

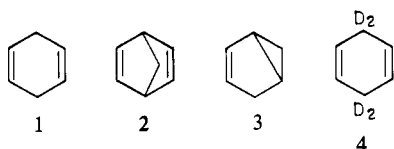
Organic Photochemistry with 6.7-eV Photons: 1,4-Cyclohexadiene and 1,4-Cyclohexadiene-3,3,6,6- d_4 [†]

R. Srinivasan,* Lloyd S. White, Angelo R. Rossi,* and Gary A. Epling*

Contribution from the IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598, and the Department of Chemistry, University of Connecticut, Storrs, Connecticut 06268. Received March 19, 1981

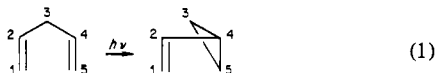
Abstract: The photolysis of 1,4-cyclohexadiene has been investigated in solution at 185 and 214 nm, as well as by sensitization by benzene in solution at 254 nm or by mercury (³P₁) atoms in the vapor phase. The reaction mechanisms under these conditions have been probed by the use of 1,4-cyclohexadiene-3,3,6,6- d_4 (**4**). Both at 185 and 214 nm, the principal products are bicyclo[3.1.0]hex-2-ene (**3**), 1,3-cyclohexadiene, 1,3,5-hexatriene, and benzene. NMR analysis of the products formed in the photolysis of **4** at 185 nm shows that the formation of **3** is exclusively by a 1,2-hydrogen migration. The other two decomposition pathways at this wavelength correspond to 1,3- and 1,4-H migration. The relative importance of these reactions is sensitive to the wavelength in the range 185–214 nm. Triplet sensitization of 1,4-cyclohexadiene gives benzene (+H₂) as a major product and **3** as a minor product. Deuterium labeling shows that in this instance **3** is formed by a di- π -methane rearrangement. Ab initio calculations on the ground state of 1,4-cyclohexadiene employing a STO-3G basis yield a dihedral angle of about 140° with a relatively flat minimum. The intermediate neglect of differential overlap (INDO-SCF-CI) method was used to calculate the energies of the low-lying singlet and triplet states in 1,4-cyclohexadiene for several values of the dihedral angle. At the experimental dihedral angle of 160°, it was computed that there were two triplet states, ³A₂ (3.7 eV) and ³B₂ (3.8 eV), and three closely spaced singlet states, ¹A₂ (5.9 eV), ¹B₂ (6.3 eV), and ¹B₂ (6.4 eV). This is in reasonably good agreement with recent electron-impact data. The ³B₂ state is deduced to undergo the di- π -methane rearrangement under triplet sensitization while all of the hydrogen migration reactions that are observed on direct irradiation are attributed to the higher ¹B₂ state. This state is derived from the excitation of an electron to the $\sigma_1^* + \sigma_2^*$ orbital and contains significant C-H antibonding character.

The properties of the excited states of 1,4-cyclohexadiene (**1**)



and its photochemistry in the far-UV are of interest from two points of view. The interaction between the double bonds in the ground state of **1** has been examined from theoretical considerations,¹ but such an analysis has not been extended to the electronically excited states in any detail. Experimental results²⁻⁴ which can identify the energies of the excited states have been a matter of controversy.⁴ The relationship of **1** to norbornadiene (**2**) whose excited states and photochemistry have been extensively studied^{4,5} made the present investigation an attractive one, the hope being that correlations between reaction pathways and the structures and energies of the excited states (a perennial hope of photochemists!) can be achieved.

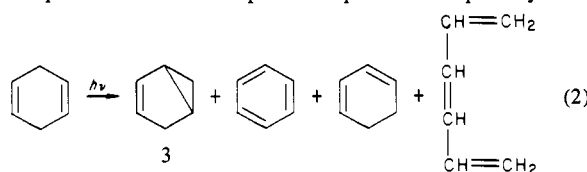
A second point of interest in the photochemistry of **1** is the presence of the 1,4-diene chromophore which leads to the di- π -methane rearrangement (eq 1) in a variety of compounds. Such



a reaction would give bicyclo[3.1.0]hex-2-ene (**3**), but this is only one of four mechanisms by which **1** can be transformed to **3**. It was planned to probe this rearrangement by the use of the deuterium-labeled compound **4**.

Results

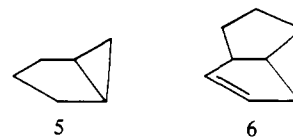
Photolysis of 1,4-cyclohexadiene in pentane solution at 185 nm gave the products shown in eq 2. The products on photolysis at



214 nm were qualitatively the same, but the ratios were quite different. This was equally true in the photolysis of 1,4-cyclohexadiene-3,3,6,6- d_4 at 185 nm which was indicative of a significant isotope effect. The relative yield of the various products is shown in Table I (see footnote *e* regarding absolute yields). The total quantum yield for the appearance of all of the listed products from 1,4-cyclohexadiene at 185 nm was 0.23. This was based on a quantum yield of 0.35 for cis \rightarrow trans isomerization of cyclooctene at this wavelength.⁶

The distribution of deuterium in the products in the photolysis of **4** was analyzed by mass spectrometry and by 200-MHz NMR spectroscopy. It was first ascertained that after 40% of **4** had been photolyzed, the residue did not show any evidence in its NMR spectrum of loss or scrambling of the deuterium atoms.

Bicyclo[3.1.0]hex-2-ene (3). NMR spectra of **3**⁷ and its partially deuterated derivative are shown in Figure 1a, b. All eight protons in **3** are nonequivalent, and in the spectrum, absorptions due to individual protons are fully resolved. The assignments which are also given in Figure 1 are based on comparisons to the spectra of bicyclo[3.1.0]hexane (**5**)^{8,9} and tricyclic compounds such as



6 in which a bicyclo[3.1.0]hex-2-ene is incorporated.¹⁰ The endo

(1) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1.

(2) Robin, M. B. "Higher Excited States of Polyatomic Molecules"; Academic Press: New York, 1975, Vol. II, p 170 ff.

(3) Dimeo, D. A. Ph.D. Thesis, University of California at Los Angeles, 1969.

(4) Frueholz, R. P.; Flicker, W. M.; Mosher, O. A.; Kuppermann, A. *J. Chem. Phys.* **1979**, *70*, 1986.

(5) (a) Reference 2, p 176 ff. (b) Dauben, W. G.; Cargill, R. L. *Tetrahedron* **1961**, *15*, 197. Hammond, G. S.; Wyatt, P.; DeBoer, D. C.; Turro, N. J. *J. Am. Chem. Soc.* **1964**, *86*, 2532. Roquette, B. C. *Ibid.* **1963**, *85*, 3700.

(6) Sonntag, C. V.; Schuchmann, H.-P.; Srinivasan, R. *J. Photochem.* **1981**, *15*, 159.

(7) Meinwald, J.; Mazzocchi, P. H. *J. Am. Chem. Soc.* **1967**, *89*, 1755.

(8) Freeman, P. K.; Grostic, M. F.; Raymond, F. A. *J. Org. Chem.* **1965**, *30*, 771.

(9) Srinivasan, R.; Brown, K. H. *J. Am. Chem. Soc.* **1978**, *100*, 4602.

[†] Dedicated to George S. Hammond on the occasion of his 60th birthday.
* Address correspondence as follows: R. S., IBM Thomas J. Watson Research Laboratories; A.R.R. and G.A.E., University of Connecticut.

Table I. Products and Yields in the Photolysis of 1,4-Cyclohexadiene and 4 under Various Conditions

reactant	wavelength, nm	solvent	% conversion	products, ^e % of total		
				bicyclo- [3.1.0]hex- 2-ene	1,3-cyclo- hexadiene + 1,3,5- hexatriene	benzene
1,4-cyclohexadiene	185 ^a	pentane	<10	30.2	30.0 ^b	39.6
4	185 ^a	pentane	<10	43.0	25.9 ^b	31.1
4	214 nm	pentane	15.8	13.3	27.5 ^c	51.7
4	254 + Hg	gas phase sensitized	~60	20.9	trace	73.0 ^d

^a The 254-nm radiation was not filtered out. ^b The ratio 1,3,5-hexatriene/1,3-cyclohexadiene \approx 4. ^c The ratio 1,3,5-hexatriene/1,3-cyclohexadiene \ll 1. ^d Yield of cyclohexene 6.1%. It varied with conversion. ^e In photolysis at 185 and 214 nm, at the low conversions listed, there were no other products observed. Therefore, the yields given are the chemical yields (not isolated yields) and equalled the percent conversion. In the sensitized reaction at 254 nm this was not the case. The products in Table I accounted for only ~40% of the 4 that was photolyzed.

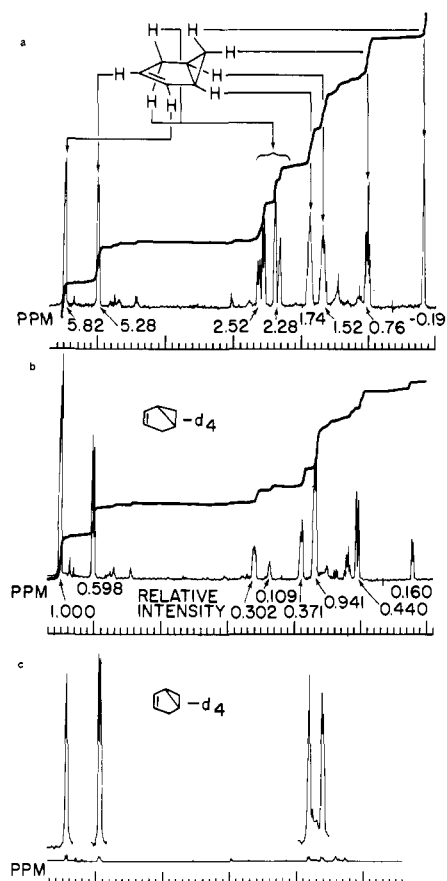


Figure 1. Proton NMR spectra at 220 MHz (CCl_4 solution, Me_4Si as internal reference): (a) bicyclo[3.1.0]hex-3-ene (3); (b) 3 derived from photolysis of 4 at 185 nm; (c) 3 derived from sensitized photolysis of 4 with mercury ($^3\text{P}_1$).

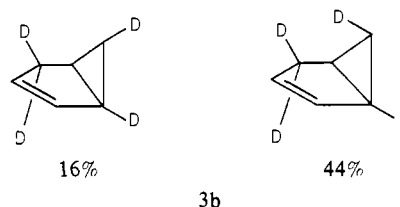
proton at C-6 in **5** is known to occur farther upfield than the exo proton and couple to it with $J = 4$ Hz.^{8,9} The corresponding protons at C-6 in **3** fall at the same chemical shift and are mutually coupled, $J = 7.5$ Hz. The olefinic protons in **6** occur as an AB pair ($J = 5$ Hz). The olefinic protons in **3** also form an AB pair, $J = 5.5$ Hz, and their chemical shifts match those in **6**. Of the remaining four protons in midfield, the pair at δ 2.27 and 2.55 shows an intense (17.5 Hz) mutual coupling which suggests that they share a geminal position. This can be identified as C-4. The exact orientations of the two protons is uncertain. In the remaining pair which corresponds to the bridgehead protons, it is reasonable to assign the downfield member to the allylic position (C-1).

The deuterated derivative (Figure 1b) was found to have four deuterium atoms from its mass spectrum. Although all of the

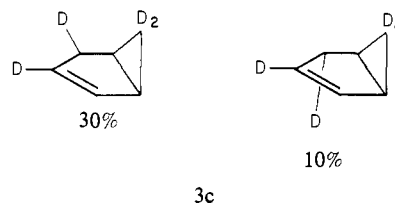
NMR absorptions in **3** were also present in the deuterated derivative, the intensities of the absorptions suggested that the distribution of deuterium was nonrandom. The possibility that the photoproduct was a mixture of two or more structures was considered.

The absorptions due to the protons at C-2 (farthest downfield) and C-5 are of unit intensity; i.e., all of the structures present in the product mixture have these positions occupied by a proton.

The proton that is farthest upfield is the endo-C-6 proton. In **3**, this absorption is a quartet since it is coupled strongly to the geminal exo-C-6 proton as well as to one of the bridgehead protons, possibly C-5. In the deuterated compound, this absorption is a doublet and its splitting (4 Hz) is nonidentical with that of the exo-C-6 proton (8 Hz). Therefore, there are two compounds (which together account for 60% of the mixture) which contain only one proton at C-6. In one the C-6 proton is endo oriented (16%) and in the other the C-6 proton, exo oriented (44%). The last proton in these two compounds can be placed at C-3 (olefinic) because the intensity of this absorption (0.6 H) equals the intensity of the absorption at C-6 (exo + endo). The first two complete structures are



Note that the proton at C-3 is a doublet since it has only one neighboring proton at C-2. The remaining absorptions in the NMR spectrum correspond to protons at C-1, C-2, C-4, and C-5. The intensity of the proton at C-1 (0.37 H) agrees with the sum of the intensities of the protons exo and endo at C-4 (0.41 H). Therefore the following structures make up the rest of the product mixture.



The stereochemical assignment of the protons at C-4 is not unequivocal. It is based merely on the chemical shift of the exo proton being at lower field than that of the endo proton.

It is worth reiterating that this NMR analysis fits only the product composition (**3b** + **3c**) proposed here. Other possible distributions of D atoms in **3**, if they amounted to more than 5% would conflict with the NMR spectrum. The product composition is listed in Table II.

Benzene. The product that was obtained on photolysis at 185 nm was analyzed only by mass spectrometry. Since it was expected

Table II. Products from the Photolysis of 1,4-Cyclohexadiene-3,3,6,6- d_4 at 185 nm and on Sensitization

formula ^a					
composition	44% 6-exo 16% 6-endo	30% 4-exo? 10% 4-endo?		85.6 (rest d_1)	8.9
formula ^b					
relative yield	20.9%	6.1%, D distribution not determined		73.0%, 4.8% d_1 , 45.1% d_2 , 51.6% d_3	

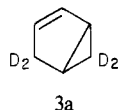
^a Wavelength, 185 nm; solvent, pentane. ^b Sensitizer, Hg(³P₁); pressure of C₆H₆, 5 torr.

that benzene-1,4- d_2 would be a major component in it, an authentic sample of this material was prepared by the pyrolysis of **4** in the vapor phase at 330 °C. Comparison of the mass spectra of this material and the photoproduct showed (Table II) that only 85.6% of the photoproduct was benzene-1,4- d_2 while 8.9% was benzene-1,2,4- d_3 , the rest being benzene- d_1 . When Hg(³P₁) atoms were used to sensitize the decomposition of **4**, the composition of the benzene that was obtained was 40.8% d_1 , 45.1% d_2 , and 51.6% d_3 .

1,3,5-Hexatriene and 1,3-Cyclohexadiene. The complex NMR spectrum of 1,3,5-hexatriene could not be analyzed. The NMR spectrum of 1,3-cyclohexadiene showed that it had 2.87 hydrogen atoms in the olefinic position and 1.13 in the allylic position. At 220 MHz, the former could be resolved into an AB pattern in which the low-field signal was 0.74 of the high-field one. This suggested a structure in which the deuteriums were at C-2, C-5 (2 H), and C-6.

Photolysis of either **1** or **4** in pentane solution at 254 nm in the presence of benzene as a sensitizer gave a few percent yield of bicyclo[3.1.0]hex-2-ene (**3**). There was a practical problem in isolating the material for NMR analysis. Therefore, photolysis of **4** in the vapor phase in the presence of mercury (³P₁) atoms as sensitizer was undertaken. The composition and structures of the products are listed in Table I.

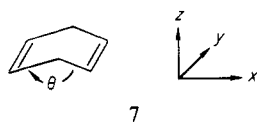
The NMR spectrum (Figure 1c) of the bicyclo[3.1.0]hex-2-ene that was isolated consisted of four absorptions of equal intensity assignable to four individual protons at C-1, C-2, C-3, and C-5. The first two are coupled to each other only and the latter two are also mutually coupled. The structure is therefore



The lower trace at a lower amplification shows that there are no absorptions corresponding to any of the other peak positions in **3**.

Theory

The purpose of the present work is to extend the theoretical analysis¹ to a detailed description of the excited states in 1,4-cyclohexadiene. In Figure 2 the relative energy of 1,4-cyclohexadiene is shown as a function of the dihedral angle, θ (**7**), which



was obtained by using the GAUSSIAN 70 program¹¹ with an STO-3G basis.¹² Although the experimental value of θ is 160°,¹³ the

(11) Hehre, W. J.; Lathan, W. A.; Ditchfield, R.; Newton, M.; Pople, J. A. *QCPE* 1973, **10**, 236.

(12) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* 1969, **51**, 2657.

(13) Oberhammer, H.; Bauer, S. H. *J. Am. Chem. Soc.* 1969, **91**, 10.

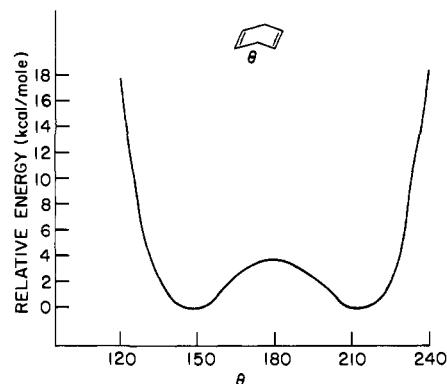


Figure 2. 1,4-Cyclohexadiene: calculated energy of ground state as a function of dihedral angle.

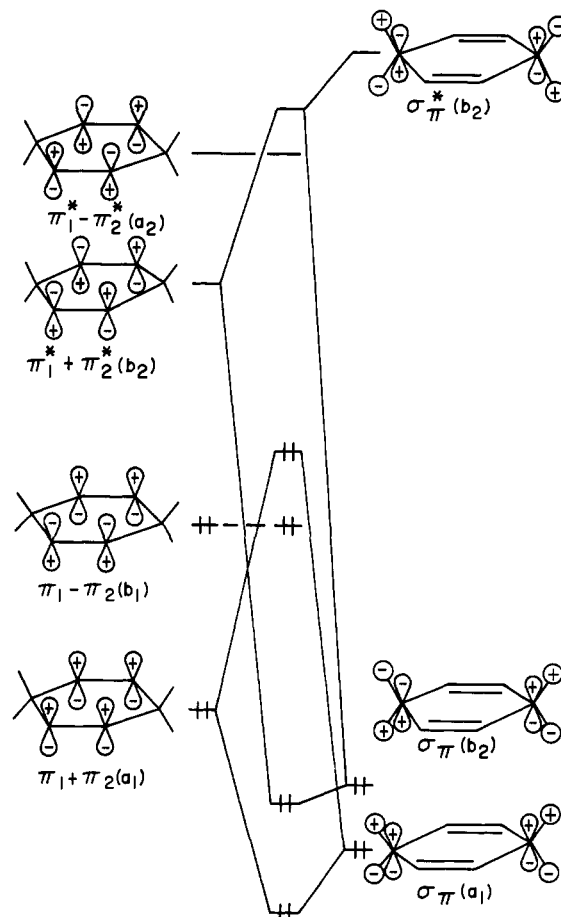


Figure 3. Orbital interaction diagram of 1,4-cyclohexadiene.

computed minimum in energy is $\sim 150^\circ$. For angles greater than 130° , however, the potential energy surface is soft since it requires only 5 kcal to achieve a planar geometry. This value represents

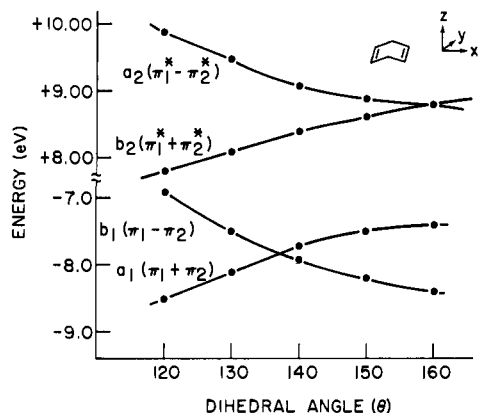


Figure 4. Orbital energies of 1,4-cyclohexadiene: calculated values of energy vs. dihedral angle.

Table III. Description and Composition of the Three Lowest Excited-State Singlets and Two Lowest Triplets for 1,4-Cyclohexadiene at a Fixed Dihedral Angle of 160°

state	excitation energy, eV	percent composition				
		$(a_1)^1-$ $(a_2)^1$	$(a_1)^1-$ $(b_2)^1$	$(b_1)^1-$ $(a_2)^1$	$(b_1)^1-$ $(b_2)^1$	$(a_1)^1-$ $(\sigma_1^* + \sigma_2^*)^1$
3A_2	3.7	64			34	
3B_2	3.8		56	41		
1A_2	5.9	92				
1B_2	6.3		59	16		20
1B_2	6.4		2-			66

an upper limit since an idealized geometry was assumed and geometry optimization was not performed.

An interaction diagram similar to that presented by Hoffmann¹ for the interaction of the methylene groups with the π orbitals in 1,4-cyclohexadiene is presented in Figure 3. One of the salient features is the manner in which the hyperconjugative interaction of the intervening methylene groups serves to destabilize the $\pi_1 + \pi_2$ combination while the $\pi_1 - \pi_2$ combination is unaffected. But the influence of the hyperconjugative interaction of the methylene groups is a sensitive function of angle as shown in Figure 4. The behavior of $\pi_1 + \pi_2$ and $\pi_1 - \pi_2$ combinations as a function of the dihedral angle, θ , indicates that the $\pi_1 + \pi_2$ combination crosses the $\pi_1 - \pi_2$ combination at $\sim 140^\circ$. There is also a crossing of the unfilled virtual $\pi_1^* + \pi_2^*$ and $\pi_1^* - \pi_2^*$ molecular orbitals. It is the relationship between the final interacted orbitals for 1,4-cyclohexadiene and the possible excited states derived from them which is the concern of the present theoretical analysis.

The combination of ethylenic π orbitals are labeled in Figure 4 according to C_{2v} symmetry with respect to the coordinate system shown in 7 as $b_1(\pi_1 - \pi_2)$, $a_1(\pi_1 + \pi_2)$, $a_2(\pi_1^* - \pi_2^*)$, and $b_2(\pi_1^* + \pi_2^*)$. The possible excited singlet or triplet states resulting from excitations of electrons from filled to unfilled orbitals within this manifold belong to the irreducible representations A_2 , B_2 and B_2 , A_2 . The lowest four singlet states and lowest two triplet states for 1,4-cyclohexadiene as a function of dihedral angle θ are given in Figure 5. The excited state energies for 1,4-cyclohexadiene were obtained by using the INDO/S program of Zerner.¹⁴ The configuration interaction for each symmetry type involved all single excitations from the ten highest occupied orbitals to the ten lowest unoccupied orbitals. A more complete description of these excited states is given in Table III for $\theta = 160^\circ$. Several important trends can be derived from this table.¹⁵ The lowest 3A_2 state is a mixture of two configurations whereas the lowest corresponding 1A_2 state is predominantly one configuration. Also, the higher excited states incorporate increasing amounts of σ^* character (from C=C) as

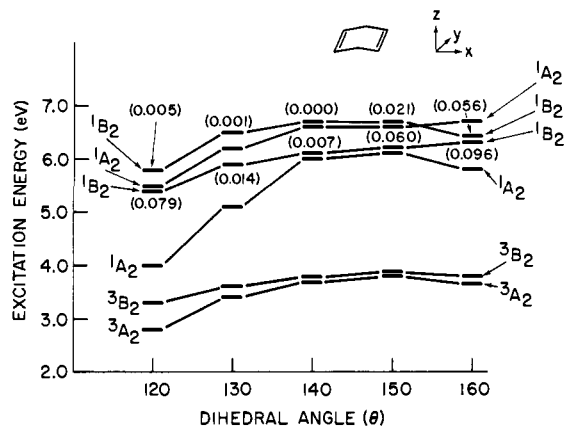
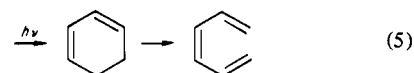
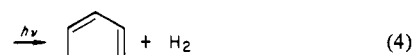


Figure 5. Energies (eV) of singlet and triplet states of 1,4-cyclohexadiene with reference to the ground state (1A_1). Numbers in parentheses indicate oscillator strengths for allowed transitions.

evidenced by the lower 1B_2 state in which there is a 66% contribution arising from an excitation originating with the $a_1(\pi_1 + \pi_2)$ orbital to a $\sigma_1^* + \sigma_2^*$ orbital. This trend of increasing σ^* (C=C) character is maintained for smaller dihedral angles and can play an important role in molecules with small dihedral angles such as norbornadiene. The results reported in Table III are also in satisfactory agreement with previous results on the electron-impact spectrum of 1,4-cyclohexadiene⁴ in which there is a low-energy spectral feature extending from 3.4 to 5.4 eV and is attributed to the lowest triplet. Other high-lying singlet states are found in the range 6.14–7.95 eV. The lower lying single state could be of Rydberg character, and, since Rydberg functions are not included in the basis, care should be used when comparing the present results with experimental values.

Discussion

The three primary photochemical reactions that are observed to take place on the irradiation of 1,4-cyclohexadiene can be represented as



Each of these reactions will be discussed in order.

Four mechanisms may be considered for the transformation of 1,4-cyclohexadiene to bicyclo[3.1.0]hex-2-ene (reaction 3). In the case of the D-labeled material, these can be depicted as in Scheme I. Although the di- π -methane rearrangement is shown as proceeding through the cyclopropyl dicarbonyl radical rather than by a concerted process, it is not pertinent to this research to analyze whether this is actually the case. The observed distribution of D atoms in **3b** and **3c** matches the 1,2-hydrogen shift exactly. The carbene mechanism can also be bent to accommodate such a product composition if it is postulated that the initial product is "hot" and undergoes a vinylcyclopropane rearrangement. But the absence of a *exo*-methylene cyclopentene as a product is a serious criticism as the carbene rearrangement invariably produces such products.^{9,16}

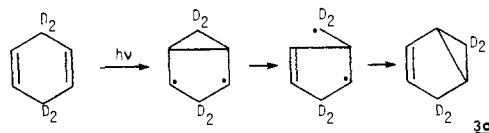
The di- π -methane rearrangement (eq 1) is a well-studied photoreaction that has been observed in acyclic, monocyclic, and bicyclic 1,4-dienes.¹⁷ The transformation has been referred to

(14) Ridley, J.; Zerner, M. *Theor. Chim. Acta* **1973**, *32*, 111–134.

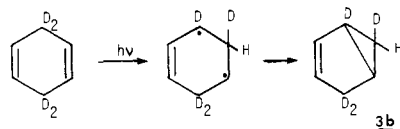
(15) Calculations on isomeric dimethyl- and tetramethyl-1,4-cyclohexadienes have also been carried out. These results will be published elsewhere.

(16) (a) Kropp, P. J.; Fravel, H. G., Jr.; Fields, T. R. *J. Am. Chem. Soc.* **1976**, *98*, 86 and earlier references. (b) Inoue, Y.; Takamuku, S.; Sakurai, H. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1635 and earlier references. (c) Srinivasan, R.; Brown, K. H. *Tetrahedron Lett.* **1978**, 3645.

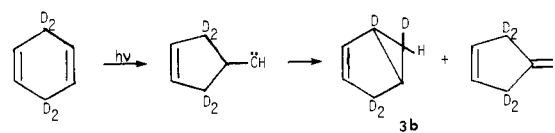
Scheme I. Formation of Bicyclo[3.1.0]hex-2-ene

Di- π -Methane Rearrangement

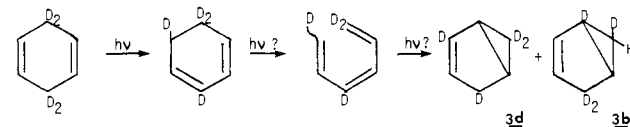
1,2-Hydrogen Shift



Carbene Mechanism



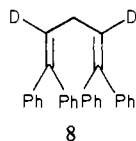
1,3-Hydrogen Shift



as "ubiquitous"¹⁷ and one review concludes that it is a "challenge in photochemistry to find a reaction which does not add another di- π -methane example".¹⁸

Equation 1 suggests that the presence of the 1,4-diene system provides a sufficient framework for the reaction. However, the inaccessibility of the ultraviolet absorption of 1,4-dienes to light of wavelengths longer than 220 nm has led to the use of conjugating substituents such as C=C, phenyl, or C=O on at least one of the double bonds and the use of sensitizers to produce triplet states of the 1,4-diene system. In turn, this has led¹⁷ to generalizations concerning the optimum multiplicity for the di- π -methane rearrangements in acyclic, monocyclic, and bicyclic systems.

It was recognized by several groups^{19,20} that the overall transformation of the 1,4-pentadiene function to a vinylcyclopropane can involve the 1,2-shift of a C-C bond (as in eq 1) or a C-H bond from C-3 to C-4 followed by bonding between C-3 and C-5. Hydrogen migration was actually observed in **8**, but



in the absence of a parallel di- π -methane rearrangement it was not possible to establish the competitive requirements for the two pathways. The behavior of 1,4-cyclohexadiene on direct irradiation

(17) Hixson, S. S.; Mariano, P. S.; Zimmermann, H. E. *Chem. Rev.* **1973**, *75*, 531.

(18) Reference 17, p 551.

(19) (a) Griffin, G. W.; Covell, J.; Petterson, R. C.; Dodson, R. M.; Close, C. *J. Am. Chem. Soc.* **1965**, *87*, 1410. (b) Griffin, G. W.; Marcantonio, A. F.; Kristinsson, H. *Tetrahedron Lett.* **1955**, 2951. (c) Hixson, S. *Ibid.* **1972**, 1155.

(20) Zimmermann, H. E.; Pincock, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 6208.

at 185 nm parallels that of acyclic 1,4-dienes without substituents at C-3. But in contrast to a compound such as **8**, triplet sensitization of 1,4-cyclohexadiene must proceed through a di- π -methane rearrangement as the structure of the product **3a** derived from **4** is compatible only with this mechanism.

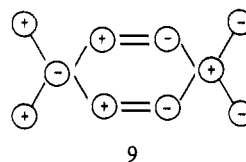
It had previously been shown by Reusch and Frey²¹ that 3,3,6,6-tetramethyl-1,4-cyclohexadiene undergoes a di- π -methane rearrangement under Hg (³P₁) sensitization in the vapor phase. However, in this compound there are no methylenic hydrogens which can promote an alternative (e.g., 1,2-H shift) reaction path. The present work shows that photochemical pathways to transform **1** to **3** (eq 3) differ fundamentally between the singlet and the triplet. This point will be discussed further after a brief consideration of the photoprocesses (4) and (5).

The decomposition of 1,4-cyclohexadiene to benzene and H₂ (eq 4) is a process that is common to both the pyrolysis²² and photolysis in the far-UV region. The former reaction is believed to occur by the concerted elimination of two H atoms from C-1 and C-4. The process is the same for the most (85.6%) part but complicating factors must prevail to account for the few percent each of benzene- d_1 and benzene- d_3 that are observed.

The formation of 1,3-cyclohexadiene is a 1,3-H shift as shown by the deuterium labeling. The question whether 1,3,5-hexatriene is formed from the 1,4-cyclohexadiene by a one-photon process or a two-photon process (by the secondary photolysis of the initially formed 1,3-cyclohexadiene) is a moot point.

The identities of the excited states of 1,4-cyclohexadiene that take part in these reactions is best discussed in terms of the descriptions of the excited states that are given in Table III. If we begin at the low-energy end, the lowest triplet state is ³A₂ and it can be identified as the one that is potentially capable of leading to (2 + 2) addition. That this reaction is not observed is not surprising since it has only 34% of (b₁)¹(b₂)¹ configuration that is required for this reaction. This can be compared to the 89% (b₁)¹(b₂)¹ configuration that is found in the conformation with $\theta = 120^\circ$ which is the geometry of norbornadiene. The only other triplet state that is available is ³B₂, and this must be identified (by a process of elimination) with the di- π -methane rearrangement.

The singlet states of 1,4-cyclohexadiene (Table III) are surprisingly closely spaced. The highest of them (¹B₂) is readily accessible with the photon energy of 6.7 eV that was used. In view of the large contribution from the (a₁)¹($\sigma_1^* + \sigma_2^*$)¹ configuration for this state, it is tempting to attribute all three of the hydrogen migration reactions that were observed in this study to this state. The representation of the $\sigma_1^* + \sigma_2^*$ orbital as in **9** shows



that there is considerable C-H antibonding character so that excitation of an electron to this orbital could promote facile cleavage of the C-H bond.

Attention should be drawn to the fact that a change in the wavelength of the exciting light from 185 to 214 nm can cause substantial changes in the compositions of the products. Wavelength effects in organic photochemistry even in the condensed phase are by no means uncommon,²³ but they are usually attributed to shifts from one electronic absorption to another. In this instance, there is no indication in the absorption spectrum² that such a shift has taken place between the specified wavelengths. Such wavelength effects have been observed only in compounds with weakly interacting chromophores.²⁴ Further experiments to establish the cause of this effect are in progress.

(21) Reusch, W.; Frey, D. W. *Tetrahedron Lett.* **1967**, 5193.

(22) Benson, S. W.; Shaw, R. *Trans. Faraday Soc.* **1967**, *63*, 985.

(23) For a brief review, see: de Mayo, P. *Afinidad* **1977**, *34*, 32.

(24) Srinivasan, R.; Rossi, A. R.; Ors, J. A.; Baum, T.; Brown, K. H.; White, L. S.; Epling, G. A. *J. Chem. Soc. D*, in press.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 137B and/or a Beckman Acculab-6 spectrometer. The solvent was carbon tetrachloride in all cases. NMR spectra were recorded on a Varian T60-1A spectrometer with CCl_4 as solvent and tetramethylsilane as reference. The mass spectra were recorded on a Du Pont 21-490B mass spectrometer. High-resolution NMR spectra were obtained on a Varian HR-220 spectrometer operated by the Consortium at The Rockefeller University in New York.

Materials. 1,4-cyclohexadiene from Chemical Samples Co. (Columbia, OH) was carefully fractionated before use. It had ~1% of benzene as the only impurity. 1,4-cyclohexadiene-3,3,6,6- d_4 was obtained from Merck and Co., Inc. It was made from the oxidation of the Diels-Alder adduct of 1,3-butadiene-1,1,4,4- d_4 to maleic anhydride. Its isotopic purity as determined by its NMR spectrum was >98%. It was used as obtained. Pentane (Baker-Photrex grade) was uniformly used as the solvent for photolysis.

Apparatus. Preparative photolysis at 185 nm was carried out in an annular quartz (Suprasil) reactor (Srinivasan type K) fitted with a 35-W hot cathode mercury resonance lamp.²⁵ In quantitative studies, the source of light was a Hanovia Ottawa-style cold cathode resonance lamp which was filtered by an Acton 185 band-pass filter to remove the radiation at 254 nm. For irradiation with 214-nm radiation, a Phillips Zn resonance lamp was used.

Procedure. Preparative Photolysis. 1,4-cyclohexadiene (0.5 g) was dissolved in 160 mL of pentane and the solution degassed with nitrogen. Irradiation in the apparatus described above was carried out at ~20 °C for 90 min. The solution was analyzed by GLC on a Perkin-Elmer 3920 B gas chromatograph fitted with a oxydiisopropionitrile column (12 ft \times 1/4 in.). At the end of this period, irradiation was stopped although the conversion was only ~50% in order to avoid secondary photolysis of

the products. The solvent was removed by distillation on a 12-in. spinning-band column. The residue was separated by gas chromatography into its component products and unreacted 1,4-cyclohexadiene. For yields, see Table I. Products were identified by comparison of their IR and NMR spectra to those of authentic materials.

The workup was identical during photolysis with 214-nm radiation. **Quantitative Studies.** A solution of freshly distilled 1,4-cyclohexadiene (5×10^{-2} M) in pentane was placed in a cylindrical (2.5 cm diameter \times 2 cm long) quartz cell with a Suprasil window and degassed with nitrogen. The lamp was operated through a constant voltage power supply and allowed to warm up in a slow stream of nitrogen in order to stabilize its light output. The Acton filter was placed in the optical path just at the commencement of the photolysis in order to minimize its destruction. During photolysis, samples were removed at 20-min intervals and analyzed by GLC using a flame-ionization detector. The photolysis was continued until sufficient data were accumulated to provide a satisfactory linear product formation curve vs. time for each of the products. The net conversion of the starting material was ~3%.

The light source was calibrated by the photolysis of *cis*-cyclooctene in the same apparatus.⁶

Sensitized Photolysis. The experiment with Hg atoms as sensitizer was carried out in a 5-L bulb with a central well in which a single 8-W mercury resonance lamp was placed. The bulb was evacuated and filled with 6 torr of 1,4-cyclohexadiene vapor and a drop of mercury. Photolysis was >60% complete in 60 min. Products and unreacted starting material were isolated by GLC and identified as before.

Pyrolysis of 1,4-Cyclohexadiene-3,3,6,6- d_4 (4). A sample of 4 (250 μL liquid) was placed in an evacuated 100 mL Pyrex bulb and pyrolyzed at 330 °C for 80 min. GC analysis showed that the material was 70% converted, and the major product (>90%) was benzene. It was separated and its mass spectrum was used as a reference for benzene-1,4- d_2 .

Acknowledgment. This work was supported in part by Grant No. CHE-8015355 from the National Science Foundation.

(25) Srinivasan, R.; White, L. S. *J. Am. Chem. Soc.* 1979, 101, 6389.

A Kinetic Scheme for Intramolecular Excimer Formation in Bis(α -naphthylmethyl) Ether, Involving Different Starting Conformations[†]

R. Todesco, J. Gelan, H. Martens, J. Put,* and F. C. De Schryver*

Contribution from the University Centre of Limburg, Universitaire Campus, B-3610 Diepenbeek, Belgium, and the Department of Chemistry, Catholic University of Leuven, Celestijnenlaan 200F, B-3030 Heverlee, Belgium. Received February 17, 1981.
Revised Manuscript Received April 28, 1981

Abstract: Fluorescence measurements under nonstationary conditions suggest that the intramolecular excimer formation in bis(α -naphthylmethyl) ether does not follow a simple kinetic scheme. Two excimers can be formed, an endo and an exo one, which have the same spectral distribution. In these excimers, the two naphthyl rings are parallel but most probably displaced with respect to each other. Besides fluorescence and radiationless deactivation, the excimers undergo reaction to an endo and an exo cyclomer, respectively. In isooctane, acetonitrile, and MTHF, the decay of the monomer fluorescence can be analyzed as a sum of two exponentials and the decay in the excimer region as a difference of two exponentials. However, the decay parameters of the excimer do not match those of the monomer fluorescence, indicating that back-reaction from the excimer to the monomer is slow in the whole temperature region measured. Preparative experiments yield evidence that the two components in the monomer region are most probably related to two sets of conformations, leading to exo and endo excimers, respectively, with different rates. A kinetic scheme involving these conformational aspects is proposed.

Intramolecular excimer formation in bichromophoric systems requires conformational changes in the linking chain, to allow the chromophores to approach each other. Until recently, the dependence of intramolecular complex formation on the conformation of bichromophoric molecules prior to excitation was not taken into consideration and a scheme analogous to that of the intermolecular process, as first proposed by Förster, was used.¹⁻¹⁰

An effect of ground-state conformations on intramolecular exciplex formation was described recently in α -phenyl- ω -dimethyl-

- (1) B. Stevens and M. J. Ban, *Trans. Faraday Soc.*, **60**, 1515 (1964).
- (2) F. Hirayama, *J. Chem. Phys.*, **42**, 3163 (1965).
- (3) H. Braun and Th. Förster, *Z. Phys. Chem. (Wiesbaden)*, **78**, 40 (1971).
- (4) E. A. Chandross and C. J. Dempster, *J. Am. Chem. Soc.*, **92**, 3587 (1970).
- (5) W. Klöppfer in "Organic Molecular Photophysics I", J. B. Birks, Ed., Wiley, New York, 1973.
- (6) G. E. Johnson, *J. Chem. Phys.*, **61**, 3002 (1974).
- (7) M. H. Hin and W. R. Ware, *J. Am. Chem. Soc.*, **98**, 4722 (1976).

[†] Dedicated to George S. Hammond on the occasion of his 60th birthday.
* Address correspondence as follows: J.P., University Centre of Limburg; F.C.D.S., Catholic University of Leuven.