

new; thus in addition to the work of Silver and Luz⁴ on the acid-catalyzed oxidation which shows an isotope effect, they also showed that proton transfers between phosphines are perceptibly slow in water,¹³ and proton transfers from trialkylphosphonium salts are slow in both directions in dimethyl sulfoxide,¹⁴ although in the gas phase phosphites equilibrate with protonated species at rates fast by ICR standards.¹⁵

Perhaps a more notable conclusion is that the halogenation after proton loss should be as general a method with PH compounds as it is with carbonyl and nitro compounds. The various phosphonates show a wide range of reactivity, thus $\text{CH}_3\text{OPHO}_2^-$ does not exchange with alkaline D_2O at a significant rate at room temperature, as shown by the stability of the PH proton NMR,¹⁰ so the range of possible reactivities is very large.

Apparently the rate law here is not entirely general, for the iodination of hypophosphorus acid is not zero order in iodine and triiodide ion is slower than iodine. The difference may merely be a slower reaction of iodine with the reactive intermediate.¹⁶

Experimental Section

Materials. Diethyl phosphonate was a commercial material distilled before use. The proton NMR showed no impurities. A sample was exchanged with heavy water containing sodium carbonate to prepare the deuterated material in D_2O solution. It showed almost complete loss of the phosphorus-bound proton in the NMR (at least 95% D). A small portion of this solution was then put into the buffer solution for the kinetic run. The small solvent kinetic isotope effect from this D_2O in the H_2O solution was neglected as was the small amount of extra base.

Kinetics. A mixture of the buffer solution, the ester, and the iodine with iodide was placed in a 1-cm cell jacketed for temperature control at 25 °C in the spectrophotometer, and the absorbance as a function of time was followed. The initial iodine concentration was in the range

0.005 to 0.017. The concentrated solutions of iodine were followed at 560 nm, at which the extinction coefficient is 99; the more dilute runs were followed at 470 nm (extinction coefficient 670). These are isobestic points for iodine and triiodide, thus avoiding the need for correction for the iodide formed in the reaction. Implicit in this method is the assumption that I_2 and I_3^- are equally reactive; the kinetics gave no reason to doubt this assumption. The ester concentration initially was not more than 2% of the buffer concentration, to allow for the 3 mol of acid produced.

At the higher pH values, there was concern about the disproportionation of iodine to iodide and iodate, which would serve as a transparent source of I_2 , and therefore give rates too low. This was suppressed by the addition of excess iodide, up to 5 M for the carbonate and the ammonia buffers, and by reducing the iodine concentration. Under these circumstances there was no evidence that the iodine concentration was too low for the zero order in iodine assumption. Nevertheless, the low rate constant for NH_3 buffers suggests the possibility of this problem. We did not study possible salt effect contributions, although Nylén found no experimentally significant salt effects up to 1 M.

In the concentrated iodine solutions the buffer and the iodine were both in excess so the A vs. time plot was an exponential fall to the infinity value, when the phosphonate was gone. This gave a pseudo-first-order constant for the particular buffer concentration used, except in the case of acetate buffers, for which much higher phosphonate concentrations and the (zero order) fall in iodine concentration were measured. For the dilute iodine solutions the A vs. time plot was also an exponential decay, when the absorbance was followed in the range 0.1 to 0.0 ($\text{I}_2 + \text{I}_3^- < 1.5 \times 10^{-4}$), giving the k_{obsd} values in Table III. In accordance with the rate law, the absorbance vs. time was linear at high absorbance, but then developed curvature leading finally to the exponential section. Because of the pseudo-first-order law, the extinction coefficient of bromine was not needed or determined. Rates not here reported in the high iodine regime with acetate buffers were also measured by the thiosulfate titration method used by Nylén;¹ it gave results in agreement with his considering the temperature difference, but in our hands it was not useful for the faster reactions at the higher pH's.

Acknowledgment. We acknowledge the support of this work by the Welch Foundation.

Registry No. Diethyl phosphonate, 762-04-9.

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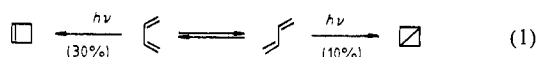
185-nm Photochemistry of Cyclobutene and Bicyclo[1.1.0]butane

Waldemar Adam,* Thomas Oppenländer,[†] and Gerald Zang[§]

Contribution from the Institute of Organic Chemistry, University of Würzburg, Am Hubland, D-8700 Würzburg, West Germany. Received August 20, 1984

Abstract: The high quantum yield of the direct 185-nm photolysis of cyclobutene ($\phi_s = 0.71$) leading to 1,3-butadiene is in accord with symmetry-allowed electrocyclic ring opening of a π, π^* -excited singlet state of cyclobutene. The formation of ethene, acetylene, and methylenecyclopropane as minor products presumably involves cyclopropylmethylene and cyclobutylidene as carbene intermediates, formed on ($\pi, 3s$)-Rydberg excitation of cyclobutene. The 185-nm photolysis of bicyclo[1.1.0]butane resembles that of the homologous bicyclo[$n.1.0$]alkanes. As main products cyclobutene ($\phi_p = 0.30$) and 1,3-butadiene ($\phi_p = 0.29$) are formed. On the other hand, the transformations of methylenecyclopropane on 185-nm irradiation, leading to ethene, acetylene, and 1,3-butadiene, are akin to radiolysis and gas-phase photolysis results of this substrate.

The symmetry-allowed disrotatory electrocyclic closure of 1,3-butadiene into cyclobutene (eq 1) is experimentally and theoretically well understood.¹ However, the reverse process, the



direct photochemical opening of simple cyclobutenes, is only

documented with a few examples.² The major reason for this is that simple cyclobutenes show no significant absorption above 200 nm. The same is the case for simple bicyclo[$n.1.0$]alkanes. It is, therefore, not surprising that very little is known on the

[†] Doctoral Dissertation, University of Würzburg, July 1984; Doctoral Fellow of the Fonds der Chemischen Industrie (1982-1984).

[§] Undergraduate research participant during autumn 1982.

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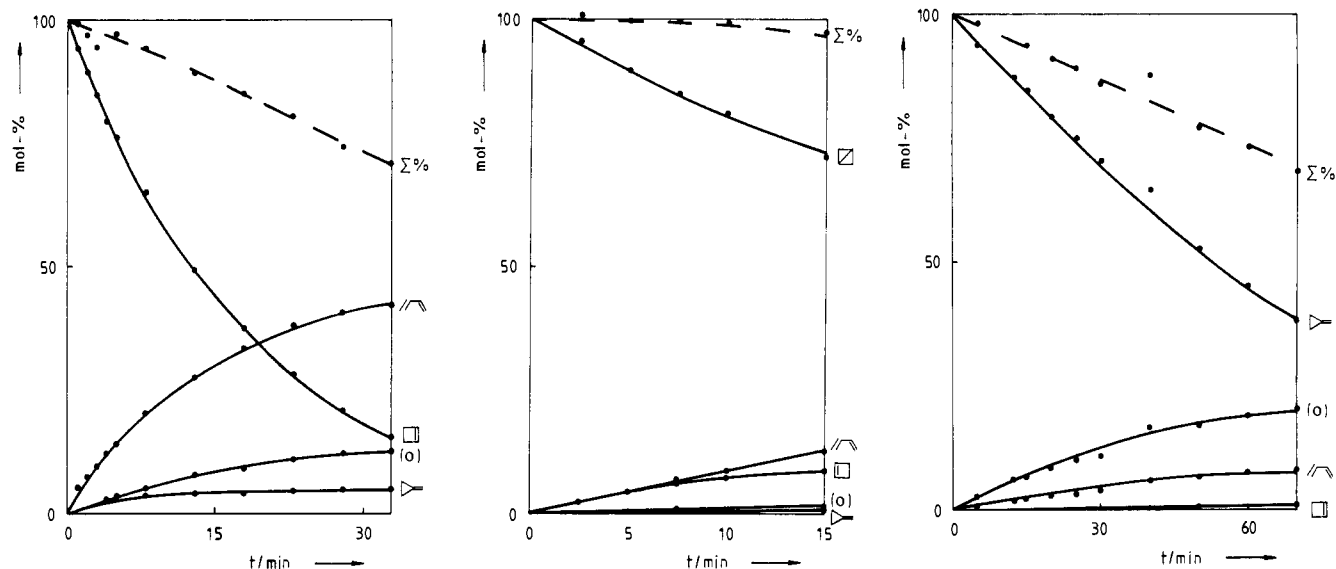








Figure 1. Concentration-time profiles of the 185-nm photolyses of cyclobutene, bicyclo[1.1.0]butane, and methylenecyclopropane; (a) represents formation of ethylene and acetylene.

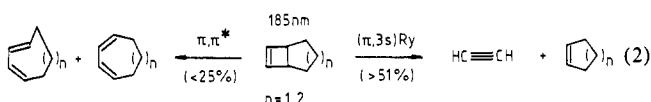
Table I. Quantum Yields of the 185-nm Photolyses of Cyclobutene, Bicyclo[1.1.0]butane, and Methylenecyclopropane

substrate	ϕ_s	photoproducts ϕ_p^a					$\Sigma\phi_p$ (mass balance)
		$\text{CH}_2=\text{CH}_2^b$	$\text{HC}\equiv\text{CH}$				
	0.71	0.07	0.04		0.43	0.12	0.66
	0.65	0.03	0.02	0.30	0.29	0.02	0.66
	0.24	0.08	0.06	<0.01	0.05		0.19

^a Only photoproducts in solution were analyzed. ^b Ethene was not photoactive under these conditions. ^c The photolysis (185 + 254 nm) of an ca. 0.01 M solution of 1,3-butadiene in *n*-heptane for 30 min gave 2.9% cyclobutene.

photochemical behavior of bicyclo[1.1.0]butane in solution, although thermal cleavage affords 1,3-butadiene.³

Recently it was shown⁴ that direct 185-nm irradiation of bicyclo[*m*.2.0]alkanes ($m = n + 2 = 3, 4$; eq 2) resulted mainly in the fragmentation to acetylene and the corresponding cycloalkene involving ($\pi,3s$)-Ry excitation. As a secondary reaction (<25%) the corresponding 1,3-cycloalkenes were formed via π, π^* -excitation.



Since cyclobutene and bicyclo[1.1.0]butane absorb appreciably in the vacuum-ultraviolet ($\lambda < 200$ nm), their photoreactivity at 185 nm should be observable. Whether π, π^* - or ($\pi, 3s$)-Ry-type photochemistry would be involved with these two substrates should be reflected by the type of photoproducts formed and their distribution. Presently we report our results on the 185-nm photochemistry of cyclobutene and bicyclo[1.1.0]butane.

Results

Control experiments at 254 nm, the major output of the 185-nm-light source, confirm that cyclobutene and bicyclo[1.1.0]butane are essentially inert (<4% consumption on 30-min irradiation) at this wavelength. Therewith it was guaranteed that any photoreactivity on irradiation with the low-pressure mercury resonance lamp was due to 185-nm excitation.

The photoproducts of the 185-nm photolyses of cyclobutene, bicyclo[1.1.0]butane, and methylenecyclopropane are for convenience exhibited in the form of concentration-time profiles in Figure 1. Also the product balance ($\Sigma\phi_p$) as a function of time is given, showing that on prolonged 185-nm photolyses significant

deterioration due to formation of intractable high molecular weight material ensued. Product identification was secured by coinjection of authentic samples in the capillary GC by using several columns (PPG, OV 101 and SE 30) and 400-MHz ¹H NMR analysis of product fractions collected by preparative GC. The ¹H NMR spectra were identical with those of the authentic samples. The quantum yields, determined by *cis,trans*-cyclooctene actinometry,⁵ are given in Table I. Control experiments confirmed that acetylene was efficiently reduced to ethylene on 185-nm photolysis in *n*-pentane solution.

The results in Table I show that both cyclobutene and bicyclo[1.1.0]butane are quite photoactive on 185-nm excitation, while methylenecyclopropane significantly less. The major photoproduct of cyclobutene is 1,3-butadiene, but appreciable amounts of methylenecyclopropane, ethylene, and acetylene are formed as well. All are primary photoproducts as established by control experiments. It is significant that no bicyclo[1.1.0]butane was formed, although the latter should have accumulated sufficiently for capillary GC and ¹H NMR detection.

In the 185-nm photolysis of bicyclo[1.1.0]butane the primary products were cyclobutene and 1,3-butadiene, formed with similar efficiencies. Secondary and minor photoproducts, as established by controls, were methylenecyclopropane, acetylene, and ethylene. On the other hand, as already stated, methylenecyclopropane was considerably less photoreactive on 185-nm irradiation with a poor product balance ($\Sigma\phi_p \sim 0.19$). Primary products were 1,3-butadiene, ethylene, and acetylene, all in low efficiencies (<10%), with cyclobutene as the secondary product.

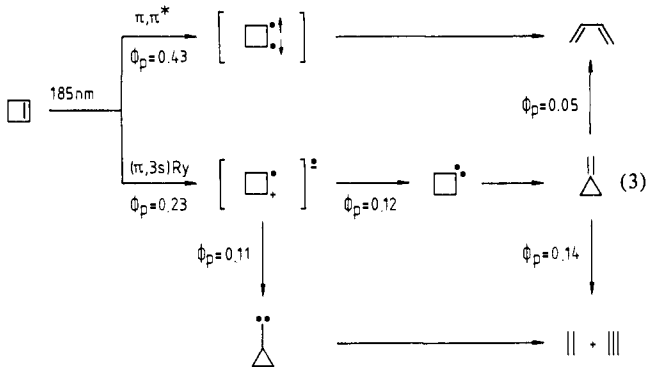
Mechanistic Discussion

In eq 3 the results of the 185-nm photochemistry of cyclobutene are rationalized mechanistically. Clearly both π, π^* - as well as ($\pi, 3s$)-Ry-type photochemistry manifest themselves in the product

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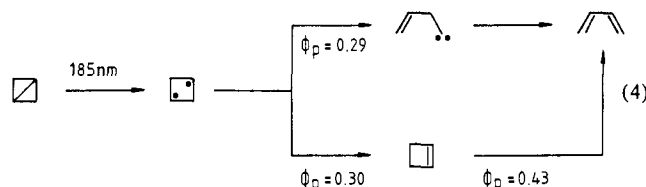
picture, the former predominating. This is not at all surprising in view of the expected efficient electrocyclic ring opening of π, π^* -excited cyclobutene. Such a photochemical process is not possible for the homologous cycloalkenes, so that cyclobutene represents a special case.



The more usual $(\pi, 3s)$ -Rydberg photochemistry of cycloalkenes⁵ is with a quantum yield $\phi_p = 0.23$ for the case of cyclobutene of subordinate importance. However, in view of the radical cation character of Rydberg excited states, retrocyclization into 1,3-butadiene⁶ cannot be rigorously excluded at this point. Still more puzzling at first sight is the fact that bicyclo[1.1.0]butane is not formed in the 185-nm photolysis of cyclobutene. Such products are typical Rydberg photoproducts of higher homologous cycloalkenes,⁵ formed from the corresponding carbenes that are derived from alkyl and hydrogen 1,2-shifts.

Relevant on this point is the established chemistry of the cyclopropylmethylene, produced in the thermolysis of the corresponding diazoalkane⁷ and tosyl hydrazone,^{8a,b} and the cyclobutylidene, produced in the thermolysis of its tosylhydrazone precursor.^{8b,c} Thus, cyclopropylmethylene mainly transforms into cyclobutene and appreciably fragments into ethylene and acetylene, while cyclobutylidene gives mainly (80%) methylenecyclopropane and some (20%) cyclobutene, but both give no bicyclo[1.1.0]butane.^{7,8} The parallelism in the product composition derived from this carbene chemistry and the 185-nm behavior of cyclobutene suggests that cyclopropylmethylene and cyclobutylidene are the precursors to the minor primary photoproducts acetylene, ethylene, and methylenecyclopropane. It would require extensive deuterium tracer experiments to sort out these mechanistic details.

In contrast, the 185-nm photochemistry of bicyclo[1.1.0]butane reflects quite well the established behavior of its congeners.⁹ The mechanistic scheme in eq 4 follows, therefore, the two-step cleavage process; but other alternatives are possible.¹⁰ σ, σ^* -



Excitation of the cyclopropane chromophore leads to homolysis

(6) (a) Haselbach, E.; Bally, T.; Lanyiova, Z. *Helv. Chim. Acta* **1979**, *62*, 577. (b) Bauld, N. L.; Bellville, D. J.; Pabon, R.; Chelsky, R.; Green, G. *J. Am. Chem. Soc.* **1983**, *105*, 2378.

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(10) For example, as suggested by a referee, homolysis of a lateral cyclopropane bond would lead to the 2-ylomethylcyclopropyl diradical, which could serve as precursor to 1,3-butadiene and cyclobutene (cf.: Eaton, D. F.; Bergman, R. G.; Hammond, G. S. *J. Am. Chem. Soc.* **1972**, *94*, 1351).

of the most strained central bond with generation of the 1,3-cyclobutadiyl-like species. Cleavage of an additional carbon-carbon bond affords 1,3-butadiene via 3-butenylidene. Alternatively, 1,2-hydrogen shift leads to cyclobutene.¹¹ Other minor products are derived from secondary processes of these primary photoproducts.

The 185-nm photolysis of methylenecyclopropane, producing acetylene, ethylene, and 1,3-butadiene, resembles quite closely the radiolysis and gas-phase photolysis results.¹² Its relatively low photoreactivity at 185 nm ($\phi_s = 0.24$) and poor product balance ($\Sigma\phi_p = 0.19$) stand out in comparison to those of cyclobutene and bicyclo[1.1.0]butane.

Experimental Section

General Aspects. All photolyses were conducted in a mercury-free apparatus with degassed spectrograde *n*-heptane^{5a} as solvent at 0 °C. ¹H NMR spectra were measured on a Bruker WM-400 NMR spectrometer in CDCl₃ with Me₄Si as reference.

Gas Chromatographic Instrumentation. Preparative gas chromatographic separations were performed on a Carlo Erba Model 4200 gas chromatograph, equipped with flame ionization detector (FID), using a packed glass column (10% Apiezon L on Chromosorb WHP, 80/100 mesh) with carrier gas flow (N₂) of 20 mL/min and column, injector, and detector temperatures of 40, 100, and 120 °C, respectively. The gaseous photoproducts (C₄ fraction) were collected with a trap filled with CDCl₃ at -50 °C.

Analytical separations and quantitative product analysis were performed on a Carlo Erba capillary gas chromatograph (GC) Fractovap 2900, equipped with FID with glass capillary columns and operated under the following conditions: *polypropylene glycol (PPG) column* (86 × 0.8 mm) carrier gas flow (N₂) = 0.56 mL/min, column, injector, and detector temperatures of 20, 100, and 150 °C, respectively; *OV 101 column* (50 m × 0.8 mm) carrier gas flow (N₂) = 0.8 mL/min, column injector, and detector temperatures of 20, 150, and 150 °C, respectively; *SE 30 column* (50 m × 0.8 mm) carrier gas flow (N₂) = 0.4 mL/min, column, injector, and detector temperatures of 20, 100, and 150 °C, respectively. Product yields were obtained by GC calibration and are reported in mol % (concentration vs. time plots). For this purpose calibration curves were constructed for methylenecyclopropane, 1,3-butadiene, cyclobutene, and bicyclo[1.1.0]butane with cyclopentane as GC standard. The calibration factors $f_i = 1.31 \pm 0.03$, 1.38 ± 0.10 , 1.46 ± 0.09 , and 1.37 ± 0.10 , respectively, were determined on the PPG column.

Light Sources. For quantitative 185-nm photolyses the unfiltered light of a 10-W low-pressure mercury arc (Grüntzel Company, Karlsruhe) was used^{5a} with an output of 10% at 185 nm and 66% at 254 nm. Preparative 185-nm photolyses were conducted with the unfiltered light of a low-pressure mercury arc (HNS-10W/Osram) with a light output of 12% at 185 nm and 78.5% at 254 nm. Control experiments at 254 nm were performed with a Vycor filter (M 235, Heraeus, Hanau) to eliminate the 185-nm output.

Materials. Bicyclo[1.1.0]butane was kindly supplied by Professor D. A. Dougherty (Cal. Tech.). Cyclobutene¹³ and methylenecyclopropane¹⁴ were prepared according to literature procedures in purities better than 99%.

Isolation and Identification of the Photoproducts. A 0.074 M solution (200 mL) of cyclobutene in *n*-heptane was irradiated for 30 min with the low-pressure mercury arc at 0 °C under external cooling of the photolysis apparatus by means of an ice bath. Thereafter the photoproducts were concentrated to 1–2 mL by distillation on a 20-cm Vigreux column

(11) The chemistry of the 1,3-cyclobutadiyl diradical has been recently investigated, generated by n, π^* -excitation of the 2,3-diazabicyclo[2.1.1]hex-3-ene (cf.: Chang, M. H.; Dougherty, D. A. *J. Org. Chem.* **1981**, *46*, 4092) or of the bicyclo[1.1.1]pentanone (cf.: Sponsler, M. P.; Dougherty, D. A. *J. Org. Chem.* **1984**, *49*, 4978) precursors. Under these conditions almost entirely bicyclo[1.1.0]butane is formed, with only traces (if any) of cyclobutene and 1,3-butadiene. However, on 185-nm irradiation (σ, σ^* - and/or Rydberg-excitation) of cyclopropanes, stepwise two-bond cleavages as depicted in eq 4 are feasible (cf. ref 9). Whether electronically and/or vibrationally excited 1,3-cyclobutadiyl diradicals are involved is difficult to define at this point, but the 185-nm data demand a more energetic species than those derived from the n, π^* -excitation of the azo and keto precursors. In this context it should be of interest to investigate the 185-nm photochemistry of 2,3-diazabicyclo[2.1.1]hex-2-ene, especially since the behavior of 2,3-diazabicyclo[2.2.1]hept-2-ene differs significantly for 185-nm vs. > 300-nm excitation (cf.: Adam, W.; Oppenländer, T.; Zang, G. *J. Org. Chem.*, in press).

(12) (a) Hill, K. L.; Doepker, R. D. *J. Phys. Chem.* **1972**, *76*, 3153. (b) Brinton, R. K. *J. Phys. Chem.* **1968**, *72*, 321.

(13) Cope, A. C.; Haven, A. C., Jr.; Ramp, F. L.; Trumbull, E. R. *J. Am. Chem. Soc.* **1952**, *74*, 4867.

(14) Köster, R.; Arora, S.; Binger, P. *Synthesis* **1971**, 322.

(temperature max 98 °C). The C₄ products were separated from the remaining *n*-heptane by means of preparative GC and identified by ¹H NMR (400 MHz) and GC coinjection of authentic materials.

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie

for financial support of our work in this area. We thank Professor D. A. Dougherty (Cal. Tech.) for supplying us with a generous sample of bicyclo[1.1.0]butane.

Registry No. Cyclobutene, 822-35-5; cyclopropylmethylene, 6142-73-0; bicyclo[1.1.0]butane, 157-33-5.

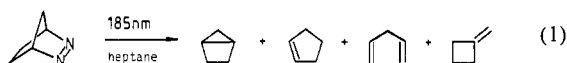
185-nm Photochemistry of Bicyclo[2.1.0]pentane and Cyclopentene

Waldemar Adam* and Thomas Oppenländer†

Contribution from the Institute of Organic Chemistry, University of Würzburg, Am Hubland, D-8700 Würzburg, West Germany. Received August 20, 1984

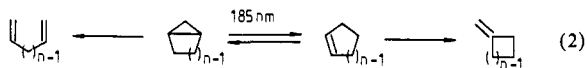
Abstract: Bicyclo[2.1.0]pentane gave 1,4-pentadiene and cyclopentene as primary and methylenecyclobutane as secondary products on irradiation with 185-nm light. Deuterium-labeling experiments revealed that cleavage of two C-C bonds in the cyclopropane chromophore took place to only 11% ($\phi_p = 0.03$), although such cleavage is the major process in the higher homologues of bicyclo[*n*.1.0]alkanes. The major process (89%) was [2 + 2]-cycloreversion into 1,4-pentadiene and rearrangement into cyclopentene, presumably via the 1,3-cyclopentadiyl as common intermediate. Stereomutation of the bicyclo[2.1.0]pentane was of minor importance ($\phi_{iso} = 0.03$). Cyclopentene afforded methylenecyclobutane and bicyclopentane as major products via the cyclobutylmethylene as intermediate, which resulted on $[\pi,3s]$ -Rydberg excitation.

In a recent communication¹ we reported that the 185-nm photodenitrogenation of 2,3-diazabicyclo[2.2.1]heptene in *n*-heptane afforded bicyclo[2.1.0]pentane, cyclopentene, 1,4-pentadiene, and methylenecyclobutane as products (eq 1). With the

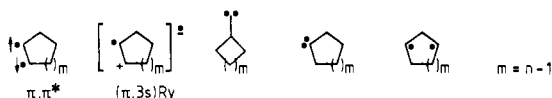


help of control experiments it was confirmed that bicyclo[2.1.0]pentane and cyclopentene were primary photoproducts, which on prolonged 185-nm irradiation converted into one another and gave 1,4-pentadiene and methylenecyclobutane as secondary products. While the 185-nm solution photochemistry of the higher homologues of bicyclo[*n*.1.0]alkanes² and cycloalkenes³ has been intensively investigated during the last decade, that of bicyclo[2.1.0]pentane and cyclopentene has received little consideration.⁴

In view of the established 185-nm photochemistry^{2,3} of the higher homologues (eq 2), it was our interest to examine the photobehavior of bicyclo[2.1.0]pentane and cyclopentene at 185 nm in detail (product studies, quantum yields, deuterium tracing, etc.), in order to establish whether these more strained substrates submit to the mechanistic features of the higher homologues (eq 2). For



example, in the rearrangement of the bicyclo[*n*.1.0]alkanes into cycloalkenes the cycloalkylmethylenes and cycloalkylidenes have been invoked as intermediates.^{2,3} 1,3-Diradicals have been



postulated⁵ as primary species in cleavage processes of bicyclo[*n*.1.0]alkanes on 185-nm excitation, leading to the final product via stepwise breakage of the cyclopropane ring.^{2,6} Such 1,3-diradicals, however, appear to be of no consequence in the 185-nm

Table I. Quantum Yields of the 185-nm Photolyses of Bicyclo[2.1.0]pentane and Cyclopentene

substrate	ϕ_s^a	photoproducts ϕ_p^a				$\Sigma \phi_p$
	0.25	0.12	0.16	0.01	0.29	
	0.15	0.03	0.01	0.04	0.08	

^a Experimental error within 10–15% of the stated values; italic values represent secondary products. ^b The 185-nm photolysis of 1,4-pentadiene led to five photoproducts in relative yields of 32%, 22.5%, 36.4%, 7.5%, and 2%. The main product (36.4%) was identified as 1,3-pentadiene by means of ¹H NMR (400 MHz) and GC coinjection with authentic samples. Bicyclo[2.1.0]pentane (7.5%) and cyclopentene (2%) were identified by GC coinjection, the rest (ca. 59%) was unidentified material. ^c The 185-nm photolysis of methylenecyclobutane led to a complex mixture of C₅ products including 2% bicyclo[2.1.0]pentane and cyclopentene. ^d Traces of cyclopentadiene were identified by GC coinjection. ^e Cyclobutene and 1,3-butadiene (<2%) were identified by GC coinjection.

photolysis of cycloalkenes.^{3a} For the latter, $(\pi,3s)$ -Ry excitation⁷ leads to rearranged products via cycloalkylmethylenes.^{3a,c} Alternatively, their (π,π^*) -singlet states lead additionally to radi-

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