J. Am. Chem. Soc. **1983**, *105*, 2492-2493

Cumulene Photochemistry: Photorearrangement of 1,2-Cyclononadiene to a Bicyclic Cyclopropene

Thomas J. Stierman and Richard P. Johnson*

Department of Chemistry, Iowa State University
Ames, Iowa 50011

Received November 4, 1982

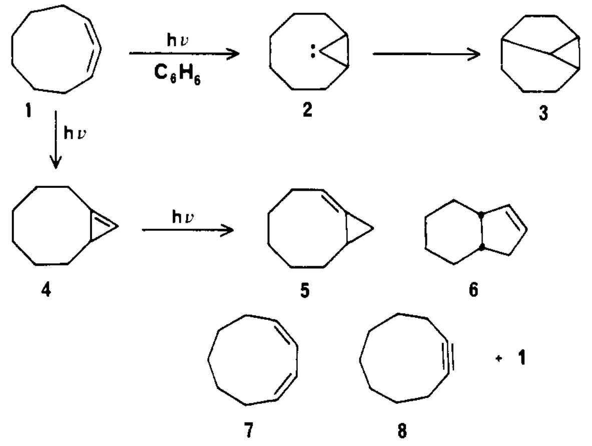
Allenes have been the subject of surprisingly little photochemistry.[1,2] Reactions reported to date often are triplet sensitized, and mechanisms usually are interpreted through radical or cyclopropylidene intermediates. A classic example is the benzene-sensitized transformation (Scheme I) of 1,2-cyclononadiene (**1**) to tricyclo[4.3.0.0^{2,9}]nonane (**3**), described some years ago by Ward and Karafiath.[2d] This was reported to occur in gas or solution phase, presumably through triplet cyclopropylidene **2**. Unsensitized irradiation of **1** yielded a mixture of C_9 isomers, one of which appeared to be **3**. Gilbert later reported a cycloadduct between **1** and benzene.[2h]

We have carefully investigated the singlet photochemistry of **1** and report here rearrangement to a stable bicyclic cyclopropene (**4**). Upon further irradiation, this cyclopropene yields products characteristic of ring opening to two isomeric vinylcarbenes. The cyclopropene is readily prepared through independent vinylcarbene generation.

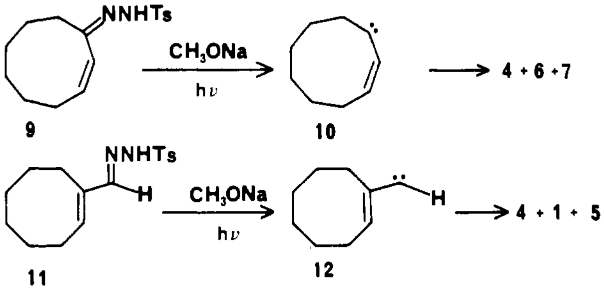
Vycor-filtered ($\lambda > 220$ nm) irradiation of dilute (5×10^{-3} M) pentane solutions of **1** did indeed produce a complex mixture (Scheme I), with **4–8** the major components.[3] Tricyclic **3** was not detected in the mixture.[4] Significantly, at low conversion (<2%) of **1**, **4** was the sole photoproduct seen by GC or 300-MHz NMR analysis. Analyses at different conversions and irradiation of pure samples showed that **4** was formed in a primary step and rearranged to **1** and **5–8** (ratio ca. 2.0:2.8:2.7:1.0:0.5) through secondary photoreactions.

Isomers **5–8** proved identical with authentic samples prepared through literature methods.[5] Cyclopropene **4** was readily isolated pure by preparative gas chromatography. Diimide reduction of **4** yielded *cis*-bicyclo[6.1.0]nonane, while brief treatment with potassium *tert*-butoxide in Me_2SO afforded isomer **5** in high yield.[5a] These experiments, spectral data,[6] and two independent syntheses (vide infra) securely characterize the structure of **4**. There are two previous reports of derivatives of **4**.[7]

Scheme I



Scheme II



At least three mechanisms are conceivable for the conversion of **1** → **4** in a singlet reaction: (a) 1,2-H shift to cyclononenylidene (**10**, Scheme II); (b) 1,2-carbon shift to isomeric vinylcarbene **12**; (c) concerted $[\sigma 2_a + \pi 2_a]$ electrocyclization. Cyclopropylidene has been suggested by Chapman as intermediate in the photoconversion of matrix-isolated allene to cyclopropene at 8 K;[2e] however, at 77 K, photogenerated cyclopropylidene yielded only allene.[2e] Steinmetz and co-workers have suggested hydrogen migration to vinylcarbenes in phenylallene photochemistry;[2g] we have observed similar reactions arising from phenyl and hydrogen migrations.[8] Extensive evidence exists for the intermediacy of vinylcarbenes in some cyclopropene photoreactions.[9]

To assess their potential intermediacy, vinylcarbenes **10** and **12** were generated photochemically as shown in Scheme II.[10] Major products[3b] from **10** (ca. 90% of volatile material) consisted of **4**, **6**, and **7** (ratio 1:1:1), while for **12**, isomers **4**, **1**, and **5** (ratio 5.6:1:1) were observed as products. Thus *both* vinylcarbenes **10** and **12** yield cyclopropene **4**, but in neither case is this the sole product. These results also are consistent with excited-state opening of **4** to **10** and **12** in a ratio of ca. 1:3 but do not explain the origin of **8** as a minor photoproduct of **4**. This may result from hydrogen transfer in the initially formed bisected vinylmethylene diradical.[11]

An alternative to discrete intermediates **10** or **12** is simultaneous 1,2-hydrogen or -carbon shift, with accompanying 1,3-bonding. Formally, this would consist of a $[\sigma 2_a + \pi 2_a]$ process, with a Hückel four-electron transition state.[12] Concerted reaction is

---

[1] Review: Huntsman, W. D. In "The Chemistry of Ketenes, Allenes and Related Compounds"; Patai, S., Ed., Wiley: New York, 1980; Part 2, pp 650–657.

[2] (a) Karan, H. I. *J. Org. Chem.* **1981**, *46*, 2186. (b) Drucker, C. S.; Toscano, V. G.; Weiss, R. G. *J. Am. Chem. Soc.* **1973**, *95*, 6482. (c) Rodriquez, O.; Morrison, H. *J. Chem. Soc., Chem. Commun.* **1971**, 679. (d) Ward, H. R.; Karafiath, E. *J. Am. Chem. Soc.* **1969**, *91*, 7475. (e) Chapman, O. L. *Pure Appl. Chem.* **1974**, *40*, 511. (f) Lankin, D. C.; Chihal, D. M.; Bhacca, N. S.; Griffin, G. W. *J. Am. Chem. Soc.* **1975**, *97*, 7133. (g) Steinmetz, M. G.; Mayes, R. T.; Yang, J.-C. *Ibid.* **1982**, *104*, 3518. (h) Berridge, J. C.; Forrester, J.; Foulger, B. E.; Gilbert, A. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2425. (i) Fujita, K.; Matsui, K.; Shono, T. *J. Am. Chem. Soc.* **1975**, *97*, 6256. (j) Klett, M. W.; Johnson, R. P. *Tetrahedron Lett.* **1983**, 1107.

[3] (a) Irradiations were conducted by using a 450-W medium-pressure Hg lamp. Analysis was by GC: 15% Carbowax 20M on Supelcoport, 10-ft glass column at 80 °C. NMR analysis (300-MHz) of product mixtures and preparative isolation of all components confirmed identities. (b) One additional product (ca. 10%) both from photolysis of **4** and **9** has been tentatively identified as a bicyclo[5.2.0]non-2-ene. Independent synthesis is in progress.

[4] Authentic **3** was prepared as previously described: Cardenas, C. G.; Shoulders, B. A.; Gardner, P. D. *J. Org. Chem.* **1967**, *32*, 1220.

[5] (a) **5**: Osborn, C. L.; Shields, T. C.; Shoulders, B. A.; Krause, J. F.; Cortez, H. V.; Gardner, P. D. *J. Am. Chem. Soc.* **1965**, *87*, 3158. (b) **6**: Crandall, J. K.; Watkins, R. J. *Tetrahedron Lett.* **1970**, 1251. (c) **7**: Vaidyanathaswamy, R.; Devaprabhakara, D. *Indian J. Chem.* **1975**, *13*, 873. (d) **8**: Meier, H.; Menzel, I. *Synthesis* **1971**, 215. (e) Shumate, K. M.; Fonken, G. J. *J. Am. Chem. Soc.* **1966**, *88*, 1073.

[6] Spectral data for **4** include the following: 300-MHz ^{1}H NMR ($CDCl_3$) δ 6.47 (1 H, s), 2.70 (1 H, m), 2.31 (1 H, m), 1.88 (1 H, m), 1.18–1.74 (10 H, m); ^{13}C NMR δ 126.6, 102.1, 33.2, 29.7, 26.7, 25.6, 25.5, 20.7, 16.7; UV (pentane) λ_{max} <185 nm; MS, *m/e* 121, 107, 93, 79, 67; high-resolution MS ($M^{+\cdot} - H$) 121.1012 (calculated 121.1017). The IR of **4** (neat) shows a strong band at 1780 cm^{-1}.

[7] Suda, M. *Tetrahedron Lett.* **1980**, *21*, 4355. Baird, M. S.; Nethercott, W. *Ibid.* **1983**, *24*, 605.

[8] Klett, M. W.; Johnson, R. P. *Tetrahedron Lett.*, submitted for publication.

[9] (a) Zimmerman, H. E.; Kreil, D. J. *J. Org. Chem.* **1982**, *47*, 2060. (b) Padwa, A. *Org. Photochem.* **1979**, *4*, 261 and references therein.

[10] Tosylhydrazones were prepared in standard fashion. Treatment with 4 equiv of CH_3ONa in THF followed by photolysis through Pyrex gave 40–60% isolated yields of volatile hydrocarbons in both cases. Product ratios were highly reproducible.

[11] Davis, J. H.; Goddard, W. A., III; Bergman, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 2427. Sevin, A.; Arnaud-Danon, L. *J. Org. Chem.* **1981**, *46*, 2346. Thermal interconversion of allene, cyclopropene, and propyne is well known: Hopf, H. F.; Priebe, H.; Walsh, R. *J. Am. Chem. Soc.* **1980**, *102*, 1210 and references therein.

0002-7863/83/1505-2492$01.50/0

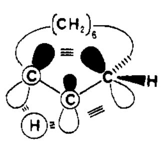
closely related to the stepwise **1** → [**10** or **12**] → **4** pathways and could be favored by constraints imposed by the carbocyclic ring.

If we assume that generation from tosylhydrazones and from photolysis of **4** define the chemistry of vinylcarbenes **10** and **12**, then it seems unlikely that either is a true intermediate in the **1** → **4** transformation. Thus, present results favor an effectively concerted mechanism. Experiments with isotopically labeled and optically active **1** should permit further mechanistic clarification.

Acknowledgment. The present work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by Ames Laboratory, U.S. Department of Energy, operated by Iowa State University under Contract W-7405-Eng-82, with the research support of the Director of Energy Research, Office of Basic Energy Science, WPAS-KD-01-03-01-2.

---

(12) Zimmerman, H. E. "Pericyclic Reactions"; Marchand, A. P., Lehr, R. E., Eds.; Academic Press: New York, 1977; Chapter 2, p 53, and references therein. The Hückel array for 1,2-H shift is depicted here:



Biosynthesis of Riboflavin. An Unusual Rearrangement in the Formation of 6,7-Dimethyl-8-ribityllumazine

Heinz G. Floss*

Department of Chemistry, Ohio State University
Columbus, Ohio 43210

Quang Le Van, Paul J. Keller, and Adelbert Bacher*

Lehrstuhl für Organische Chemie und Biochemie
Technische Universität München
D-8046 Garching, Federal Republic of Germany

Received January 3, 1983

In the course of our continuing studies[1] on the biosynthesis of riboflavin, we have encountered an apparently novel biochemical carbon skeletal rearrangement. Riboflavin (**3**, Scheme I) has been shown[2] to form by a disproportionation of two molecules of 6,7-dimethyl-8-ribityllumazine (**2**). The eight carbon atoms of the xylene ring of **3** thus originate from two biochemically identical four-carbon units, namely, carbons 1α, 6, 7, and 7α of **2**. The regiochemistry of this condensation is depicted in Scheme I through the use of an arbitrary numbering system (1*-4*) for the biosynthetically equivalent carbon atoms. The pyrimidinedione **1** is known to be the direct precursor of **2**, but the origin of the four carbon atoms that eventually form the pyrazine ring of **2** is not clear. Several authors have suggested[3] the involvement of a pentose; hence, formation of **2** would require the elimination of one carbon atom from the pentose precursor.

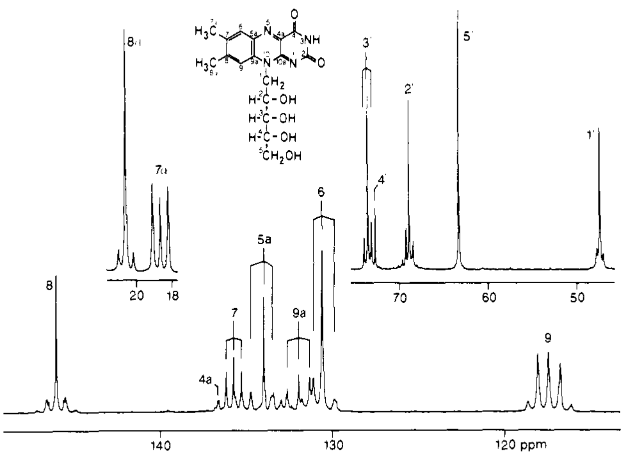
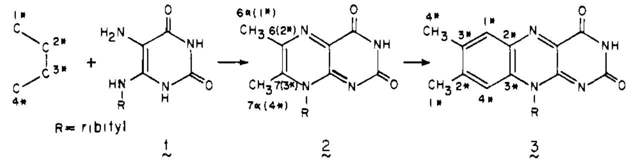


Figure 1. Selected regions from 50.3-MHz proton-decoupled ^{13}C NMR spectrum of riboflavin derived biosynthetically from [1,3-^{13}C$_2$]glycerol. Conditions: 60° pulse, repetition time 2 s, 11-KHz spectral width, 32K data points, solvent Me$_2$SO-d_6.

Scheme I



In earlier studies, we had investigated this proposal through incorporation of ^{13}C-labeled precursors into riboflavin followed by ^{13}C NMR spectroscopic analysis of the products. In such experiments, the ribityl side chain of **3** can serve as a probe for the labeling pattern of the pentose pool, since its origin from the ribose moiety of GTP is firmly established.[4] The results showed that position 1* is labeled by the same precursors as carbon 1′ in the side chain, whereas carbon 2* corresponds to C-2′ and 3* to C-3′ in their respective labeling patterns. However, position 4* is efficiently labeled from [6-^{13}C$_1$]glucose even though this precursor contributes its label almost exclusively to the 5′ carbon of the ribityl side chain.[1b] Furthermore, incorporation of [2-^{13}C$_1$]glycerol gave riboflavin that was highly labeled at C-4′ but not at position 4*,[1c] thus suggesting extrusion of C-4 of a pentose or its equivalent (e.g., C-2 of a triose) in the formation of **2**. In addition, a feeding experiment with [U-^{13}C$_6$]glucose had indicated the transfer of C-3* and C-4* as coupled pair of carbons from the same glucose molecule.[5] In summary, the available evidence suggested that the carbon atoms 4 and 6 of an individual hexose molecule can give rise to the directly connected carbons 3* and 4* of **2** and **3**. This apparent paradox can be explained by the assumption of an intramolecular skeletal rearrangement. The present paper reports proof for such a process.

[1,3-^{13}C$_2$]Glycerol (0.2 g, 90% ^{13}C, MSD Inc.) was fed to the flavinogenic fungus *Ashbya gossypii* (ATCC 10859), and the resulting riboflavin was isolated and purified as previously described.[1a,6] The ^{1}H-decoupled ^{13}C NMR spectrum of this material (Figure 1) was measured at 50.3 MHz on a Bruker WP-200 spectrometer.

It was expected on the basis of previous studies that the proffered glycerol would label the ribityl moiety at C-3′ and C-5′ due to the straightforward derivation of C-3′–C-5′ from a triose. Additionally, C-1′ and C-2′ should be labeled by the action of transketolase and oxidative decarboxylation of glucose, respec-

---

(1) (a) Bacher, A.; Le Van, Q.; Bühler, M.; Keller, P. J.; Eimicke, V.; Floss, H. G. *J. Am. Chem. Soc.* **1982**, *104*, 3754-3755. (b) Bacher, A.; Le Van, Q.; Bühler, M.; Keller, P. J.; Floss, H. G. In "Chemistry and Biology of Pteridines"; Blair, A., Ed.; Walter de Gruyter Verlag: Berlin, in press. (c) Manuscript in preparation.

(2) For reviews see: (a) Plaut, G. W. E.; Smith, C. M.; Alworth, W. L. *Ann. Rev. Biochem.* **1974**, *43*, 899-922. (b) Brown, G. M.; Williamson, J. M. *Adv. Enzymol.* **1982**, *53*, 345-381.

(3) (a) Alworth, W. L.; Dove, M. F.; Baker, H. N. *Biochemistry* **1977**, *16*, 526-531. (b) Bresler, S. E.; Perumov, D. A.; Chernik, T. P.; Glazunov, E. A. *Genetika* **1976**, *12*, 83-91. (c) Hollander, I. J., Braman, J. C.; Brown, G. M. *Biochim. Biophys. Res. Commun.* **1980**, *94*, 515-521. (d) Logvinenko, E. M.; Shavlovskii, G. M.; Zakal'skii A. E.; Zakhodylo, I. V. *Biokhim.* (*Moscow*) **1982**, *47*, 931-936.

(4) (a) Mailänder, B.; Bacher, A. *J. Biol. Chem.* **1976**, *251*, 3623-3628. (b) Burrows, R. B.; Brown, G. M. *J. Bacteriol.* **1978**, *136*, 657-667. (c) Logvinenko, E. M.; Shavlovskii, G. M.; Zakal'skii, A. E.; Senyuta, E. A. *Biokhim.* (*Moscow*) **1980**, *45*, 1284-1292.

(5) (a) Keller, P. J.; Le Van, Q.; Bacher, A.; Kozlowski, J. F.; Floss, H. G. *J. Am. Chem. Soc.*, in press. (b) Keller, P. J.; Le Van, Q.; Bacher, A.; Floss, H. G. *Tetrahedron*, in press.

(6) Bacher, A.; Mailänder, B. *J. Biol. Chem.* **1973**, *248*, 6227-6231.

0002-7863/83/1505-2493$01.50/0