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

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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 Me₂SO 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

(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.;

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 Crandall, J. K.; Watkins, R. J. Tetrahedron Lett. 1970, 1251. (c) 7: Vaid-yanathaswamy, 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.

(7) Suda, M. Tetrahedron Lett. 1980, 21, 4355. Baird, M. S.; Nethercott, W. Ibid. 1983, 24, 605.



Scheme II



At least three mechanisms are conceivable for the conversion of $1 \rightarrow 4$ 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

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⁽⁶⁾ Spectral data for 4 include the following: 300-MHz ¹H NMR (CDCl₃) δ (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); ¹³C NMR δ 126.6, 102.1, 33.2, 29.7, 26.7, 25.6, 25.5, 20.7, 16.7; UV (pentane) $\lambda_{max} < 185$ nm; MS, m/e 121, 107, 93, 79, 67; high-resolution MS (M⁺ - H) 121.1012 (calculated 121.1017). The IR of 4 (neat) shows a strong band at 1780 cm-

⁽⁸⁾ Klett, M. W.; Johnson, R. P. Tetrahedron Lett., submitted for publication

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⁽¹⁰⁾ Tosylhydrazones were prepared in standard fashion. Treatment with 4 equiv of CH₃ONa 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.

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 \rightarrow 4 transformation. Thus, present results favor an effectively concerted mechanism. Experiments with isotopically labeled and optically active 1 should permit further mechanistic clarification.

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(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

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In the course of our continuing studies¹ on the biosynthesis of riboflavin, we have encountered an apparently novel biochemical carbon skeletal rearrangement. Riboflavin (3, Scheme I) has been shown² to form by a disproportionation of two molecules of 6,7dimethyl-8-ribityllumazine (2). The eight carbon atoms of the xylene ring of 3 thus originate from two biochemically identical four-carbon units, namely, carbons $l\alpha$, 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 suggested³ 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 ¹³C 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_2SO-d_6 .



In earlier studies, we had investigated this proposal through incorporation of ¹³C-labeled precursors into riboflavin followed by ¹³C 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-13C6]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.

[1,3-13C2]Glycerol (0.2 g, 90% 13C, 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 ¹H-decoupled ¹³C 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-

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