

Figure 9. A derivative-intensity plot of time-resolved kinetic parameter, according to the equation $((\Delta I_t/\Delta t)/I_t) + (k_1 + k_2 + k_3[\text{CH}_3\text{COOH}]) = (k_4/f)(I_{545}/I_{447})$, as a function of acetic acid concentration at 298 K for lumichrome in ethanol.

(dioxane). Although we have not deconvoluted the rise time of **2***, the above values of k_3 are consistent with the slower rise time of **2*** than the excitation pulse rise time, assuming $f \sim 1$.¹³

The fact that the fluorescence of **2*** is not resolved within the nanosecond range examined (Figure 7) in aqueous solution of **1** at pH 5.53 [this pH being lower than $\text{p}K_a^*(\text{N}_1) = 3.6$]⁵ suggests that the photodissociation of the N_1 proton in aqueous solution is substantially slower than is the phototautomeric transfer of the proton from N_1 to N_{10} in dioxane and ethanol in the presence of

pyridine and acetic acid, respectively. For 2-naphthol in water, photodissociation shows rate constants ranging from 4.1×10^{14} to $5.1 \times 10^7 \text{ s}^{-1}$.¹² Furthermore, the temperature dependence of the time-resolved fluorescence due to **2*** (Figure 8) suggests that the phototautomeric proton transfer is strongly viscosity dependent, in contrast to the dissociation of proton and the resulting ion-pair formation between N_1^- and the conjugated acid (pyridinium cation) in the excited state of **1**. The long-wavelength fluorescence of **1** at pH 11.5 (Figure 7) is probably due to a ca. 1:1 mixture of N_1 and N_3 anions.^{5,15}

Conclusion

The nanosecond time-resolved fluorescence spectra of lumichrome in dioxane and ethanol in the presence of pyridine and acetic acid, respectively, have been obtained by a PAR boxcar averaging system. Inspection of these spectra strongly suggests that the excited lumichrome (**1***) undergoes a tautomeric proton shift from N_1 to N_{10} , yielding the excited flavinic tautomer (**2***) which emits maximally at 540–545 nm. Both steady-state and time-resolved fluorescence data yield rate constants of $3\text{--}4.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for the phototautomeric reaction, and these rate constants are an order of magnitude lower than diffusion-controlled processes. The driving force for the phototautomeric proton shift is the redistribution of the electron density at N_1 and N_{10} upon excitation of lumichrome.³ A strong temperature dependence, and that the photodissociation of the N_1 proton is substantially slower at neutral and acidic pHs than is the phototautomerism in dioxane and ethanol in the presence of pyridine and acetic acid, respectively, has been observed.

Acknowledgments. We are grateful to Professor S. Georgiou for his valuable advice in constructing the nanosecond time-resolved spectrofluorometer used in this work. Funds for the construction of this equipment were provided by the Dean of the College of Arts and Sciences, Texas Tech University.

(14) Weller, A. *Prog. React. Kinet.* 1961, 1, 187.

(15) Lasser, N.; Feitelson, J. *Photochem. Photobiol.* 1977, 25, 451.

Organic Photochemistry with 6.7-eV Photons: Photoisomerization of Tricyclo[3.2.1.0^{2,4}]oct-6-ene (Endo and Exo) and Tricyclo[3.2.2.0^{2,4}]non-6-ene (Endo and Exo)

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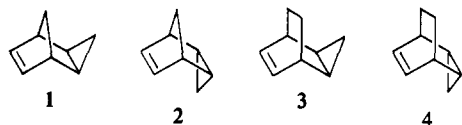
Contribution from the IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598, and Chemistry Department, The University of Connecticut, Storrs, Connecticut 06268. Received October 26, 1979

Abstract: Photolysis of the title compounds at 185 nm in solution leads to internal addition of the olefinic group to the cyclopropane ring and cleavage of the cyclopropane to a bicyclic 1,4-diene. A theoretical analysis of the interactions between the π -orbitals of the double bond and the σ orbitals of the cyclopropane in each of these compounds has been carried out. The effect of through-bond interactions superimposed upon the through-space effects when extended to the valence excited states gives rise to three low-lying excited states which are (in order of decreasing energy) $\sigma_A \rightarrow \sigma_A^* + \pi^*$ (forbidden), $\sigma_S + \pi \rightarrow \pi^* + \sigma_A^*$ (allowed), and $\pi - \sigma_S \rightarrow \pi^* + \sigma_A^*$ (allowed). The internal addition reaction is identified with the $\pi - \sigma_S \rightarrow \pi^* + \sigma_A^*$ state and the cleavage of the cyclopropane to yield a 1,4-diene with the $\sigma_S + \pi \rightarrow \pi^* + \sigma_A^*$ state. The low reactivity of the *endo*-tricyclo[3.2.2.0^{2,4}]non-6-ene is believed to relate to a departure from the ordering of the excited states as described above.

Introduction

The tricyclic compounds **1–4** which incorporate an allylcyclopropane function in a rigid tricyclic framework have been of interest to both spectroscopists and photochemists. The inter-

actions between the π electrons of the double bond and the Walsh orbitals of the cyclopropane have been examined in **1**, **2**, and **3** by photoelectron (PE) spectroscopy by Heilbronner and his co-workers² and by Bruckmann and Klessinger.³ These workers

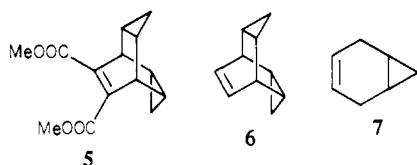


focused their attention on obtaining the ionization energies of higher lying filled levels and relating the splittings obtained to the interplay of through-space vs. through-bond interactions. Unfortunately, PE spectra do not produce direct information concerning the nature of the excited states in these strained molecules.

Previous work on the photochemistry of these compounds has been concerned mainly with the internal addition reaction which in the case of **1** proceeds according to eq 1. Prinzbach and his



co-workers⁴ have discovered numerous examples of such internal additions and attempted to correlate the facility for such additions to the geometry of the molecule^{4b} or the interaction energies between the olefin and the cyclopropane groups which were derived from their PE spectra. Reaction 1 was studied by Freeman and his co-workers⁵ with radiation >200 nm. They noted that it proceeded at half the chemical yield in the endo isomer **2**. They also observed that both **1** and **2** have the same ultraviolet absorption maxima. Neither **3** nor **4** has been investigated photochemically previously, but from the photolysis of **5**^{4b,e} and **6**,⁶ it had been found that internal addition of the olefin to the exo-oriented cyclopropane is overwhelmingly favored.



This work was motivated by our earlier study⁷ of the photochemistry of bicyclo[4.1.0]hept-3-ene (**7**) at 185 nm which showed that >83% of the photon energy that was absorbed resulted in the decomposition of the cyclopropane ring. At the same time, there was no evidence for the internal addition of the olefin to the cyclopropane. It was considered desirable to extend the study to compounds **1-4** which incorporate **7** so that a comparison may be made of the photochemistry at 185 nm of rigid systems with varying degrees of strain.

Results

The ultraviolet absorption spectra of **1-4** in a hydrocarbon solvent are shown in Figures 1 and 2. The spectra of pairs of isomeric compounds were obtained at identical concentrations in order that subtle differences may be detected by subtraction. These difference spectra are also shown in these figures. Both exo isomers show an absorption at ~210 nm which is absent in

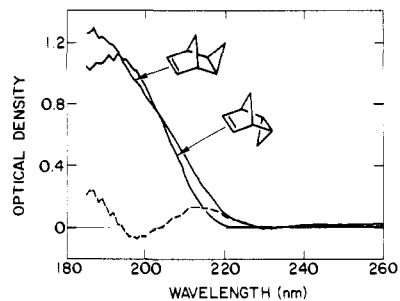


Figure 1. Ultraviolet absorption spectra of **1** and **2**. Solvent, pentane 2.64×10^{-4} M; path 1.0 cm.

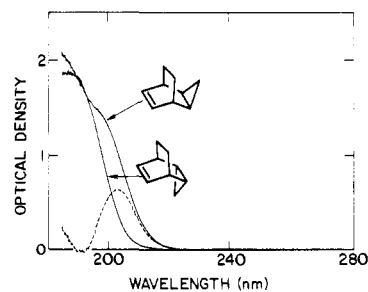


Figure 2. Ultraviolet absorption spectra of **3** and **4**. Solvent, pentane 3.07×10^{-4} M; path 1.0 cm.

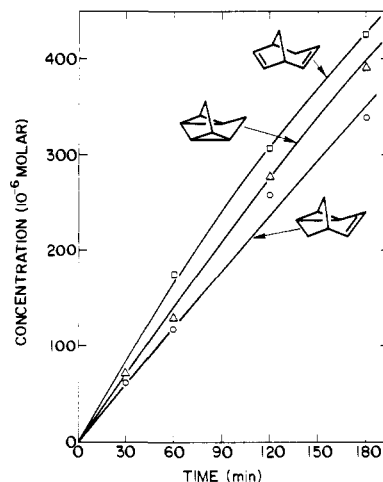
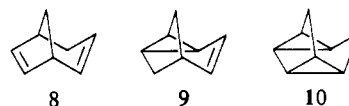


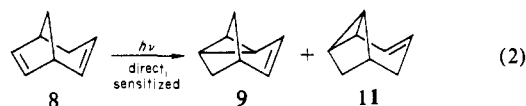
Figure 3. Rate of formation of products in the photolysis of **2** at 185 nm. Solvent, pentane; mercury resonance lamp with band-pass filter.

the endo isomers. The intensity of this absorption is weak in **1** but strong in **3**.

Photolysis of the endo isomer **2** at 185 nm in pentane solution gave the diene **8**, the vinylcyclopropane **9**, and the internal adduct **10**. Compound **9** has been observed by Sauers and Shurpik⁸ to



be a product of the direct or sensitized photolysis of **8**. Since this reaction which is presumably a di- π -methane rearrangement gives **11** as well, a careful search for **11** was made in the photolysis of



3. At low conversions, its presence could not be detected (<2%), but at high (~50%) conversions, it was observed to amount to one-third of **9**.⁹

(1) (a) IBM; (b) The University of Connecticut; Visiting scientist, IBM Thomas J. Watson Research Center, 1979.

(2) P. Bischof, E. Heilbronner, H. Prinzbach, and H. D. Martin, *Helv. Chim. Acta*, **54**, 1072 (1971).

(3) P. Bruckmann and M. Klessinger, *Angew. Chem., Int. Ed. Engl.*, **11**, 524 (1972).

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(5) (a) P. K. Freeman, D. G. Kuper, and V. N. Mallikarjuna Rao, *Tetrahedron Lett.*, 3301 (1965); (b) P. K. Freeman and D. M. Balls, *J. Org. Chem.*, **32**, 2354 (1967).

(6) A. de Meijere, C. Weitemeyer, and O. Schallner, *Chem. Ber.*, **110**, 1504 (1977).

(7) R. Srinivasan and J. A. Ors, *J. Am. Chem. Soc.*, **101**, 3411 (1979).

(8) R. R. Sauers and A. Shurpik, *J. Org. Chem.*, **33**, 799 (1968).

Table I. Rates^a of Formation of Products in Photolysis of Compounds 1-4

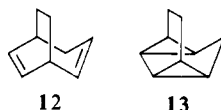
compd	total rate of disappearance	rate of internal cycloadduct formation	rate of diene product(s) ^b formation
1	575.0	418.8	156.3
2	775.0	250.0	537.5
3	437.5	431.3	~0 ^c
4	287.5	50.0	243.8

^a Rate in M/min $\times 10^6$; 185-nm radiation; pentane solvent; all values at 10% conversion of reactant. ^b Includes secondary rearrangement product of dienes. ^c Not detected.

In Figure 3, the formation of **8**, **9**, and **10** from the photolysis of **2** is plotted as a function of time. The total conversion represented here is 18%. Up to 12% conversion, both the mass balance and the linearity of the rates of formation of the products were satisfactory within the uncertainty in the analysis ($\pm 6\%$).

Photolysis of the exo isomer **1** gave the diene **8** and the internal adduct **10** as the only significant products. The di- π -methane rearrangement products, **9** and **11**, amounted to less than 2% each.

Photolysis of the endo isomer **4** gave the diene **12**¹⁰ and the internal adduct **13**. There were also three other minor products



(<5% each) which were not identified. The structure of **13** was derived from the similarity of its infrared [3008 (s), 3001 (s), and 850 (m) cm^{-1}] and NMR [δ 0.4-0.9 (br m, 2 H) and 0.9-2.1 (br m, 10 H)] spectra to those of **10**. The presence of **12** as a product suggested that the minor products may be derived from it by a di- π -methane rearrangement. However, efforts to sensitize the photorearrangement of **12** (in a separate experiment) were inconclusive. Isomeric products amounted to <10% while addition products of the carbonyl sensitizer to the olefin predominated. Direct irradiation of **12** at 185 nm led to loss of material with no significant accumulation of any product other than a polymer.

Photolysis of the exo isomer **3** gave the internal adduct **13** as the major product and small amounts (<4%) of two minor products which were the same (according to GC retention times) as the first two from the photolysis of **4**. There was no detectable amount of the diene **12** formed in this instance.

Rate data similar to those in Figure 2 were obtained for **1**, **3**, and **4**. For the purpose of comparing them, the smoothed values are given in Table I. In all experiments, the absorbed intensities were constant so that the rates of formation of the products are proportional to their quantum yields. On the basis of the stereoisomerization of *cis*-cyclooctene¹¹ as the actinometer, the quantum yield for the photoisomerization of **1** is close to unity.

Theory

An interaction diagram indicating the through-space interaction of cyclopropane and ethylene fragments is given in Figure 4. This was obtained by placing the cyclopropane and ethylene molecules in precisely the same position as they are in the parent molecule **1**.¹²⁻¹⁶

(9) The difference in the degree of conversion of **3** affects the relative yield of **11**. Thus, in the early stages of photolysis of **3**, we shall argue (see Discussion) that the source of **11** is probably an excited **8** that is formed from **3**. In the later stages of photolysis of **3**, the **8** that has accumulated in solution can absorb some of the 185-nm radiation directly and give **11** (as well as **9**).

(10) J. Japenga, G. W. Klumpp, and M. Kook, *Recl. Trav. Chim. Pays-Bas*, **97**, 7 (1978).

(11) The correct value for this quantum yield is 0.35 (C. von Sonntag, H.-P. Schuchmann, and R. Srinivasan, to be published).

(12) All the calculational results were obtained by using the extended Hückel¹³ and GAUSSIAN 70¹⁴ programs with an STO-3G¹⁵ basis. The bond distances used in **1-4** and **18** are C-C, 1.54 Å; C-C (attached to double bond), 1.51 Å; C=C, 1.34 Å; and C-H, 1.10 Å. The dihedral angles θ_1 , θ_2 , and θ_3 shown in **17** were maintained at 120° for all molecules.

ISOLATED CYCLOPROPANE FRAGMENT ORBITALS

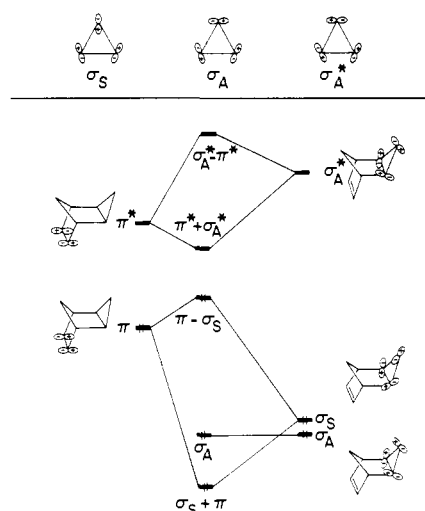


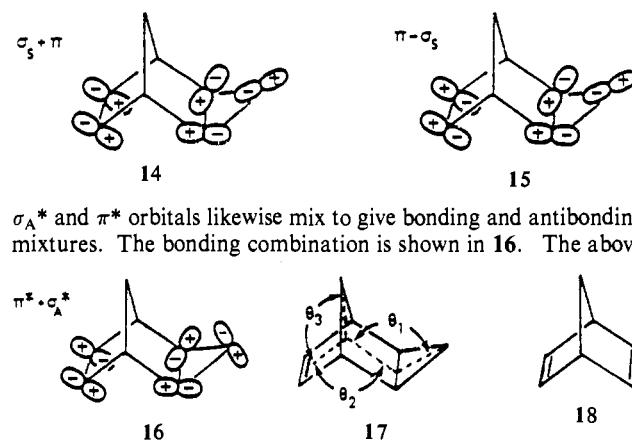
Figure 4. Interaction diagram showing through-space mixing of cyclopropane Walsh orbitals with ethylene π orbitals. The orbitals are designated by S or A with respect to the symmetry plane of the molecule.

Table II. Overlaps of Walsh Orbitals on Cyclopropane with the Olefinic π and π^* Orbitals

	1	2	3	4	18 ^a
$\langle \pi \sigma_S \rangle$	0.052	0.012	0.061	0.014	0.078 ^b
$\langle \pi \sigma_A \rangle$	0.031	0.012	0.037	0.015	0.053 ^c
$\langle \pi^* \sigma_A^* \rangle$	0.035	0.006	0.042	0.007	

^a Overlap of the π orbitals in norbornadiene are included for comparison. ^b Overlap of π_1 and π_2 . ^c Overlap of π_1^* and π_2^* .

The σ_S orbital of the cyclopropane combines with the ethylene to give in-phase and out-of-phase combinations **14** and **15**. The



results are analogous to the discussion of norbornadiene (**18**) previously given by Hoffmann.¹⁷ Thus, excitation of an electron from **15** to **16** will promote ring closure to **10** by removing an electron which is antibonding beneath the carbon skeleton and placing it in an orbital which is bonding in that region. An idea of the difference between through-space effects in **1-4** and norbornadiene can be obtained by looking at the overlaps given in

(13) J. Howell, A. Rossi, D. Wallace, K. Haraki, and R. Hoffmann, *QCPE*, **10**, 344 (1977).

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

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

(16) The interaction diagram given in Figure 4 is the result of extended Hückel calculations.¹³

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

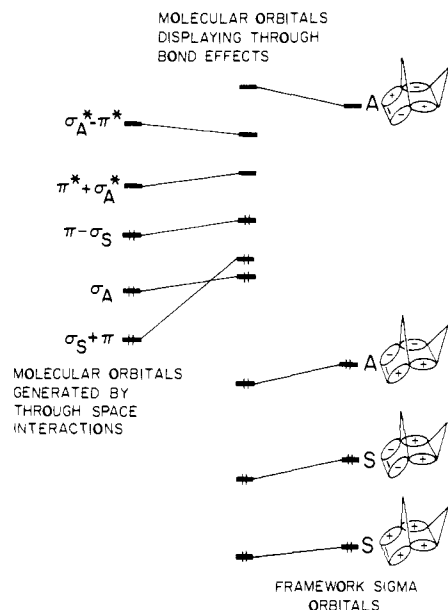


Figure 5. Effect of through-bond coupling on the orbitals obtained from through-space interactions.

Table II. In general, the overlaps are larger for **1** and **3** compared to **2** and **4**, and those of **3** are more similar to the overlaps in **18**. The larger overlaps for **3** give rise to a greater through-space splitting, as confirmed by calculation.

The effect of through-bond interactions superimposed upon the through-space effects is given in Figure 5. All the filled valence levels are pushed up in energy by through-bond interactions, but the $\sigma_S + \pi$ combination is pushed above the σ_A orbital. It is also possible to have the $\sigma_S + \pi$ orbital above the $\pi - \sigma_S$ orbital if the through-bond interaction is very strong (or the through-space interaction weak). The relative splittings of these two levels have been studied with photoelectron spectroscopy by Heilbronner et al.² Another interesting result from Figure 5 is that the $\pi^* + \sigma_A^*$ level is also low enough to be destabilized by the through-bond effects of the valence orbitals. However, the $\sigma_A^* - \pi^*$ combination appears to be stabilized by through-bond coupling of high-lying unoccupied levels. The influence of through-bond coupling in virtual orbitals with the concomitant effect on excited-state photochemistry is an area which has not been previously studied.

A general trend of the orbital energies for the series of compounds **1-4** calculated by GAUSSIAN 70¹⁸ is shown in Figure 6. The first result to note is that the splitting between the two highest occupied levels is smaller for **3** than for **1**. Through-space effects would favor the reverse trend, but the opposing through-bond interactions dominate to give the overall result in Figure 6. Photoelectron spectroscopy results appear to give approximately the same splitting of the two highest levels in these compounds.^{2,3} Another important result to be derived from Figure 6 is that the σ_A and $\pi^* + \sigma_A^*$ orbitals are significantly destabilized in compound **4**. Not only should the splitting of the highest two orbitals be smallest for **4** compared to **1**, **2**, and **3**, but the level ordering for **4** has important consequences for its photochemistry, as will be discussed below. The photoelectron spectrum of **4** has not been measured.

In Figure 7, the three lowest transition energies for compounds **1-4** are plotted on a relative scale. The configuration interaction (CI) was carried out by allowing the mixing of singly excited configurations formed from transitions involving the filled σ_A , $\sigma_S + \pi$, and $\pi - \sigma_S$ orbitals to the unoccupied $\pi^* + \sigma_A^*$ and $\sigma_A^* - \pi^*$ orbitals. It is important to emphasize that the actual values obtained for the excitation energies cannot be taken too seriously since only a small CI was performed. In addition, the CI calculations presented here are not sufficiently extensive to accurately

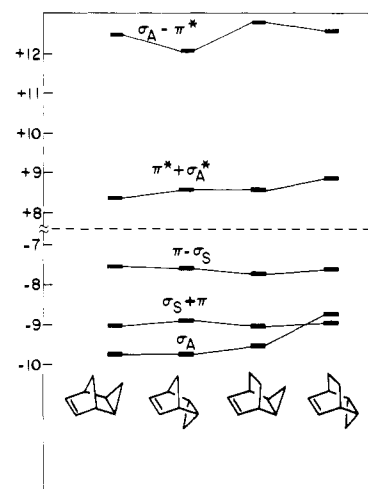


Figure 6. Orbital energies for the molecules **1-4**.

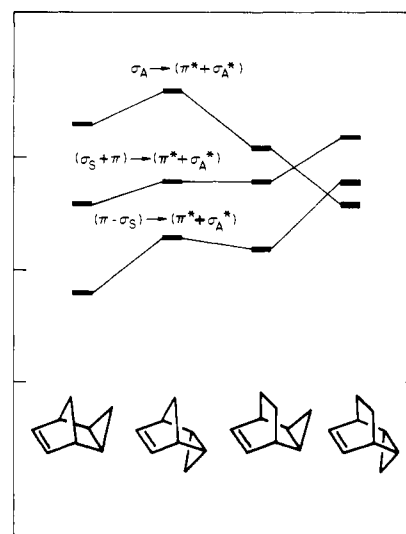


Figure 7. The three lowest excitation energies for the molecules **1-4**.

determine either the precise nature or the value of the excited states in these saturated compounds. More extensive calculations could allow different excited states than the ones given in Figure 7 to be lower, but an encouraging aspect of the results presented here is that in all cases one or two configurations corresponding to the specific excitations given in Figure 7 appear to dominate the CI calculation.

Discussion

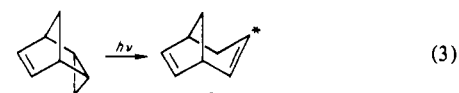
An examination of the experimentally obtained ultraviolet spectra suggests that the computed differences in the transition energies for the exo-endo pair made of **3** and **4** is probably a true reflection of the significant difference in their UV spectra (Figure 2). The corresponding computed values for the pair **1** and **2** probably exaggerate the true differences which, according to their UV spectra (Figure 1), are small.

The observed $2\pi + 2\sigma$ cycloaddition (reaction 1) must, in every instance, come from the $\pi - \sigma_S \rightarrow \pi^* + \sigma_A^*$ transition which is similar to the $\pi \rightarrow \pi^*$ transition in norbornadiene which leads to quadricyclane. This transition is the lowest of the excited states for **1**, **2**, and **3**. All three of these compounds undergo this process as a principal photochemical reaction. In **4**, the lowest excited state is no longer this transition, and the internal cycloaddition is only marginally favored. The transition $\sigma_S + \pi \rightarrow \pi^* + \sigma_A^*$ can be identified as the one which results in the formation of diene products. This transition involves removing an electron from an orbital that is localized to a large extent on the cyclopropane moiety. Removal of an electron from the $\sigma_S + \pi$ orbital tends to weaken the C-C bond in the cyclopropane and promotes bond cleavage which, in turn, leads to diene products.¹⁹

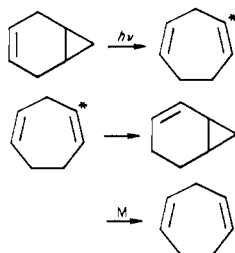
(18) The transition energies were obtained with a CI program written to interface with GAUSSIAN 70 by Professor M. H. Whangbo.

The quantum yields for the decomposition of all four compounds (Table I) fall within a small range (a factor of two), the least efficient molecule being **4**. Nevertheless, the partitioning of the reaction path between the two principal modes (which we shall refer to as "diene formation" and "cycloaddition") shows much greater differences. Since the excitation energy (i.e., 185 nm) is constant in all cases, the differences can be explained as follows. The two allowed transitions in each compound represent the mixing of the excited states of the π system of the olefin and the Walsh orbitals of cyclopropane to different degrees. At a given photon energy in a given compound, there will be a fixed distribution of $\pi - \sigma_S \rightarrow \pi^* + \sigma_A^*$ and $\sigma_S + \pi \rightarrow \pi^* + \sigma_A^*$ transitions. This distribution will differ from compound to compound, which would explain the distribution of diene and cycloaddition products even if the total quantum yield for isomerization does not change severely. Note that even in **4**, in which the forbidden transition is the lowest in energy, the quantum yield is not greatly different. A simple test of this explanation would be to use photons of slightly different energy when the same reactions should be observed but with a different ratio of diene formation to cycloaddition. Experiments to verify this idea are in progress.

A subtle difference between the photochemistry of **1** and **2** may be noted. Photolysis of the endo isomer **2** gave not only the 1,4-diene, **8**, but one of its di- π -methane rearrangement²⁰ products, **9**, as well. Since **9** was to be observed even when the fraction



of **2** decomposed was a few percent, this reaction probably occurs by a carry-over of the electronic energy in the initially formed **8**. A similar carry-over of electronic energy followed by a di- π -methane rearrangement has been reported previously in the photochemistry of **7**.⁷

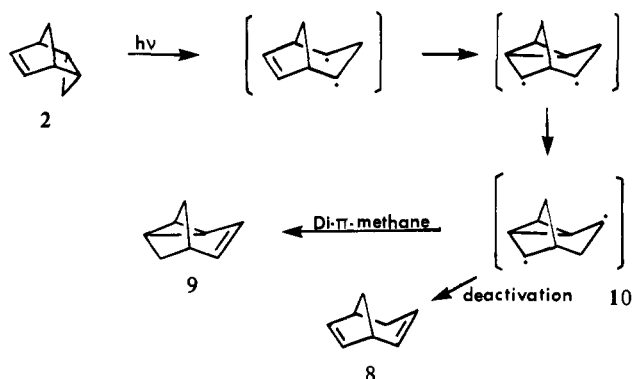


Evidence for the nature of the electronic state of **8** that is formed in reaction 3 can be obtained from the work of Sauers and Shurpik.⁸ These workers studied this rearrangement in detail and demonstrated that the singlet of **8** gives more **11** than **9** whereas the triplet formed by sensitization gave more **9** than **11**. In the present instance, the excited state of **8** that is formed by reaction 3 is probably a triplet. This is reasonable from a consideration

(19) Another cautionary comment should be given when discussing the idea that different transitions can lead to different products. The transition energies presented here are for molecules **1-4** in their ground-state equilibrium geometries. In order to provide a detailed analysis of how these compounds proceed from reactant to product for each excited state, it would be necessary to obtain a complete multidimensional potential energy surface, an impossible task because of the number of degrees of freedom involved. Rather, it is hoped that qualitative concepts of reactivity can be inferred by observing incipient bonding or antibonding interactions resulting from transitions from the occupied to unoccupied orbitals.

(20) The extensive literature on the di- π -methane rearrangement has been reviewed: S. S. Hixson, P. S. Marino, and H. E. Zimmerman, *Chem. Rev.*, **73**, 531 (1973).

Scheme I



of the energy balance as well. The initial photon energy of 155 kcal/mol (≈ 6.7 eV) which goes to excite **2** would be barely sufficient to excite **8** to its singlet state when it is formed as a product in step 3. But less than 4.5 eV would be needed to excite **8** to its triplet state, and this may be available from reaction 3.

An alternative to reactions 3, 4, and 5 which does not involve an electronically "hot" state of **8** as an intermediate is also possible. This would consist of the sequence shown in Scheme I. The intermediate **10** can be viewed as a configuration of the triplet state of **8**. In that case, the two mechanisms do not differ in a fundamental way. Nevertheless, the second scheme, since it foresees a common intermediate for the formation of **8** and **9**, would predict a constant ratio of **8** to **9**. Once again, this can be readily verified by the use of photons of an energy other than 185 nm.

It is puzzling that the di- π -methane product from **8** is formed only in the photolysis of **2** and not from **1** even though the same diene (**8**) is formed in comparable quantity in this instance. This suggests a third possibility in which the intermediate **10** is avoided and the diradical which is its precursor undergoes a 1,2 shift of the carbon bridge to give **9** directly. Deuterium labeling studies which can help to resolve these ambiguities are currently in progress.

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.

Product separations and purifications of reactants were carried out on a Hewlett-Packard 5750B gas chromatograph by using one of the following columns: (a) 10% Carbowax 20M, 24 ft \times 0.25 in.; (b) 20% β,β -oxybis(propionitrile), 20 ft \times 0.25 in.; (c) 10% silicone gum rubber, 24 ft \times 0.25 in., 14 ft \times 0.25 in.; (d) Ucon-550X 20%, 12 ft \times 0.25 in.

exo-Tricyclo[3.2.1.0^{2,4}]oct-6-ene (1) was prepared by the method of Simmons, Blanchard, and Smith.²¹ Cyclopropanation was achieved by the addition of methylene iodide to norbornadiene with a Zn/Cu catalyst. The product was purified by gas chromatography (Column d). The IR²² and NMR²¹ spectra agreed with the published values.

endo-Tricyclo[3.2.1.0^{2,4}]oct-6-ene (2) was prepared by the procedure of Closs and Krantz.²³ Freshly generated cyclopropene was bubbled directly into freshly distilled cyclopentadiene in CH_2Cl_2 at 0 °C. The product was purified by gas chromatography (Column d). The IR²² and NMR²² spectra agreed with the published values.

exo-Tricyclo[3.2.2.0^{2,4}]non-6-ene (3) was prepared by the method of Schueler and Rhodes.²⁴ The product was purified by gas chromatography on Column a: IR 3050, 3010, 2940, 2865, 1640, 1550, 1460, 1435, 1365, 1318, 1250, 1160, 1088, 1040, 1000, 953 cm^{-1} ; NMR δ 0.53 (1 H, complex), 0.82 (1 H, m), 0.95–1.55 (6 H, complex), 2.60 (2 H, br s), 6.32 (2 H, d).

endo-Tricyclo[3.2.2.0^{2,4}]non-6-ene (4) was prepared by the addition of cyclopropene (prepared by the method of Closs and Krantz²³) to a

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solution of 1,3-cyclohexadiene in CH_2Cl_2 at 0 °C. The product was purified by gas chromatography on Column a; IR 3050, 2950, 2900, 1465, 1440, 1380, 1315, 1280, 1215, 1155, 1085, 1055, 1040, 950, 925, and 858 cm^{-1} . The NMR spectrum agreed with the published one.²⁵

Pentane (Baker-Photrex grade) was uniformly used as the solvent for photolysis.

Apparatus. The equipment for photolyses at 185 nm in solution either on a preparative scale (0.1–0.5 g) or for kinetic studies has been described.²⁶ An Acton 185 band-pass filter was used to isolate the 185-nm line in quantitative studies. Ultraviolet absorption spectra were recorded on a Cary 17D spectrometer. The digitized output could be stored in a computer. Solutions of two compounds (e.g., **3** and **4**) at an identical concentration were separately scanned in the spectrometer by using the same cell to obtain the difference spectrum between the compounds. The spectra were stored, then subtracted, and displayed. The difference spectra could be amplified suitably to emphasize minor dissimilarities.

Procedure. A solution of the tricyclic ene ($\sim 5 \times 10^{-3}$ M) in pentane was placed in a cylindrical cell (volume, 9.3 mL) with a Suprasil window and flushed with nitrogen. Photolyses were carried to conversions of <20%. Aliquots were withdrawn at various time intervals and analyzed on a Perkin-Elmer 3920B gas chromatograph fitted with a Carbowax column (14 ft \times 1/8 in.) and both thermal conductivity and flame ionization detectors. In the case of **2**, a gum rubber column was used in addition to separate **2** from **1**. The detectors were calibrated from time to time with bicyclo[2.2.2]octane as reference.

Photolysis of 1. Irradiation was carried out as described above. Separation by gas chromatography (Columns a and c) showed the presence of diene **8** (14%) and tetracyclic hydrocarbon **10** (36%). Diene **8** was prepared by the method of Moore, Moser, and LaPrade.²⁷ The

NMR spectrum [δ 6.07 (1 H, q), 5.86 (1 H, q), 5.53 (1 H, br d), 5.03 (1 H, complex), 1.5–2.7 (6 H)] agreed with the published²⁷ one. Product **10** agreed in its IR and NMR spectra [δ 1.8 (5 H), 1.4 (5 H)] with the published²⁷ spectra.

Photolysis of 2. Following irradiation as described above, separation was carried out by gas chromatography on Columns a and b. The three major products were **8** (28%), **9** (23%), and **10** (26%). Product **9** [NMR δ 5.9 (2 H), 2.6 (1 H), 1.6 (5 H), 1.2 (1 H), 0.9 (1 H), and 0.7 (1 H)] fully agreed in its NMR spectrum with the spectra in the literature.⁸

Photolysis of 3. There was a single product, **13**, formed in 55% yield. Remaining products amounted to <5%. Separation was carried out by gas chromatography on Columns a and b.

Tetracyclo[4.3.0.0^{2,9}.0^{5,7}]nonane (13): M_r (mass spectrum) 120 (base peak 79); IR 3008 (s), 3001 (s), 2900 (s), 1470, 1460, 1440, 1340, 1050, 940, 850, 690 cm^{-1} ; NMR δ 0.4–0.9 (10 H, m), 0.9–2.1 (2 H, m).

Photolysis of 4. There were two main products which were separated by gas chromatography on Columns a and b. These were **12** (22%) and **13** (5%). The spectra of **12** agreed with those of an authentic sample kindly furnished by Professor G. W. Klumpp.

Photolysis of Diene 8 at 185 nm. A solution of **8** in pentane (3×10^{-3} M) was photolyzed with the isolated 185-nm radiation. The products that were observed (in decreasing importance) were **11**, **9**, and an unknown. The ratio of **9** to **11** was $\sim 1:3$, which is of the same order as was reported by Sauer and Shurpik⁸ in direct photolysis at longer wavelengths. Note that the ratio of **9** to **11** is reversed in importance when triplet sensitization in solution is used.⁸

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Potential Surfaces for $(\text{NH})_3^{2+}$

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Abstract: Potential surfaces for the lowest triplet and two lowest singlet states of the triaziridenyl dication, a molecule isoelectronic with the cyclopropenyl carbanion, have been obtained from ab initio calculations. It is found that when the σ core is allowed to deviate from D_{3h} symmetry, the two lowest singlet states, at the SCF or π CI level of theory, are nondegenerate by 13 kcal/mol at D_{3h} geometries. The lower state, 1A_1 , also fails to exhibit even qualitatively correct behavior on molecular distortion to geometries of C_{2v} symmetry. It is shown by group-theoretical arguments that CI in the σ space must accompany π CI in order to obtain satisfactory $^1E'$ wave functions. σ - π CI calculations are, in fact, found to yield singlet wave functions that exhibit both D_{3h} degeneracy and the correct Jahn-Teller behavior on molecular distortions to C_{2v} symmetry. A modified CI protocol has been developed to explore nonplanar molecular geometries. It is found that all three of the lowest states of $(\text{NH})_3^{2+}$ prefer such geometries; the stationary points on the global surfaces for these states have been obtained. A substantial barrier to pseudorotation is predicted for the lowest singlet, which is calculated to be the ground state of the molecule. The driving force for nitrogen pyramidalization in $(\text{NH})_3^{2+}$ is discussed in light of population analyses at planar and nonplanar geometries.

Several years ago, as part of a continuing series of studies of the potential surfaces for molecules containing open-shell π systems, we carried out calculations on the planar cyclopropenyl anion.¹ The aim of this project was to verify computationally a prediction of the location of the minima on the potential surface for the lowest singlet state, based on consideration of first- and second-order Jahn-Teller effects. Despite the fact that the computed surface was found to have the form expected, several aspects of our calculations were somewhat unsatisfactory, as we ourselves noted.¹

First, the energy of the $^3A_2'$ ground state of the planar anion was found to be 6.7 eV above that of the lowest doublet state of

the planar cyclopropenyl radical, for which we also carried out calculations.¹ Therefore, if increasingly diffuse basis functions had been added to the minimal STO-3G set used, the energy of the anion would have been greatly reduced, until, if a complete basis set were used in the π space, the extra electron in the planar anion would almost certainly not have been found to be bound.²

(2) It would, in fact, be rather surprising if the planar cyclopropenyl anion were bound in the gas phase, since the pyramidal methyl anion is found experimentally to be bound by less than 2 kcal/mol³ and Breslow's study of a presumably nonplanar cyclopropenyl anion in solution shows that even this species is conjugatively destabilized.^{4,5}

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