I, 180 °C). Although the minor product was not obtained in a pure form, the GLC–MS analysis and the 500-MHz ^{1}H NMR of the mixture indicated that it would be **3d**. **3d**: ^{1}H NMR δ 2.95 (quint, J = 5 Hz, 1 H), 3.21 (dq, J = 9, 7 Hz, 1 H), 3.43 (s, 3 H), 3.52 (dq, J = 9, 7 Hz, 1 H), 3.90 (d, J = 13 Hz, 1 H), 4.00 (d, J = 13 Hz, 1 H) (The other signals were not resolved from those due to **3d**); MS (23 eV) m/z 222 (M^+, 33), 193 (26), 191 (29), 190 (24), 179 (100), 177 (39), 165 (21), 162 (20), 147 (69), 119 (55), 107 (22); HRMS calcd for $C_{14}H_{11}O_2$ 222.1620, found 222.1634. **3d′**: ^{1}H NMR δ 1.18 (t, J = 7 Hz, 3 H), 1.3–1.5 (m, 4 H), 1.6–1.8 (m 4 H), 2.90 (dt, J = 5, 4 Hz, 1 H), 3.33 (s, 3 H), 3.43 (q, J = 7 Hz, 2 H), 3.87 (d, J = 13 Hz, 1 H), 4.03 (d, J = 13 Hz, 1 H), 5.84 (s, 1 H), 5.90 (d, J = 10 Hz, 1 H), 6.10 (dd, J = 5, 10 Hz, 1 H); IR (film) 2980, 2925, 2850, 1445, 1380, 1100, 1075, 845 cm^{-1}; MS (23 eV) m/z 222 (M^+, 12), 191 (15), 190 (100), 177 (50), 175 (56), 149 (80), 147 (28), 121 (18), 107 (18); HRMS calcd for $C_{14}H_{22}O_2$ 222.1620, found 222.1616.

Irradiation of 1c in 1% (v/v) CF_3CO_2H/Ethanol. Photolysis of **1c** (80 mg, 0.42 mmol) in a mixture of 0.2 mL of CF_3CO_2H and 20 mL of ethanol was carried out as described for the reaction of **1a** in methanol and monitored by GLC (column A, 100–200 °C), which showed the formation of two major products in a ratio of 5:6. This ratio remained almost constant throughout the irradiation. After 5 h, the photolysis was almost complete. The reaction was worked up as described for the reaction of **1a** in CF_3CO_2H/2-propanol, and the crude product mixture was subjected to chromatography on silica gel eluted with ether/hexane (1:9) to give 32 mg of **3e** (32%) and 29 mg of **3e′** (29%). **3e**: ^{1}H NMR δ 1.14 (t, J = 7 Hz, 3 H), 1.4–1.9 (m, 7 H), 2.2–2.4 (m, 1 H), 2.95–3.1 (m, 1 H), 3.20 (dq, J = 9, 7 Hz, 1 H), 3.45 (dq, J = 9, 7 Hz, 1 H), 3.78 (s, 3 H), 5.8–6.1 (m, 2 H), 6.99 (d, J = 6 Hz, ^{1}H); IR (film) 3040, 2970, 2930, 2850, 1725, 1665, 1630, 1440, 1430, 1270, 1255, 1245, 1215, 1100, 1075, 800 cm^{-1}; MS m/z 236 (M^+, 13), 193 (30), 189 (17), 177 (18), 175 (55), 165 (43), 134 (15), 133 (100), 120 (20), 107 (16), 91 (24), 77 (15); Anal. ($C_{14}H_{20}O_3$) C, H. **3e′**: ^{1}H NMR δ 1.20 (t, J = 7 Hz, 3 H), 1.3–1.6 (m, 4 H), 1.6–1.9 (m, 4 H), 3.41 (q, J = 7 Hz, 2 H), 3.46 (m, 1 H), 3.78 (s, 3 H), 5.88 (dd, J = 2, 10 Hz, 1 H), 6.10 (dd, J = 5, 10 Hz, 1 H), 7.10 (d, J = 2 Hz, 1 H); IR (film) 3040, 2975, 2930, 2855, 1720, 1665, 1630, 1440, 1270, 1260, 1245, 1110, 1080, 1065, 805 cm^{-1}; MS, m/z 236 (M^+, 22), 194 (27), 193 (100), 177 (56), 165 (39), 149 (21), 135 (23), 121 (34), 107 (33), 91 (15); Anal. ($C_{14}H_{20}O_3$) C, H.

Irradiation of 9 in Methanol. A solution of 7 mg of **9** in 7 mL of methanol in a quartz tube was bubbled with argon and irradiated with a high-pressure Hg lamp. The GLC analysis (column H, 170 °C) of the photolysate showed the formation of a single volatile product. The IR spectrum of the product collected by preparative GLC was superimposable to that of authentic **13**.[9] The yield of **13** determined by GLC was 58%. The expected methanol adduct **11** was not detected in the photolysate.[20]

Measurement of Electronic Absorption Spectra Observed upon Irradiation of 1a–1c with 254-nm Light at 77 K. A solution of **1** in an appropriate solvent [ethanol, EPA, pentane/isopentane (1:1)] was placed in a quartz tube (12-mm i.d.) and degassed by freeze–pump (2 × 10^{-3} Torr)–thaw cycles. The sealed quartz tube was immersed in liquid N_2 in a Dewar having two parallel windows (22-mm diameter) facing each other and irradiated through the window.

(a) **1a.** When a solution of 5 mg of **1a** (37 μmol) in 5 mL of ethanol was irradiated with 254-nm light, development of an absorption with λ_{max} 260 ± 2 and 340 ± 2 nm (relative intensity, ca. 2:1) was observed. The continued irradiation brought about development of another absorption with λ_{max} 285 and 300 nm at a much slower rate. Absorbances at 340 nm after 5, 10, 20, and 30 min of irradiation were 0.24, 0.35, 0.43, and 0.46, respectively, and it was not increased appreciably upon further irradiation, while the intensity of the latter absorption continued to increase. When irradiated with 366-nm light, the former absorption had largely been bleached after 1 min. The absorption at 340 nm remained unchanged for more than 1 h at 77 K in the dark but had disappeared when the frozen solution was thawed in an ethanol bath at −100 °C and immediately refrozen in liquid N_2. Irradiation of **1a** in EPA or pentane/isopentane (1:1) also led to development of an absorption with λ_{max} 260 and 340 nm (relative intensity, ca. 2:1) that showed similar thermal and photochemical behaviors.

(b) 1b. When a solution of 8 mg of **1b** (45 μmol) in 6 mL of ethanol was irradiated with 254-nm light at 77 K, development of an absorption with λ_{max} 267 ± 2 and 346 ± 2 nm (relative intensity, ca. 2:1) was observed. Absorbances at 346 nm after 5 and 9 min of irradiation were 0.35 and 0.47, respectively. By subsequent irradiation with 366-nm light for 2 min, the generated absorption was largely bleached but a broad band in the 270–310-nm region (absorbance <0.10) remained unbleached. The absorption at 346 nm remained unchanged for more than 1 h at 77 K in the dark but had disappeared when the frozen solution was thawed in an ethanol bath at −100 °C and immediately refrozen in liquid N_2.

(c) 1c. When a solution of 10 mg of **1c** (53 μmol) in 6 mL of ethanol was irradiated with 254-nm light at 77 K, development of an absorption with λ_{max} 280 ± 2, 348 ± 2, and 425 ± 3 nm (relative intensity, ca. 7:2:1) was observed. Absorbances after 4, 8, 12, and 16 min of irradiation were 0.24, 0.38, 0.47, and 0.50, respectively. By subsequent irradiation with 366-nm light, the generated absorption was bleached and the original absorption spectrum of **1c** was cleanly restored. The newly developed absorption remained unchanged for more than 1 h at 77 K in the dark but had disappeared when the frozen solution was thawed in an ethanol bath at −100 °C and immediately refrozen in liquid N_2. Irradiation of **1c** in pentane/isopentane (1:1) with 254-nm light led to development of an absorption with λ_{max} 278 ± 2, 347 ± 2, and 425 ± 3 nm (relative intensity, ca. 6:2:1) that showed similar thermal and photochemical behaviors.

Trapping of Intermediate Exhibiting Absorption at 340 nm with Ethanol. To a chilled solution of 20 mg of **1a** (0.15 mmol) in 6 mL of ethanol was added 6 mL of 2% (v/v) ethanolic solution of sulfuric acid. In two quartz tubes (12-mm i.d.) were placed 5-mL portions of the above solution and degassed by freeze–pump–thaw cycles. The solution in the first tube was frozen in liquid N_2 in the Dewar used for the measurement of the electronic absorption spectra, irradiated with 254-nm light for 5 min through one of the windows and for additional 5 min from the opposite direction through the other window, and then warmed up to room temperature. This freeze–irradiation (2 × 5 min)–thaw cycle was repeated 10 times. The solution in the second tube was irradiated with 254-nm light in the same manner, but each time before the frozen solution was thawed, the generated absorption was bleached by irradiating the solution with 366-nm light through the two windows for 1 min at a time. Each photolyzed mixture was neutralized with aqueous $NaHCO_3$, concentrated in vacuo, and extracted with pentane. The extract was washed with water, dried with $MgSO_4$, concentrated, and analyzed by GLC (columns C and F, 135 °C) and GLC–MS. The ethanol adduct **3b** was detected in both the photolysates, but the amount of **3b** produced in the second tube was only ca. one-tenth of that formed in the first tube. A residual 2 mL of the acidic ethanolic solution of **1a** was worked up after standing 16 h in the dark at room temperature. The GLC analysis showed that **1a** largely remained unconsumed and that **3b** was not formed in a detectable amount in the dark. When the above experiment was repeated, good reproducibility was observed.

Trapping of 14 Generated in Photolysis of 1a with 254-nm Light at 77 K. A solution of 10 mg of **1a** (76 μmol) in 15 mL of pentane/isopentane (1:1) was distributed among three quartz tubes (12-mm i.d.). The solution in each tube was bubbled with N_2 for 15 min at 0 °C, frozen in liquid N_2, and irradiated with 254-nm light for 4.5 h, whereupon absorbance at 300 nm went up to over 2. A dilute solution of bromine in dichloromethane was added, and the frozen mixture was warmed up to room temperature while agitating it well. The mixtures in the three tubes were combined, washed with aqueous $Na_2S_2O_3$ and water, and dried with $MgSO_4$. The analysis of the mixture by GLC (column F, 150 °C) and HPLC [μ-Porasil eluted with ether/hexane (1:99)] showed peaks at the retention times coinciding with those of *p*-xylylene dibromide. The product mixture was subjected to chromatography on silica gel eluted with ether/hexane (1:99), and the eluent containing the product was analyzed by GLC-MS. The fragmentation pattern of the product was superimposable to that of authentic *p*-xylylene dibromide.[33]

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Direct and Sensitized Photoisomerization of 1,4-Diphenylbutadienes

W. Atom Yee,*[1a] Stephan J. Hug,[1b] and David S. Kliger[1b]

Contribution from the Department of Chemistry, Santa Clara University, Santa Clara, California 95053, and the Department of Chemistry, University of California, Santa Cruz, California 95064. *Received September 8, 1987*

Abstract: Photoisomerization of the three stereoisomers of 1,4-diphenylbutadiene (DPB) in room-temperature cyclohexane solution was studied by direct excitation and by triplet sensitization. The photostationary mixtures in both singlet and triplet experiments contain only trans,trans and cis,trans isomers; no cis,cis isomer or any photoproducts were observed. The two cis isomers exhibit no measurable fluorescence or triplet formation. Results are interpreted in terms of allylmethylene-like intermediates. Efficient internal conversion of singlet DPBs is inferred from low isomerization quantum yields by direct excitation. Triplet-sensitized isomerizations show a marked DPB concentration dependence of photostationary compositions and quantum yields. Analysis of these data reveals a quantum chain process involving excited triplet DPB as the chain-carrying species. Transient absorption measurements show that sensitized excitation of any DPB isomer leads directly to a fast equilibrium between triplet all-trans and trans-twisted forms.

Linear aliphatic polyenes[2] and α,ω-diphenylpolyenes[3,4] have been extensively investigated in recent years as models for important biological chromophores that undergo cis–trans photoisomerization. This has led to a great deal of theoretical interest in the electronic structure of polyene excited states[5] and in their dynamical behavior.[6]

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