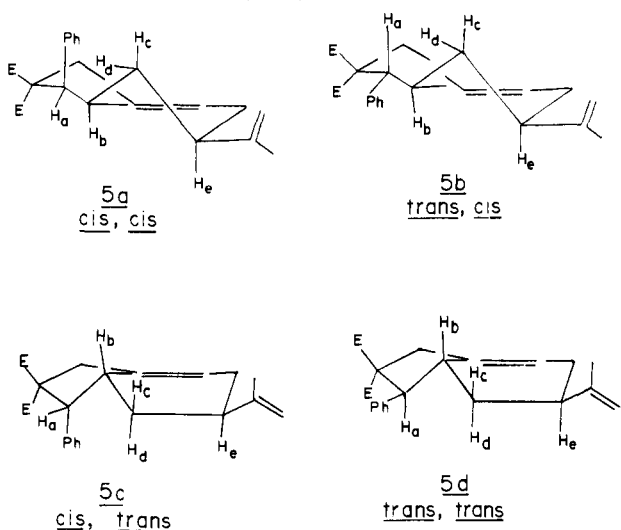


Chart I. Diastereomeric Adducts



products⁷—neither of which corresponds to those obtained from **3**.¹² Again, the regioselectivity is established as corresponding to **5** not **4** by the presence of an isolated AM pattern for a CH₂ unit (major, δ 3.58 and 2.90, $J = 18.9$ Hz; minor, δ 3.42 and 2.63, $J = 16.2$ Hz) as well as a doublet for the benzylic proton (major, δ 3.99, $J = 7.5$ Hz; minor, δ 3.60, $J = 12.8$ Hz). The presence of an upfield proton as a ddd in both cases (major, δ 1.01, $J = 13.5, 9.8, 4.2$ Hz; minor, δ 1.24, $J = 13.4, 9.0, 4.0$ Hz) corresponds to the axial proton at C(4) in a trans-3,5-disubstituted cyclohexene⁹—i.e., H_c in **5c** and **5d**. In addition, the minor isomer reveals H_d also as a ddd at δ 1.82, $J = 13.4, 5.7, 5.3$ Hz. Double irradiation confirms these assignments. The stereochemistry of the phenyl group derives from models which suggests an approximately 20° dihedral angle for the cis,trans isomer but a nearly 180° dihedral angle for the trans,trans isomer. The smaller J_{ab} is associated with the smaller dihedral angle—a fact that suggests the major isomer is cis,trans-**5c**.

The chemo-, regio-, and diastereoselectivity of these reactions are remarkable. From a mechanistic point of view, they demonstrate that the new C–C bond is formed with net retention of stereochemistry with respect to the face of the allyl unit. Since the initial Pd-assisted ionization occurs with inversion of configuration,^{9,13} the new C–C bond also results from an inversion process—i.e., the distal approach as in eq 1, path b. To our knowledge, this example represents the first demonstration of a metal-catalyzed olefin addition not involving prior coordination of the olefin to the metal. A secondary stereochemical benefit is the selectivity for the phenyl group to become endo which can be interpreted to arise from an extended approach of the acceptor in which steric interactions are minimized.¹⁴ As expected,^{9,15} even though the starting materials are optically active, the products are racemic—a result of the symmetry expected from the initial ionization of the carbonate by palladium (i.e., **7**) as well as the likelihood that the TMM–Pd equilibrates (i.e., **8** \rightleftharpoons **9**).^{3a} The complexity of the TMM unit employed here bodes well for the generality of this cycloaddition approach to five-membered rings.¹⁶

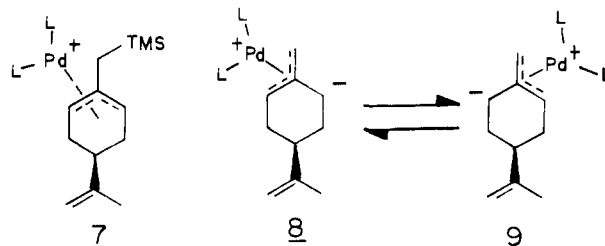
(11) An alcohol inversion of **2** using the Mitsunobu procedure which proceeds in 90% yield at 40% conversion also provides **6** after exchange of the initially formed benzoate to the carbonate. The benzoate also serves as a donor in the cycloaddition but in somewhat lower yields.

(12) Here, too, a trace amount of a third product that does not correspond to **5a** nor **5b** can be detected in the NMR spectrum. It is tentatively assigned as the alternative regioisomer but was present in insufficient amounts to isolate.

(13) Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1976**, *98*, 630; *J. Org. Chem.* **1976**, *41*, 3215. Hayashi, T.; Hagihara, T.; Konishi, M.; Kumada, M. *J. Am. Chem. Soc.* **1983**, *105*, 7767.

(14) This point will be discussed in more detail in future publications.

(15) Trost, B. M.; Schmuff, N. R. *Tetrahedron Lett.* **1981**, *22*, 2999. However, also see: Fiaud, J. C.; Malleron, J. L. *Tetrahedron Lett.* **1981**, *22*, 1399.



It does illustrate the importance of the choice of the leaving group for successful reactions.¹⁷

Acknowledgment. We thank the National Science Foundation and the National Institutes of Health, General Medical Sciences, for their generous support for our programs.

Registry No. **2**, 94348-83-1; **3b**, 94348-84-2; (\pm)-**5** (isomer 1), 94369-80-9; (\pm)-**5** (isomer 2), 94348-85-3; (\pm)-**5** (isomer 3), 94348-86-4; (\pm)-**5** (isomer 4), 94348-87-5; **6**, 94348-88-6; Pd(OAc)₂, 33571-36-7; BuLi, 109-72-8; Ph₃P, 603-35-0; *cis*-carveol, 1197-06-4; *trans*-carveol, 1197-07-5; dimethyl benzylidenemalonate, 6626-84-2.

(16) The most complex TMM units previously employed involved intramolecular cycloadditions. See: Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1982**, *104*, 3733.

(17) For the first case of an allyl carbonate, see: Trost, B. M.; Masse, G., unpublished work, quoted in the following. Trost, B. M.; Runge, T. A. *J. Am. Chem. Soc.* **1981**, *103*, 7550. For extensive studies of this leaving group, see: Trost, B. M.; Hung, M.-H. *J. Am. Chem. Soc.* **1983**, *105*, 7757. Tsuji, J.; Shimizu, I.; Minami, I.; Ohashi, Y. *Tetrahedron Lett.* **1982**, *23*, 4809.

Competing Pathways in the Photolysis of Bicyclo[1.1.0]butane

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The vacuum ultraviolet (VUV) photochemistry of simple cyclopropane derivatives in the gas phase¹⁻³ and in solution^{4,5} is dominated by a two-bond scission to give an olefin and a carbene. In the gas phase at 167 and 147 nm, the methylene-extrusion channel is stereospecific for retention: *cis*- and *trans*-1,2-dimethyl cyclopropane give *cis*- and *trans*-2-butene, respectively.³ This result supports a concerted mechanism. In the solution-phase photolysis at 185 nm, the results are less easily interpreted, but a sequential rather than a concerted cleavage of the two bonds seems likely.⁵

Applied to bicyclo[1.1.0]butane (**1**), the latter mechanism might offer a hydrocarbon route to cyclobutane-1,3-diyl (**2**), a biradical⁶

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(1) Currie, C. L.; Okabe, H.; McNesby, J. R. *J. Phys. Chem.* **1963**, *67*, 1494.

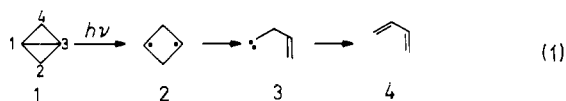
(2) (a) Lopez, E.; Doepker, R. D. *J. Phys. Chem.* **1979**, *83*, 573. (b) Lopez, E.; Doepker, R. D. *Ibid.* **1978**, *82*, 753. (c) Dhingra, A. K.; Vorachek, J. H.; Koob, R. D. *Chem. Phys. Lett.* **1971**, *9*, 17. (d) Scala, A. A.; Ausloos, P. J. *J. Chem. Phys.* **1968**, *49*, 2282.

(3) (a) Dhingra, A. K.; Koob, R. D. *J. Phys. Chem.* **1970**, *74*, 4490. (b) Dees, K.; Koob, R. D. *Ibid.* **1973**, *77*, 759. (c) Pendleton, T. S.; Kaplan, M.; Doepker, R. D. *Ibid.* **1980**, *84*, 472.

(4) (a) Srinivasan, R.; Baum, T.; Epling, G. *J. Chem. Soc., Chem. Commun.* **1982**, 437. (b) Srinivasan, R.; Baum, T.; Ors, J. A. *J. Am. Chem. Soc.* **1978**, *100*, 7089. (c) Adam, W.; Oppenlander, T. *Photochem. Photobiol.* **1984**, *39*, 719. (d) Adam, W.; Oppenlander, T. *Tetrahedron Lett.* **1982**, 5391.

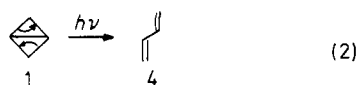
(5) (a) Srinivasan, R.; Ors, J. A.; Baum, T. *J. Org. Chem.* **1981**, *46*, 1950. (b) Srinivasan, R.; Ors, J. A. *Ibid.* **1979**, *44*, 3426.

that is implicated in the photolysis and thermolysis of 2,3-diazabicyclo[2.1.1]hex-2-ene^{7a} but is not thermally accessible from hydrocarbon **1**.^{7b} Cleavage of the bridge bond (C₁-C₃) of **1** followed by cleavage at C₁-C₂ of biradical **2** would give the carbene **3**, which would be expected to rearrange to butadiene **4** (eq 1).⁸



In fact, we find that the 185-nm photolysis⁹ of **1**¹⁰ in either cyclohexane¹¹ or heptane¹¹ gives butadiene as the major product along with a small amount of cyclobutene. The product ratio determined by carefully calibrated capillary gas chromatography was 10:1 in repeated runs. That both hydrocarbons were primary products was established by measurement of the ratio at only 5% conversion, conditions under which the secondary photochemistry of butadiene was insignificant.

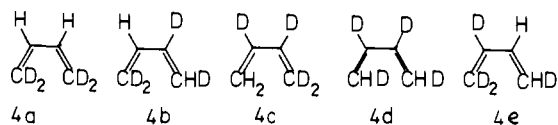
A plausible alternative to eq 1 is a mechanism analogous to the thermal rearrangement of bicyclobutanes^{8,12} and shown in eq 2, in which the C₁-C₃ bond remains intact but the side bonds



cleave to give **4** directly.⁸ Two independent isotope position labeling experiments now permit us to assign the relative contributions of the pathways of eq 1 and 2.

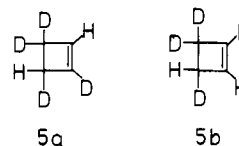
Photolysis of 2,2,4,4-tetradeuteriobicyclo[1.1.0]butane (**1-d₄**)¹³ in cyclohexane was followed by gas chromatographic (GC) isolation of the starting material and products, and the positions of the deuterium label were deduced by proton magnetic resonance (¹H NMR) spectroscopy. Recovered **1-d₄** showed no scrambling of the label away from the original sites; moreover, the labeling pattern in the products did not change between 3% and 50% conversion and was not dependent on wavelength (185 vs. 214 nm). The total deuterium content in the butadiene product was the same as that in the starting material (NMR analysis with pentane internal standard).

The ¹H NMR spectrum of product **4** showed an intensity ratio



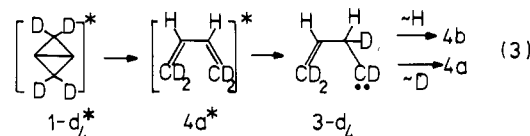
of the methine and methylene resonances of 2:1. Since **4a** is the only **4-d₄** isomer that could give a ratio of these absorptions greater than 1:1, its presence is immediately established. The intensity ratio could be achieved by any of four mixtures of products: (a) **4a**:**4b** = 1:2; (b) **4a**:**4c** = 2:1; (c) **4a**:**4d** = 2:1; (d) **4a**:**4e** = 1:2. However, only mixture a is compatible with the details of the

250-MHz ¹H NMR spectrum. The methine absorption appeared as a broad singlet at δ 6.35, whereas the methylene absorption appeared as two partially resolved triplets of approximately equal intensity at δ 5.06 ($J = 1.3$ Hz) and 5.16 ($J = 2.5$ Hz). That the methylene and methine protons were spin-spin coupled was established by decoupling of the latter, which caused increased resolution of the methylene triplets. The intensity ratio within each methylene triplet was very close to 1:1:1, as would be required by coupling to the methine deuterium of **4b**. Multiplication of the coupling constants by 6.5 (J_{HH}/J_{HD}) gives values in the range normally expected for cis and trans vicinal olefinic couplings. Integration of the two ¹H NMR absorptions in the cyclobutene product gave an intensity ratio of 1:1. Two structures **5a** and **5b**



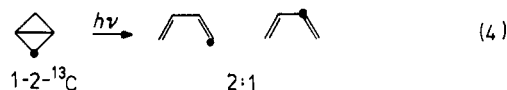
are compatible with this ratio but are not readily distinguishable by ¹HMR because both $J_{1,3}$ and $J_{1,4} \approx 0$. Structure **5a** is preferred on mechanistic grounds (see below).

The deuterium labeling distribution in the butadiene product is thus consistent with two competing mechanisms, with two-thirds of the product, **4b**, coming from the carbene pathway (eq 1, with nonstereospecific hydrogen shift) and one-third, **4a**, from a direct rearrangement (eq 2). However, at this stage the data permit one other interpretation, namely, that there is only one photochemical pathway, which produces excited **4a** (**4a***) by an adiabatic version (eq 3) of the direct mechanism (eq 2) and that **4a***



produces **4a** and **4b** via the carbene **3-d₄**. This would avoid the postulate of competing mechanisms. The preference for product **4b** over **4a** would then be interpreted as a kinetic isotope effect on the hydrogen rearrangement in carbene **3-d₄** ($k_H/k_D \approx 2$). Note also that if the carbenic center of **3-d₄** inserts into the CD₂ group, the cyclobutene product would be **5b** instead of **5a**.

The adiabatic alternative¹⁴ was eliminated by the preparation¹⁵ and photolysis of bicyclo[1.1.0]butane-2-¹³C. Equation 3 predicts exclusive location of ¹³C at the methylene position of **4** derived from 1-2-¹³C, but quantitative ¹³C NMR integration [0.05 M Cr(acac)₃, pulse delay, gated decoupling] of the **4**-¹³C from the photolysis gave a methylene to methine ¹³C ratio of 2:1 (eq 4, ● = ¹³C). The result quantitatively confirms the 2:1 competition



ratio favoring eq 1 over eq 2 for product **4**. The cyclobutene product **5** is most easily explained by a hydrogen shift in biradical **2**, although we cannot exclude other processes such as a concerted hydrogen shift and bridge-bond cleavage in **1** or a vinyl C-H insertion reaction of carbene **3**.

The existence of competing pathways of butadiene formation shown by the present experiments suggests the possibility that two energetically neighboring excited states of bicyclo[1.1.0]butane, one with a strong bridge bond and one with strong side bonds, may be accessible to VUV radiation. Preliminary ab initio the-

(6) Dervan, P. B.; Dougherty, D. A. In "Diradicals"; Borden, W. T., Ed.; Wiley: New York, 1982; pp 107-149.

(7) (a) Chang, M. H.; Jain, R.; Dougherty, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 4211. (b) Wiberg, K. B.; Lavanish, J. M. *Ibid.* **1966**, *88*, 5272.

(8) A formal variant of this mechanism would generate carbene **3** via initial side-bond cleavage to a cyclopropylcarbinyl biradical. The latter species also could give **4** by cleavage of the remaining side bond.

(9) Osram low-pressure, 10-W Hg arc. Solutions were 0.01 M. Control experiments with a Vycor filter showed that the 254-nm radiation was without effect on **1**.

(10) Prepared by the method of: Sieja, J. B. *J. Am. Chem. Soc.* **1971**, *93*, 130.

(11) Commercial spectrograde solvents. Further purification of solvents did not affect the product composition.

(12) Closs, G. L.; Pfeffer, P. E. *J. Am. Chem. Soc.* **1968**, *90*, 2452.

(13) Wiberg, K. B.; Peters, K. S. *Spectrochim. Acta, Part A* **1977**, *33A*, 261. We found that the use of a 3:1 (v/v) THF/D₂O mixture raised the yield for deuteration of 3-ethoxycyclobutanone from 1.4% to 25% of 97% **d₄** material.

(14) Photolysis of authentic **4a**, prepared by thermolysis of **1-d₄**, caused no scrambling of deuterium. However, this experiment is less decisive than that in the text because it is not clear that **4a** generated by eq 3 would have to be in the same excited state as that generated from **4**.

(15) From ¹³CO₂ following a sequence in the unlabeled series: (a) Mazur, R. H.; White, W. N.; Semenov, D. A.; Lee, C. C.; Silver, M. S.; Roberts, J. D. *J. Am. Chem. Soc.* **1959**, *81*, 4390. (b) Young, L. B.; Trahanovsky, W. S. *J. Org. Chem.* **1967**, *32*, 2349. (c) Reference 8.

