

(temperature max 98 °C). The C<sub>4</sub> products were separated from the remaining *n*-heptane by means of preparative GC and identified by <sup>1</sup>H NMR (400 MHz) and GC coinjection of authentic materials.

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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.

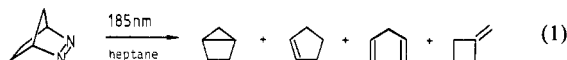
## 185-nm Photochemistry of Bicyclo[2.1.0]pentane and Cyclopentene

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

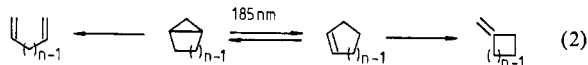
**Abstract:** Bicyclo[2.1.0]pentane gave 1,4-pentadiene and cyclopentene as primary and methylenecyclobutane as secondary products on irradiation with 185-nm light. Deuterium-labeling experiments revealed that cleavage of two C-C bonds in the cyclopropane chromophore took place to only 11% ( $\phi_p = 0.03$ ), 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 bicyclo[2.1.0]pentane as major products via the cyclobutylmethylene as intermediate, which resulted on  $[\pi,3s]$ -Rydberg excitation.

In a recent communication<sup>1</sup> 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

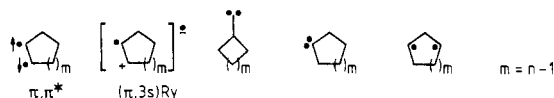


help of control experiments it was confirmed that bicyclo[2.1.0]pentane and cyclopentene were primary photoproducts, which on prolonged 185-nm irradiation converted into one another and gave 1,4-pentadiene and methylenecyclobutane as secondary products. While the 185-nm solution photochemistry of the higher homologues of bicyclo[*n*.1.0]alkanes<sup>2</sup> and cycloalkenes<sup>3</sup> has been intensively investigated during the last decade, that of bicyclo[2.1.0]pentane and cyclopentene has received little consideration.<sup>4</sup>

In view of the established 185-nm photochemistry<sup>2,3</sup> 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 cycloalkylenes have been invoked as intermediates.<sup>2,3</sup> 1,3-Diradicals have been



postulated<sup>5</sup> 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.<sup>2,6</sup> 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

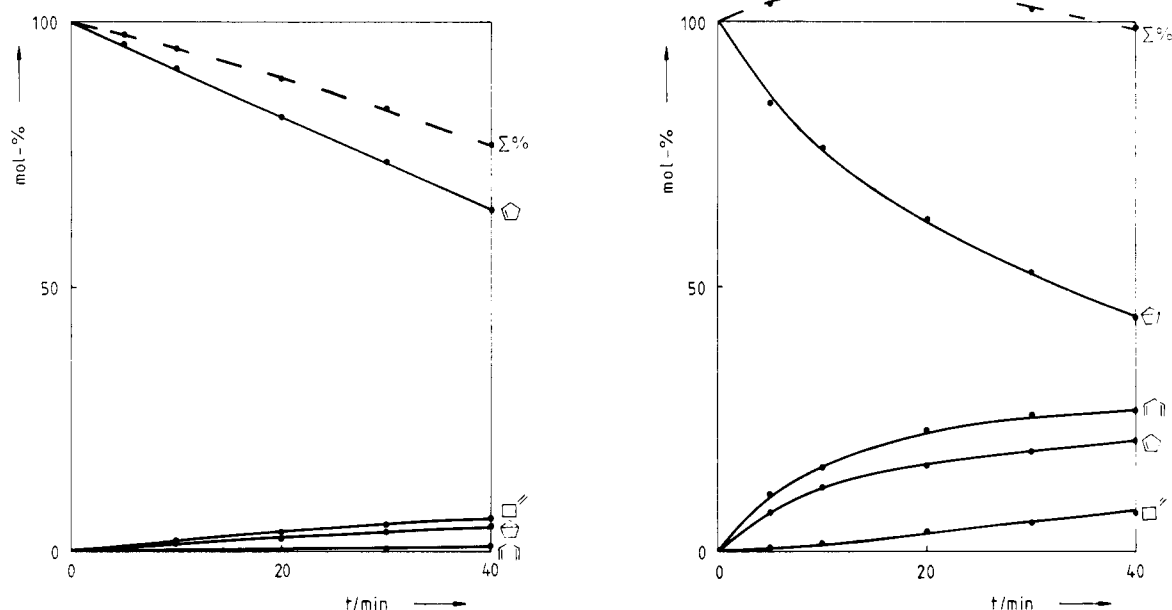
sub- strate	$\phi_s^a$	photoproducts $\phi_p^a$				$\Sigma \phi_p$
<sup>a,e</sup>	0.25	0.12	0.16	0.01		0.29
<sup>c</sup>	0.15	0.03	0.01	0.04		0.08

<sup>a</sup> Experimental error within 10–15% of the stated values; italic values represent secondary products. <sup>b</sup> 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 <sup>1</sup>H 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. <sup>c</sup> The 185-nm photolysis of methylenecyclobutane led to a complex mixture of C<sub>5</sub> products including 2% bicyclo[2.1.0]pentane and cyclopentene. <sup>d</sup> Traces of cyclopentadiene were identified by GC coinjection. <sup>e</sup> Cyclobutene and 1,3-butadiene (<2%) were identified by GC coinjection.



















photolysis of cycloalkenes.<sup>3a</sup> For the latter,  $(\pi,3s)$ -Ry excitation<sup>7</sup> leads to rearranged products via cycloalkylmethylenes.<sup>3a,c</sup> Alternatively, their  $(\pi,\pi^*)$ -singlet states lead additionally to radi-

- (1) (a) Adam, W.; Oppenländer, Th. *Tetrahedron Lett.* **1982**, 23, 5391. (b) Adam, W.; Oppenländer, Th.; Zang, G. *J. Org. Chem.*, in press.
- (2) (a) Srinivasan, R.; Baum, T.; Ors, J. A. *Tetrahedron Lett.* **1981**, 22, 4795. (b) Srinivasan, R.; Ors, J. A.; Baum, T. *J. Org. Chem.* **1981**, 46, 1950. (c) Srinivasan, R.; Ors, J. A. *J. Am. Chem. Soc.* **1978**, 100, 7089.
- (3) (a) Srinivasan, R.; Brown, K. H. *J. Am. Chem. Soc.* **1978**, 100, 4602. (b) Inoue, Y.; Takamuku, S.; Sakurai, H. *J. Chem. Soc., Chem. Commun.* **1975**, 577. (c) Inoue, Y.; Takamuku, S.; Sakurai, H. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1635. (d) Schuchmann, H.-P.; von Sonntag, C.; Srinivasan, R. *J. Photochem.* **1981**, 15, 159.
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†Doctoral Fellow of the Fonds der Chemischen Industrie (1982–1984); Dissertation, University of Würzburg, July 1984.



**Table II.** Relative Distribution in the Photoproducts of the 185-nm Photolyses of Bicyclo[2.1.0]pentane-2,3-*d*<sub>2</sub> and Cyclopentene-3,4-*d*<sub>2</sub>

substrate	deuterium distribution <sup>a</sup>
	
	
	
	
	
	
	
	
	

<sup>a</sup> Normalized for two deuterium atoms; error of <sup>2</sup>H NMR (61.4 MHz) integration ca. 5–10% of the stated values. <sup>b</sup> Initial exo/endo ratio of 1.2. <sup>c</sup> Initial exo/endo ratio of 2.94.

cal-type products.<sup>4</sup> Besides these complex transformations, [2 + 2]-cycloreversion of the cyclobutane can be expected for bicyclo[2.1.0]pentane, a unique feature of this bicyclo[*n*.1.0]alkane (*n* = 2). The feasibility of such direct photochemical retro-cyclization has been recently<sup>8</sup> postulated.

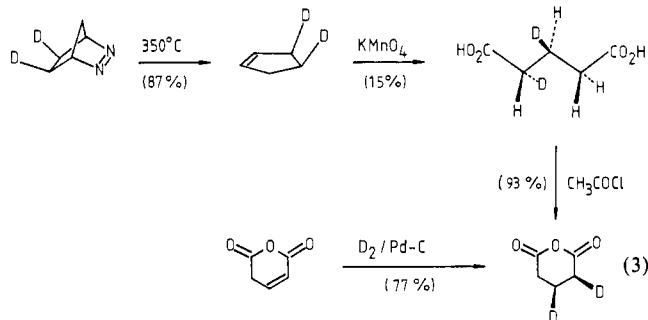
## Results

**Product Studies.** The photoproducts derived from bicyclo-[2.1.0]pentane and cyclopentene on 185-nm irradiation were identified by means of coinjection with authentic materials on several capillary GC columns and 400-MHz  $^1\text{H}$  NMR spectra of fractions collected by preparative GC. Concentration-time profiles for each substrate are given in Figure 1. In the case of bicyclopentane, the product balance ( $\Sigma\%$ ) was excellent, while for cyclopentene considerable deterioration of the photolysate on prolonged photolysis set in as evidenced by precipitation and turbidity. For quantitative work it was essential to conduct the photolyses to less than 20% substrate consumption.

Since all 185-nm photolyses were carried out under unfiltered conditions (major output of the mercury resonance lamps used was 254-nm radiation), it was necessary to test for the photo-reactivity of these substrates and products at 254 nm. These controls confirmed, as expected, that these substances were essentially inert at 254 nm.

**Quantum Yields.** The quantum yields of substrate consumption ( $\phi_s$ ) and product formation ( $\phi_p$ ) were determined by the previously established<sup>9</sup> *cis,trans*-cyclooctene actinometry. The results are summarized in Table I. Differentiation between primary and secondary photoproducts was achieved by examining the yield of a particular product (% $P_i$ ) relative to the sum of all product yields ( $\sum \%P_i$ ) as a function of time. When the quotient  $\%P_i / \sum \%P_i$  stayed constant with respect to time, that particular product was a primary one. In this way it became evident that methylene-cyclobutane was a secondary product in the photolysis of bicyclopentane, while 1,4-pentadiene was a secondary product in the case of cyclopentene (Table I, italic entries).

**Deuterium Labeling.** An ca. 3:1 mixture of *exo,endo*-2,3-dideuteriobicyclo[2.1.0]pentane was prepared by gas-phase pyrolysis<sup>10</sup> of 2,3-diaza-*exo*-5,6-dideuteriobicyclo[2.1.0]heptane at 180 °C; pyrolysis at 350 °C afforded predominantly *cis*-3,4-dideuteriocyclopentene (eq 3). For the latter the *cis* configuration



of the deuteriums was established by means of permanganate oxidative cleavage to glutaric acid and cyclization to glutaric anhydride with acetyl chloride. Cis deuteration of glutaconic anhydride and spectral comparison (IR,  $^1\text{H}$  NMR at 400 MHz,  $^2\text{H}$  NMR at 61.4 MHz,  $^{13}\text{C}$  NMR at 100 MHz) established the cis configuration beyond doubt (eq 3).

(8) (a) Leigh, W. J.; Srinivasan, R. *J. Org. Chem.* **1983**, *48*, 3970. (b) Steinmetz, M. G.; Stark, E. J.; Yen, Y.-P.; Mayes, R. T.; Srinivasan, R. *J. Am. Chem. Soc.* **1983**, *105*, 7209. (c) Adam, W.; Oppenländer, T. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 641.

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(10) (a) Roth, W. R.; Martin, M. *Liebigs Ann. Chem.* **1967**, *702*, 1. (b) Criegee, R.; Rimmelin, A. *Chem. Ber.* **1957**, *90*, 414.

The 185-nm photolysis of bicyclopentane-2,3- $d_2$  in heptane gave *cis*-cyclopentene-3,4- $d_2$  and 1,4-pentadiene- $d_2$  with the relative deuterium distribution as shown in Table II.  $^1\text{H}$  and  $^2\text{H}$  NMR spectroscopy were employed to establish the deuterium distribution. However, prolonged 185-nm photolysis of an *exo/endo*  $d_2$  mixture of the bicyclopentanes showed that after 60 min the original *exo/endo* ratio of 2.94 had dropped to 2.24 in the recovered material. By means of cyclooctene actinometry<sup>9</sup> the quantum yield for this photoisomerization ( $\phi_{\text{iso}}$ ) was determined to be  $0.030 \pm 0.003$ . Again, a control experiment established that no photoisomerization occurred at 254 nm.

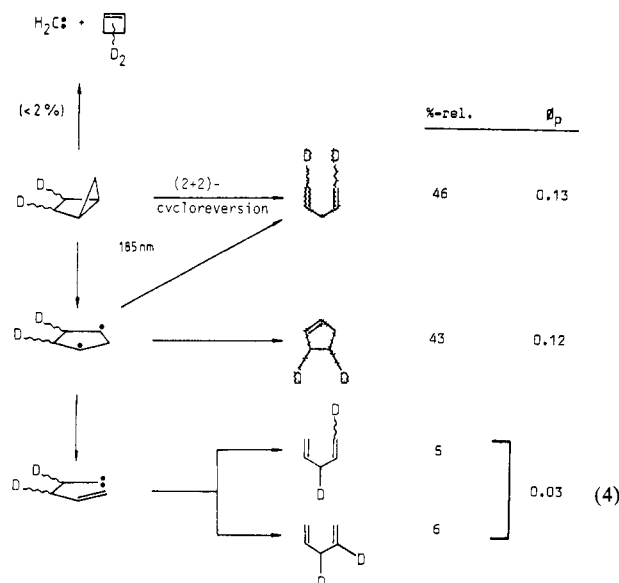
The deuterium distribution in 1,4-pentadiene was independent of the *exo/endo* ratio of the deuteriums in the starting bicyclopentane. Using the 2-position as reference point, which corresponded to 5.5% of the total deuterium content, the relative amounts of various isomers were assessed (eq 4).

In the 185-nm irradiation of *cis*-cyclopentene-3,4- $d_2$   $^2\text{H}$  NMR analysis on the recovered substrates revealed that only ca. 1% of deuterium migration into the double bond had taken place after ca. 45 min. The methylenecyclobutane showed traces (<2%) of deuterium at the *exo*-methylene position.

In contrast, the bicyclopentane that was formed in the 185-nm photolysis of cyclopentene exhibited extensive deuterium labeling at all positions (Table II). The *exo/endo* ratio was found to be  $1.10 \pm 0.01$ . Remarkable is the preferential placement of deuterium at the 5-*anti* position and at the bridgehead positions in the bicyclopentane.

## Discussion

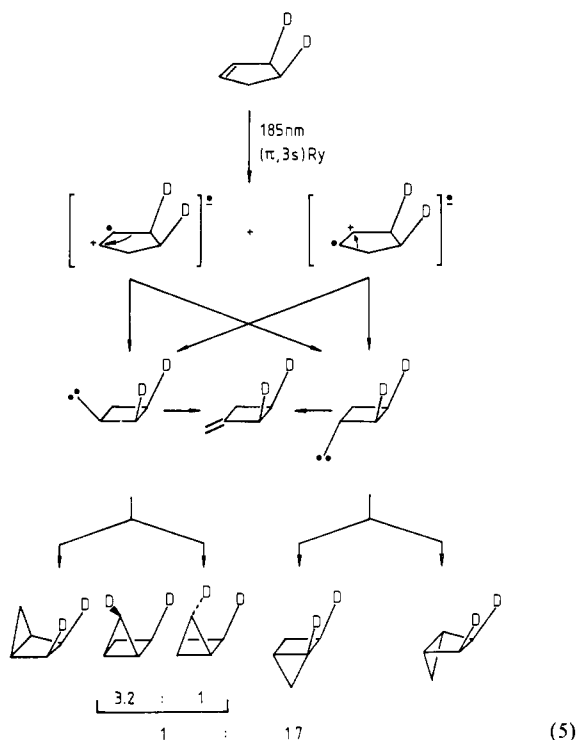
The 185-nm photolysis of bicyclopentane generates cyclopentene and 1,4-pentadiene as primary and methylenecyclobutane as secondary products (Table I). On the basis of the deuterium labeling (Table II) we propose the mechanistic scheme in eq 4 to rationalize these results. In accord with the higher homologues of the bicyclo[*n*.1.0]alkanes,<sup>2a</sup> two-bond cleavage of the cyclopropane chromophore to give methylene and cyclobutene is unimportant (<2%). The alternative two-bond cleavage leading to pent-4-en-1-ylidene, which affords in essentially equal amounts the 1,3- $d_2$  and 2,3- $d_2$  1,4-pentadienes, takes place to a greater extent, i.e., ca. 11% ( $\phi_p = 0.03$ ).



By far the dominant isomer is the 1,4-pentadiene-1,5- $d_2$ , which is formed in 46% ( $\phi_p = 0.13$ ). Whether this isomer is formed exclusively by direct [2 + 2]-retrocycloversion of excited bicyclopentadiene or whether some is additionally produced via the 1,3-cyclopentadienyl (eq 4) cannot be decided on the basis of the present results. However, the fact that *cis*-cyclopentene-3,4- $d_2$  is formed efficiently, i.e., 43% ( $\phi_p = 0.12$ ), which requires a 1,3-cyclopentadienyl-type intermediate, suggests that some of the 1,4-pentadiene-1,5- $d_2$  could be derived from a stepwise process

involving this species.<sup>11</sup> Thus, bicyclopentane differs from its higher homologues in its 185-nm photochemistry in that breakage of one C-C bond in the cyclopropane chromophore (leading to 1,4-pentadiene-1,5- $d_2$  and *cis*-cyclopentene-3,4- $d_2$ ) predominates over breakage of two C-C bonds (leading to 1,4-pentadiene-1,3- $d_2$  and -2,3- $d_2$ ) to the extent of 89% vs. 11%.

The 185-nm photochemistry of cyclopentene is considerably more complex. The primary products are bicyclopentane (minor) and methylenecyclobutane (major); the secondary product is 1,4-pentadiene. The extensive deuterium scrambling in the bicyclopentane implies carbene-type chemistry. In eq 5 the results are mechanistically interpreted in terms of the two possible ( $\pi,3s$ )-Ry states that are formed on 185-nm excitation. From these two distinct (in terms of deuterium labeling) Rydberg states the two respective cyclobutylmethylenes are generated by ring contraction. A 1,2-shift of the adjacent cyclobutane hydrogen affords methylenecyclobutane as major process ( $\phi_p = 0.04$ ), cf. Table I. The latter is >98% deuterium labeled at the 2,3-positions.



As competing process ( $\phi_p = 0.03$ ) figures 1,3-hydrogen insertion (Table I), producing a complex mixture of isomeric bicyclopentanes- $d_2$ . The pronounced *anti/syn* selectivity (*anti*-5- $d$  vs. *syn*-5- $d$  isomers ca. 3.2) relates presumably to steric factors, since deuterium migration above the cyclobutane plane (*syn*-5- $d$  isomer) vs. laterally (*anti*-5- $d$  isomer) should be unfavorable during 1,3-insertion. A similar selectivity was found in the 185-nm photolysis of cyclohexene-3,3,6,6- $d_4$ .<sup>3a</sup>

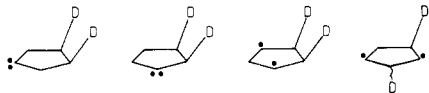
An additional clue that cyclobutylmethylenes intervene in the cyclopentene 185-nm photolysis is the appreciable isotope effect ( $k_H/k_D = 1.7$ ) in the 1,3-insertion leading to the *syn,anti*-bicyclopentane-1,2- $d_2$  and -2,5- $d_2$ , respectively. Isotope effects of this magnitude are typical for 1,3-hydrogen insertions of carbenes.<sup>12</sup> But probably the most compelling evidence for cyclobutylmethylene as intermediate in the 185-nm photolysis of cyclopentene is the fact that the ratio of methylenecyclobutane and bicyclopentane products corresponds to that observed in the base-catalyzed decomposition of the tosylhydrazone of cyclo-

(11) As suggested by a reviewer, an alternative two-bond cleavage pathway leading to scrambled 1,4-pentadienes could be homolysis of a lateral cyclopropane bond affording an excited 2-ylomethylcyclobutyl 1,3-diradical, which subsequently fragments to the 4-penten-1-ylidene (cf.; White, D. H.; Condit, P. B.; Bergman, R. G. J. Am. Chem. Soc. 1972, 94, 1348, 7931).

(12) Kirmse, W.; von Scholz, H.-D.; Arold, H. Liebigs Ann. Chem. 1968, 711, 22.

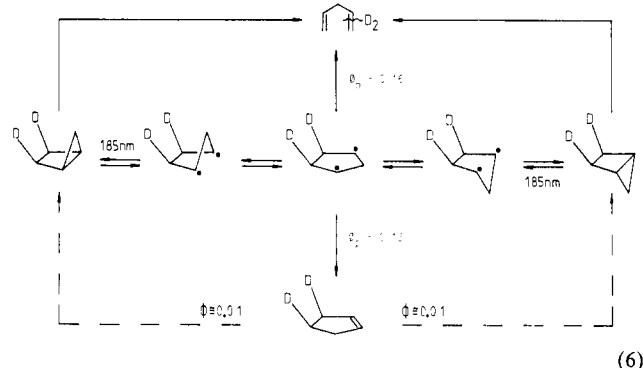
butanecarboxaldehyde,<sup>13</sup> i.e., respectively 1.3 vs. 1.4. Unfortunately, a deuterium-labeling experiment has not been performed for the cyclobutylmethylene derived from the tosylhydrazide, which would allow a more detailed comparison of these two drastically distinct modes of generating this carbene.

The temptation to invoke cyclopentylidenes and 1,3-cyclopentadiyl as possible reaction intermediates in the 185-nm photochemistry of *cis*-cyclopentene-3,4-*d*<sub>2</sub> can be excluded, at least as major species, on the basis of the present results. The cy-



clopentylidenes would have caused extensive deuterium scrambling in the recovered substrate. This is not observed. Besides, this carbene, generated from denitrogenation of tetramethylenediazirene,<sup>14</sup> leads exclusively to cyclopentene. On the other hand, the 1,3-cyclopentadiyls would have resulted in little if any syn/anti selectivity in the bicyclopentane formation.<sup>1b</sup>

A final feature concerns the stereomutation (*exo/endo*-isomerization) of bicyclo[2.1.0]pentane-2,3-*d*<sub>2</sub> during its 185-nm photolysis (eq 6). Such stereomutation competes inefficiently ( $\phi_{iso} = 0.03$ ) with fragmentation into 1,4-pentadiene ( $\phi_p = 0.16$ ) and rearrangement into cyclopentene ( $\phi_r = 0.12$ ). In fact, the prevalent amount of *exo/endo*-isomerized substrate must derive from secondary photolysis of the cyclopentene that is formed in the 185-nm irradiation of bicyclopentane.



## Experimental Section

**General Aspects.** All photolyses were performed in spectrograde *n*-heptane<sup>9</sup> under nitrogen atmosphere at room temperature (25 °C). Before photolysis, the solutions were deaerated by purging with a slow stream of purified nitrogen. During photolysis the mixture was stirred efficiently by means of a magnetic spinbar.

Melting points were measured on a Büchi SMP-20 instrument in sealed tubes and are uncorrected. <sup>1</sup>H NMR (400 MHz), <sup>2</sup>H NMR (61.4 MHz), and <sup>13</sup>C NMR (100.6 MHz) were taken on a Bruker WM-400 NMR spectrometer with internal standard Me<sub>4</sub>Si or CDCl<sub>3</sub>. IR spectra were conducted on a Beckman IR spectrophotometer Acculab-4.

**Gas Chromatographic Instrumentation.** For quantitative analyses a Carlo Erba, Fractovap Model 2900 capillary gas chromatograph, equipped with glass capillary columns and flame ionization detector (FID), was used. The following column was employed:

**Column A:** 86 m × 0.8 mm, polypropylene glycol (PPG), carrier gas flow (N<sub>2</sub>) = 0.56 mL/min, column, injector, and detector temperatures of 20, 150, and 150 °C, respectively.

Preparative gas chromatographic separations were conducted on a Carlo Erba Model 4200 (FID) gas chromatograph with the following packed glass columns:

**Column B:** 1.5 m × 8 mm, 10% Apiezon L on Chromosorb WHP (80/100 mesh), carrier gas flow (N<sub>2</sub>) = 25 mL/min, column, injector, and detector temperatures of 40, 100, and 150 °C, respectively.

**Column C:** 1.5 m × 8 mm, 5% AgNO<sub>3</sub> and 20% ethylene glycol<sup>15</sup> on Volaspher (80/100 mesh), carrier gas flow (N<sub>2</sub>) = 30 mL/min, column, injector, and detector temperatures of 40, and 80 °C, respectively.

**Light Sources.** Photolyses (185 nm) on preparative scale (25–200 mL) were carried out in a reaction vessel equipped with nitrogen inlet and a Suprasil tube, containing a low-pressure mercury arc (HNS 10W/UoZ-Osram). Quantitative photolyses were performed in a Suprasil cuvette (4 mL), equipped with a nitrogen inlet, placed directly in front of a sigmoidal low-pressure mercury arc (capillary lamp No. 4, Gräntzel Co., Karlsruhe). Control experiments at 254 nm (and higher wavelength) were conducted by selecting the 254-nm line by means of a Vycor filter (M 235, Heraeus, Hanau). Quantum yields at 185 nm were determined as previously<sup>9</sup> described with the *cis*-*trans* isomerization of cyclooctene as actinometer.

**Product Analysis.** All photoproducts were identified by <sup>1</sup>H NMR (400 MHz) and/or <sup>2</sup>H NMR (61.4 MHz) and GC coinjection on column A with authentic samples. For quantitative GC analysis the C<sub>5</sub> products were calibrated against 2-methyl-1,3-butadiene (isoprene) as GC standard on column A affording calibration factors (*f*<sub>i</sub>) for cyclopentene, bicyclo[2.1.0]pentane, 1,4-pentadiene, and methylenecyclobutane of *f*<sub>i</sub> = 1.11 ± 0.01, 0.50 ± 0.01, 1.14 ± 0.01, and 0.92 ± 0.01, respectively.

**Materials.** Cyclopentene, 1,3-pentadiene, nonane (GC standard) and 2-methyl-1,3-butadiene (GC standard) were commercially available in purities better than 99% (GC). Methylenecyclobutane and 1,4-pentadiene were gift samples from Dr. P. Binger (Max-Planck-Institut für Kohleforschung/Mühlheim).

**Bicyclo[2.1.0]pentane,**<sup>16</sup> bp 45–46 °C (760 torr), was synthesized in a purity >99.4% (GC) by pyrolyzing a sample of 2,3-diazabicyclo[2.2.1]hept-2-ene<sup>16</sup> at 260 °C (760 torr).<sup>10b</sup>

**2,3-Dideuteriobicyclo[2.1.0]pentane**<sup>10b</sup> was obtained in 75% yield by thermolysis of 2,3-diaza-*exo*-5,6-dideuteriobicyclo[2.2.1]hept-2-ene as a mixture of *exo/endo* isomers. At 250 °C (760 torr) a mixture of 54.3 ± 1.2% *exo*- and 45.7 ± 0.8% *endo*-bicyclo[2.1.0]pentane-2,3-*d*<sub>2</sub> was obtained, whereas at 180 °C (140 torr) the composition of the mixture was 74.6 ± 0.5% and 25.4 ± 0.2%, respectively. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 0.51 (mc, 1 H, *syn*-H), 0.67 (mc, 1 H, *anti*-H), 1.35 (mc, 1.09 H, *endo*-H), 1.51 (mc, 2 H, 1-H, 4-H), 2.11 (mc, 0.91 H, *exo*-H). <sup>2</sup>H NMR (CFCl<sub>3</sub>, 61.4 MHz): δ 1.45 (br s, 0.91 D, *endo*-D), 2.19 (br s, 1.09 D, *exo*-D). IR and <sup>1</sup>H NMR data were in agreement with published data.<sup>10a</sup>

***cis*-3,4-Dideuteriocyclopentene** was obtained by pyrolysis<sup>10b</sup> of 1.00 g (10.2 mmol) of 2,3-diaza-*exo*-5,6-dideuteriobicyclo[2.2.1]hept-2-ene at 350 °C (760 torr), affording 0.51 g (71%) of a pale yellow liquid which contained ca. 80% cyclopentene-3,4-*d*<sub>2</sub> and 20% bicyclo[2.1.0]pentane-2,3-*d*<sub>2</sub>. Pure (99% by GC) *cis*-3,4-dideuteriocyclopentene (bp 44 °C (760 torr)) was obtained by processing this mixture by preparative GC on column C. IR (CFCl<sub>3</sub>): 3050, 2930, 2900, 2850, 2120, 1660, 1365, 910, 830, 735 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 1.79 (mc, 1 H, 4-H), 2.22–2.28 (br m, 1 H, 3-H), 2.28 (br d, 2 H, 5-H), 5.68 (br s, 2 H). <sup>2</sup>H NMR (CFCl<sub>3</sub>, 61.4 MHz): δ 1.80–1.98 (br m, 1 D, 4-D), 2.38 (br d, 1 D, 3-D).

***cis*-3,4-Dideuterioglutaric Anhydride from Cyclopentene-3,4-*d*<sub>2</sub>.** Cyclopentene-3,4-*d*<sub>2</sub> (0.60 g, 8.6 mmol) was dropped continuously within 30 min into a mixture of 5.00 g (31.6 mmol) of KMnO<sub>4</sub>, 5 mL of benzene, 13 mL of water, and 0.1 mL of triethylmethylammonium chloride. The temperature of the mixture was kept by external cooling at less than 40 °C. Thereafter, the brown reaction mixture was heated to 50 °C and after filtration the colorless mixture was extracted with ether (50 mL). After the mixture was dried over MgSO<sub>4</sub>, the solvent was evaporated at 20 °C (18 torr) to yield 170 mg (15%) of colorless needles, mp 98–99 °C, of dideuterated glutaric acid. Afterwards, 100 mg of glutaric acid-*d*<sub>2</sub> were refluxed with 174 mg (2.25 mmol) of freshly distilled acetyl chloride (bp 52 °C (760 torr)) for the period of 1 h. Excess acetyl chloride was removed by distillation (50 °C (18 torr)) to yield an oily residue, which was redistilled at 90 °C (0.1 torr). After recrystallization from 1:1 ether/hexane, there were obtained 80 mg (92%) of *cis*-glutaric-3,4-*d*<sub>2</sub> anhydride: colorless needles, mp 53–55 °C. IR (KBr): 3538, 2990, 2925, 2220, 1810, 1770, 1423, 1140, 1128, 643 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 1.97–2.06 (m, 1 H), 2.73 (mc, 1 H), 2.75 (d, *J* = 6.5 Hz, 2 H). <sup>2</sup>H NMR (CFCl<sub>3</sub>, 61.4 MHz): δ 1.85 (br s, 1 D), 2.54 (br s, 1 D). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100.6 MHz): δ 15.98 (dt, C-4), 29.61 (dt, C-3), 29.87 (t, C-5), 166.34 (s, C-2, C-6).

***cis*-3,4-Dideuterioglutaric anhydride from glutaconic anhydride** was obtained by deuteration of 0.50 g (4.5 mmol) of glutaconic anhydride with D<sub>2</sub>/Pd-C in 100 mL of ethyl acetate at 20 °C in a yield of 77% (0.40 g) as colorless needles, mp 54–55 °C. IR, <sup>1</sup>H NMR, <sup>2</sup>H NMR, and <sup>13</sup>C NMR data coincided with previous data.

**General Procedure for Isolation and Characterization of the Photoproducts.** Solutions (25 mL, 0.01 M) of the appropriate substrate in *n*-heptane were saturated with nitrogen at 25 °C and photolyzed for 30 min. Thereafter, the volatile photoproducts were concentrated by means

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of fractional distillation with a 20-cm Vigreux column (bp max 98 °C), affording 1–2 mL of a *n*-heptane solution. This solution was processed by preparative GC with column B to isolate the C<sub>5</sub> fraction with a retention time of 2.3 min. Characterization was achieved by <sup>1</sup>H NMR and <sup>2</sup>H NMR, respectively. Relative product yields and deuterium distributions were obtained by means of electronic integration of the <sup>1</sup>H NMR or <sup>2</sup>H NMR resonances (Table II).

**Time Dependence of the Exo/Endo Ratio during 185-nm Photolysis of 2,3-Dideuteriobicyclo[2.1.0]pentane.** Three solutions (25 mL, 0.0171 M) of *exo/endo*-bicyclo[2.1.0]pentane (*exo/endo* ratio = 2.94) in *n*-heptane were photolyzed under exactly the same conditions for 20, 40, and 60 min, respectively. The C<sub>5</sub>-product fraction was isolated as described above and analyzed by means of <sup>2</sup>H NMR spectroscopy. The actinometric measurement<sup>9</sup> was conducted by irradiating a 0.040 M solution of *cis*-cyclooctene and *n*-nonane as GC standard (0.027 M) in *n*-pentane in the same vessel and under the same conditions. The *cis*-*trans* isomerization was monitored by GC with column A (but column temperature 72 °C and carrier gas flow (N<sub>2</sub>) = 1.1 mL/min). The quantum yield of *exo/endo* isomerization ( $\phi_{iso}$ ) was calculated according to eq 7 with  $\phi_{Z \rightarrow E} = 0.32$ ,<sup>3d</sup> the quantum yield of formation of *trans*-cyclooctene,

$$\phi_{iso} = \frac{R_{iso}\phi_{Z \rightarrow E}}{R_{Z \rightarrow E}} \quad (7)$$

$R_{iso} = (2.1 \pm 0.1) \times 10^{-5}$ , the rate of *exo/endo* isomerization of bicyclo[2.1.0]pentane-2,3-*d*<sub>2</sub>, and  $R_{Z \rightarrow E} = (2.4 \pm 0.1) \times 10^{-4}$ , the rate of formation of *trans*-cyclooctene (M<sup>-1</sup> min<sup>-1</sup>).

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**Registry No.** Bicyclo[2.1.0]pentane, 185-94-4; *exo*-5,6-dideuterio-bicyclo[2.2.1]hept-2-ene, 3675-40-9; *exo*-2,3-dideuteriobicyclo[2.1.0]pentane, 51794-28-6; *endo*-2,3-dideuteriobicyclo[2.1.0]pentane, 60426-74-6; bicyclo[2.1.0]pentane-2,3-*d*<sub>2</sub>, 96442-65-8; *cis*-3,4-dideuteriocyclopentene, 96349-02-9; glutaric acid-*d*<sub>2</sub>, 96349-03-0; *cis*-glutaric-3,4-*d*<sub>2</sub> anhydride, 96349-04-1; glutaconic anhydride, 5926-95-4; cyclopentene, 142-29-0.

## Application of the Gassman–Fentiman Tool of Increasing Electron Demand to the <sup>13</sup>C NMR Spectroscopic Study of 1-Aryl-3-methylbut-2-enyl (Allylic) and 2-Arylpent-3-yn-2-yl (Propargylic) Cations<sup>1</sup>

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**Abstract:** The Gassman–Fentiman tool of increasing electron demand has been applied to 1-aryl-3-methylbut-2-enyl (allylic) and 2-arylpent-3-yn-2-yl (propargylic) cations **2** and **3**, using <sup>13</sup>C NMR spectroscopy as the structural probe. A plot of C<sub>α</sub> and C<sub>γ</sub> chemical shifts of **2** and **3** vs. the cationic center chemical shifts of model 1-aryl-1-cyclopentyl cations **8** indicates deviations which can be rationalized by an increased resonance effect (allylic resonance in **2** and mesomeric vinyl cation character in **3**).

Although the Gassman–Fentiman tool of increasing electron demand<sup>2</sup> has been used extensively in conjunction with <sup>13</sup>C NMR spectroscopy to probe the structures of a variety of “ordinary” and “extraordinary” unconjugated carbocations, as well as some aryl conjugated carbocations,<sup>3–22</sup> no systematic study of the tool applied

to ordinary conjugated allylic cations has been reported. Since there is dispute over the interpretation of the response of the diarylcarbenium ions to the probe,<sup>9,21</sup> and since the probe has been applied to the allylic carbocation 2-aryl-3-methylenenorbornyl (**1**),<sup>22</sup> and an interpretation offered, we thought that it is imperative to determine the response of an “ordinary” conjugated system to the probe to serve as a model for detection of “extraordinary” conjugated carbocations. It is well-known that <sup>13</sup>C NMR shifts cannot be directly equated with charge densities and<sup>2a</sup> such

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