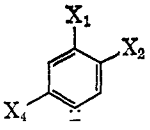
butoxide-*t*-butyl alcohol–dimethyl sulfoxide deiodination, which probably involves nucleophilic displacement on iodine as a key step,[5] redistribution according to Scheme II is believed to proceed faster than by Scheme III. Schemes involving attack by the 3-anion of 1,2,4-triiodobenzene or by **1b** or **7b** on X_4 in **2b** or **8b** are unlikely because the products of such steps would be highly energetic.

Our experiments do not rule out mechanisms involving 1,2 shifts of iodine atoms, *e.g.*, **7b** → **15**, but



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such shifts are disfavored because they cannot account for halogen transfer between rings.[1,2]

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J. F. Bunnett, D. J. McLennan
University of California
Santa Cruz, California 95060
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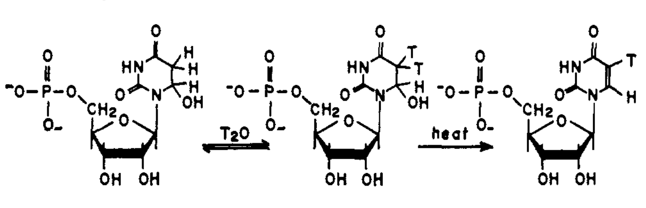
Synthesis of Tritiouridine 5′-Phosphate *via* the Photohydrate of Uridylic Acid

Sir:

During some nmr studies on the photohydrate of uridine 5′-phosphate (I) we observed that deuterium was incorporated into the pyrimidine ring. After the exchange was complete, the solution was heated to convert the photohydrate to deuteriouridine 5′-phosphate. The nmr spectrum[1] showed no signal at δ 6.50 ppm where the H-5 doublet is found in the uridine 5′-phosphate (U5′P) spectrum. The H-6 doublet at 8.63 ppm seen in the U5′P spectrum was replaced by a singlet in the deuterated compound. Thus, the deuterium is attached to the 5 position in deuterated U5′P.

These results suggested a simple method for detecting uridylate photohydrates in RNA by incorporation of tritium. The synthesis of tritiouridine 5′-phosphate (III) described in this communication establishes the feasibility of this scheme.



I II III

A mechanically stirred, aqueous solution of disodium uridine 5′-phosphate (6 μmol in 3.5 ml) was irradiated[2] at 254 nm in a stoppered 1-cm quartz spectrophotometer cell until the absorbance dropped to 0.15 (6 hr). The solution was evaporated to dryness under reduced pressure at room temperature.[3] The residue (invisible) was transferred to a 1.5-ml ampoule with three 50-μl portions of water. The solution was lyophilized and the residue taken up in 0.1 ml of tritiated water (3.6 μCi/μmol). The ampoule was sealed and allowed to stand for 17 hr at room temperature. The sealed ampoule was heated in a 70° water bath for 2.5 hr and cooled. The ampoule was opened at the tip and the condensation washed down the wall with several small portions (totaling 0.1 ml) of water. The solution was evaporated to dryness in a vacuum desiccator over P_2O_5 under reduced pressure (water pump). The residue was dissolved in 25 μl of H_2O and transferred to a 4.5 × 22.5 cm strip of Whatman 3 MM paper that had been washed with distilled water and air dried just before use. Electrophoresis was carried out at 1000 V for 2 hr at pH 3.5 (0.02 *M* ammonium citrate).

The electropherogram was scanned with a Nuclear Chicago Actigraph III (windowless). A small amount of radioactivity remained at the origin. A trace of activity was found in a minor uv-absorbing spot with a mobility 0.47 that of U5′P. The major activity was found in the U5′P spot. The U5′P spot was cut out and eluted with 2 ml of 0.1 *M* sodium phosphate buffer, pH 7.0 (3.8 μmol, 63% recovery).[4] A 0.2-ml aliquot was counted in Bray's solution[5] in a Nuclear Chicago Mark I scintillation spectrophotometer. The specific activity of the U5′P was 5.8×10^5 cpm/μmol. Since our counting efficiency was 22%, this corresponds to 1.2 μCi/μmol. After three recrystallizations from aqueous methanol in the presence of unlabeled U5′P (20 mg), the specific activity was 1.0 μCi/μmol. This demonstrates unequivocally that the tritium is bound to U5′P and is nonexchangeable. If the original exchange and reversal had been quantitative, the specific activity should have been 3.6 μCi/μmol. The reason for this discrepancy is not clear. However, the observed specific activity of 1 μCi/μmol is adequate to detect a single photohydrate in transfer RNA.

A more detailed account of the kinetics of the exchange and dehydration reactions as well as the application of this labeling technique to photochemical studies on transfer RNA will be reported subsequently.[5a]

Acknowledgments. The expert technical assistance of Mrs. Lelde V. Riekstins and Mrs. Irene Rosenberg

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(1) Nmr was measured with a Varian A-60A spectrophotometer using D_2O as a solvent. The spectra were calibrated externally with TMS in a capillary tube.

(2) Irradiation was performed with a low-pressure mercury lamp (Mineralight, 9 W) equipped with the low-wavelength filter (model SL 2537) and a piece of Vycor glass (2 mm thick) between the filter and the cell.

(3) A neutral, aqueous solution of the photohydrate I can be evaporated to dryness under reduced pressure at room temperature without appreciable conversion to III.

(4) Estimated from absorbance measurements. A large and variable blank makes this correction difficult. Therefore 63% represents the minimum recovery.

(5) G. A. Bray, *Anal. Biochem.*, 1, 279 (1960).

(5a) Note Added in Proof. It should be pointed out that the formation of 5-deuterio- (or tritio-) uridine 5′-phosphate constitutes strong evidence that the photohydrate of uridine 5′-phosphate has structure I. This is in agreement with recent chemical evidence of Miller and Cerutti on the structure of the uridine photohydrate.[6] In addition, we have studied the uridine 5′-phosphate photohydrate directly by nmr. A multiplet at δ 3.47 ppm disappears slowly in D_2O. Concurrently, another multiplet centered at δ 6.21 ppm changes to two single proton peaks located at δ 6.16 and 6.26 ppm, respectively. These latter two peaks are assigned to the H-6 protons in the two diastereoisomers of I. Therefore, the multiplet at δ 3.47 ppm is assigned to H-5. This provides *direct* evidence for assignment of structure I to the photohydrate of uridine 5′-phosphate. It does not rule out the possibility that the "hydrate" may not be a water addition product, but a phosphodiester formed by photoaddition of the 5′-phosphate to the 5,6-double bond.

(6) S. I. Miller and R. U. Cerutti, *Proc. Natl. Acad. Sci. U. S.*, **59**, 34 (1968).

during part of this work is gratefully acknowledged. This work was supported by grants from the U. S. Public Health Service (Grant No. 3 R01 GM07262-07S1 PC), the Health Research Council of the City of New York (Grant No. U-1530), and the American Cancer Society (Grant No. P-476).

[7] Career Research Scientist (I-200) of the Health Research Council of the City of New York.

Robert Warner Chambers[7]
Department of Biochemistry
New York University School of Medicine
New York, New York 10016

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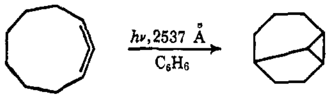
The Photolytic Conversion of an Allene to a Cyclopropylidene. The Photolysis of 1,2-Cyclononadiene[1]

Sir:

The ring opening of cyclopropylidenes to allenes is an efficient process. For example, the carbenoid species formed by the treatment of 9,9-dibromobicyclo[6.1.0]-nonane with methyllithium[2] gives 1,2-cyclononadiene in 81% yield.

The reverse of this process has been treated theoretically[3] but has not been observed experimentally. The first excited singlet and the lowest triplet states of allenes are both expected to have the substituents on the terminal carbon atoms of the allenic bond coplanar[4] which is the correct molecular geometry for closing to the cyclopropylidene. We have investigated the photolysis of 1,2-cyclononadiene, a compound in which the strain imposed by the ring should facilitate ring closure.

The benzene-sensitized photolysis of 1,2-cyclononadiene in vapor phase[5] at 2537 Å yields one major product, tricyclo[3.3.0.0^{2,9}]nonane (I). The structure of I was assigned on the basis of the identity of spectra and of chromatographic behavior with that of an independently synthesized sample.[6] The nmr spectrum[7] (CCl_4) consisted of four unresolved multiplets at τ 7.4, 8.2, 8.6, and 9.2. The ir spectrum showed an absorption band at 3045 cm^{-1}; the mass spectrum[7] had a parent peak at *m/e* 122 and a fragmentation pattern similar to that of *cis*-hydrindan, but displaced by two mass units. The synthetic product and the photoproduct had identical glpc retention times on three columns.[8]



I

Compound I did not hydrogenate over 10% palladium on carbon in ethanol but under more drastic conditions (Pt, HOAc, $HClO_4$) yielded two products (*m/e* 124). One of these was identified as *cis*-hydrindan by glpc retention times and mass spectra.

The most reasonable pathway for the formation of I is the closing of the allene to the cyclopropylidene and subsequent transannular insertion of this species into the C–H bond. Such transannular insertions are known to occur in medium-ring carbenoid reactions.[9] At very low conversions (0.1%), a plot of % conversion *vs.* time gives a straight line, indicating that I is a primary product. At higher conversions (~10%) polymer formation is noticeable. The quantum yield for the formation of I was 0.17, based on a benzene–*cis*-2-butene actinometer.[10]

The benzene-photosensitized isomerization of olefins is generally assumed[11] to proceed by energy transfer from the first triplet state of benzene to give the antiplanar triplet of the olefin. If the allene photosensitization occurs by this path, it must be a nonvertical excitation, since transfer from benzene $^3B_{1u}$ (85 kcal)[12] to give planar triplet allene (~100 kcal)[4] is endothermic and therefore unlikely. Energy transfer from the $^1B_{2u}$ or the $^3E_{1u}$ states[13] seems improbable because of the short lifetimes of these states and the relatively high efficiency of the observed photosensitization. Since only 63% of the light absorbed by benzene produces the triplet state,[14] and if the sole energy transfer mode is triplet–triplet, then the actual conversion of excited allene to I is 28%.

We conclude, then, that most probably the triplet allene is either formed in its planar configuration[15] or is quickly deactivated to that state by collision. This molecular arrangement is suitable for closing to the cyclopropylidene, but Borden[3] has predicted on the basis of orbital symmetry considerations that this conversion should not occur in either a concerted conrotatory, disrotatory, or nonrotatory fashion. Closing from the first excited singlet allene can be excluded by similar arguments.

If the triplet allene is prevented from closing to the cyclopropylidene, the most reasonable remaining path for its disappearance is a radiationless transition to a planar, and therefore highly vibrationally excited, ground electronic state. This species, at the instant of its formation, is also suitably arranged for closure to the cyclopropylidene, and this closure appears to be symmetry allowed by a nonrotatory process. This crossing from one energy surface to another in "multi-

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[1] This research was supported by the National Aeronautics and Space Administration.

[2] W. R. Moore and H. R. Ward, *J. Org. Chem.*, **27**, 4179 (1962).

[3] W. T. Borden, *Tetrahedron Letters*, 447 (1967).

[4] W. T. Borden, *J. Chem. Phys.*, **45**, 2512 (1966).

[5] Benzene/allene = 0.5, total pressure ~9 mm.

[6] C. G. Cardenas, B. A. Shoulders, and P. D. Gardner, *J. Org. Chem.*, **32**, 1220 (1967).

[7] The nmr and mass spectrometers were purchased with funds supplied by the National Science Foundation.

[8] Retention times relative to 1,2-cyclononadiene: 10% Carbowax 20M (80°), 0.7; 15% TCEP (100°), 0.68; and 10% QF-1 (50°), 0.82.

[9] A. C. Cope and S. S. Hecht, *J. Am. Chem. Soc.*, **89**, 6920 (1967).

[10] M. Tanaka, M. Kato, and C. Sato, *Bull. Chem. Soc. Japan*, **39**, 1423 (1966).

[11] R. B. Cundall and P. A. Griffiths, *Trans. Faraday Soc.*, **61**, 1968 (1965).

[12] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1960, p 332.

[13] The idea of energy transfer from the $^3E_{1u}$ state is attractive because a vertical excitation to give the antiplanar triplet allene is both energy and spin allowed. However, since the $^3E_{1u}$ and $^3B_{1u}$ states are separated by only ~15 kcal (G. Herzberg, "Electronic Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1966, p 350), the lifetime of the $^3E_{1u}$ state is not expected, *a priori*, to allow time for efficient energy transfer. This possibility cannot be eliminated, particularly since a suggestion of just such an energy transfer from the second triplet of anthracene has appeared: R. S. H. Liu and J. R. Edman, *J. Am. Chem. Soc.*, **90**, 213 (1968).

[14] W. A. Noyes, Jr., and D. A. Harter, *J. Chem. Phys.*, **46**, 674 (1967).

[15] Calculations indicate that the excited allene is slightly bent (165°) out of planarity, but that the minimum is shallow: R. Hoffman, *Tetrahedron*, **22**, 521 (1966).