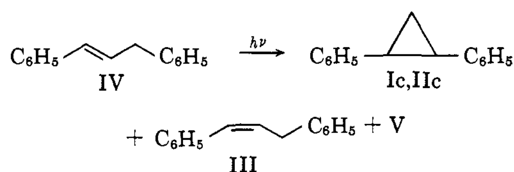
The olefins III and IV may form from VII by an unusual but not unprecedented 1,2-hydrogen migration. Pitts and Norman[11] invoked such a mechanism to explain the vapor-phase photoconversion of acetylcyclopropane to 2-penten-4-one. There is reason to doubt that the *cis* isomer III has been isolated before.[12] We obtained it as an oil, $\lambda_{max}^{2,2,4\text{-trimethylpentane}}$ 243 mμ (ϵ 13,700), ν_{max}^{neat} (cm.$^{-1}$) 915 w, 765 m, 735 m, and 700 s. The structure of III was established by its reduction to 1,3-diphenylpropane and confirmed by n.m.r. and mass spectral analysis. Independent synthesis of III was achieved by photoisomerization of IV (*vide infra*) and by pyrolysis of 2-acetoxy-1,3-diphenylpropane at 500°.

The indan probably arose by cyclization of VII followed by rearomatization and presumably is the precursor of the indene VI.[13]

When IV was exposed to 2537 Å. light[8] for 17 hr. in benzene (0.1 *M*) at 40° the products included both *cis*- and *trans*-1,2-diphenylcyclopropane (each in 6% yield) in addition to III (5%) and the indan V (5%).[5b]



This remarkable, unsensitized[14] photocyclization of an olefin to a cyclopropane *in solution*, in which *hydrogen or phenyl migration is required*, appears to be without analogy.

Mercury ($^3P_1$) photosensitized cyclization with *hydrogen migration* has been observed in the vapor phase in the conversions of 1-butene to methylcyclopropane,[15a] 1,5-hexadiene to allylcyclopropane,[15b] and 1,5-cyclooctadiene to bicyclo[5.1.0]octene-3.[15c] On the other hand the photocyclizations of dienes and trienes to cyclopropane derivatives in the condensed phase reported previously[16] can be explained by mechanisms not involving hydrogen migration. In one case,[16a] the photoisomerization of 1,3,6-cyclooctatriene to 3,4-homotropilidene, hydrogen migration was definitely excluded by deuterium labeling.

The cyclic irradiation products of the olefin IV could have arisen from VIII produced in turn by a 1,2-phenyl migration.[17] The absence of branched chain products suggests that this is not the case. It appears that the reaction proceeds primarily *via* the more stable intermediate VII, generated from the π–π^* excited state of IV by a 1,2-hydrogen shift. At this time we cannot completely exclude a photochemical chain mechanism, perhaps initiated by an adventitious radical species.

Acknowledgments. We are indebted to the Army Research Office (Durham) and to the Petroleum Research Fund (Grant No. 1090) for support of this work.

G. W. Griffin, J. Covell
Department of Chemistry, Tulane University
New Orleans, Louisiana
R. C. Petterson
Department of Chemistry, Loyola University, New Orleans
New Orleans, Louisiana
R. M. Dodson, G. Klose
Department of Chemistry, University of Minnesota
Minneapolis, Minnesota

Received October 3, 1964

(11) J. N. Pitts and I. Norman, *J. Am. Chem. Soc.*, **76**, 4815 (1954).

(12) G. H. Beaven and E. A. Johnson, *J. Chem. Soc.*, 658 (1957).

(13) Authentic samples of V and VI were made by the method of W. E. Parham and C. D. Wright, *J. Org. Chem.*, 22, 1473 (1957).

(14) Benzene may act as a sensitizer, but the same products were produced in cyclohexane.

(15) (a) R. J. Cvetanović and L. C. Doyle, *J. Chem. Phys.*, **37**, 543 (1962); (b) R. Srinivasan, *J. Phys. Chem.*, **67**, 1367 (1963); (c) R. Srinivasan, *J. Am. Chem. Soc.*, **86**, 3318 (1964).

(16) (a) W. R. Roth and B. Peltzer, *Angew. Chem.*, **76**, 378 (1964); (b) G. R. Evanega, W. Bergmann, and J. English, Jr., *J. Org. Chem.*, 27, 13 (1962); G. R. Evanega, Ph.D. Dissertation, Yale University, New Haven Conn., 1960; H. Prinzbach and H. Hagemann, *Angew. Chem.*, **76**, 600 (1964); W. G. Dauben and F. G. Willey, *Tetrahedron Letters*, **No.** 20, 893 (1962); R. Srinivasan, *J. Am. Chem. Soc.*, **85**, 4045 (1963).

(17) Irradiation of 1,1,3,3-tetraphenylpropene affords *trans*-1,1,2,3-tetraphenylcyclopropane, conclusively demonstrating that phenyl migration can accompany cyclization in a π–π^* system. A related cyclization with phenyl migration has been observed independently by D. W. Boykin, Jr., and R. E. Lutz (personal communication) with 1,1,3-triphenyl-3-benzoylpropene.

Enzymatic Stereospecificity in the Conversion of Oleic Acid to 10-Hydroxystearic Acid[1]

Sir:

The microbiological conversion of oleic acid (I) to 10-hydroxystearic acid[2] provides a unique model for the study of the stereochemistry of enzymatic reactions at an isolated double bond in an acyclic compound. In the course of a previous investigation we found that the 10-hydroxystearate produced by the action of a *Pseudomonas* species on oleic acid is optically active[3,4] and has the D-configuration.[4] This finding raised two additional questions. First, is a hydrogen atom from the solvent incorporated into the hydroxystearate during its enzymatic formation from oleate, and second, if this is the case, is the incorporation of the hydrogen atom also stereospecific? Accordingly the organism was incubated with oleic acid in a medium enriched with deuterium oxide (99.8 atom % excess deuterium). Methyl 10-hydroxystearate (II; m.p. 55.5–56.0°; λ 4.70 μ (C–D stretch)), isolated and purified as previously described,[4] contained 99% monodeuterated molecules. Location of the deuterium on C-9 was established by a combination of chemical and mass spectrometric studies. A major peak in the spectrum of methyl 10-hydroxystearate is at *m/e* 201, representing the fragment $HO\text{–}C^+H(CH_2)_8COOCH_3$.[5] In the spectrum of the deuterated sample this peak occurs at *m/e* 202, indicating that the deuterium is located on one of the carbon atoms from C-2 to C-10. Another prominent peak is that at *m/e* 172 which has been assigned[5] to $^+(CH_2)_8COOCH_3$ plus a hydrogen atom. In the spectrum of the deuterated sample this peak occurs at *m/e* 173, indicating that the deuterium is on one of the carbon atoms from C-2 to C-9.[6] Moreover, since the

(1) Supported by a grant (HE 09501) from the United States Public Health Service.

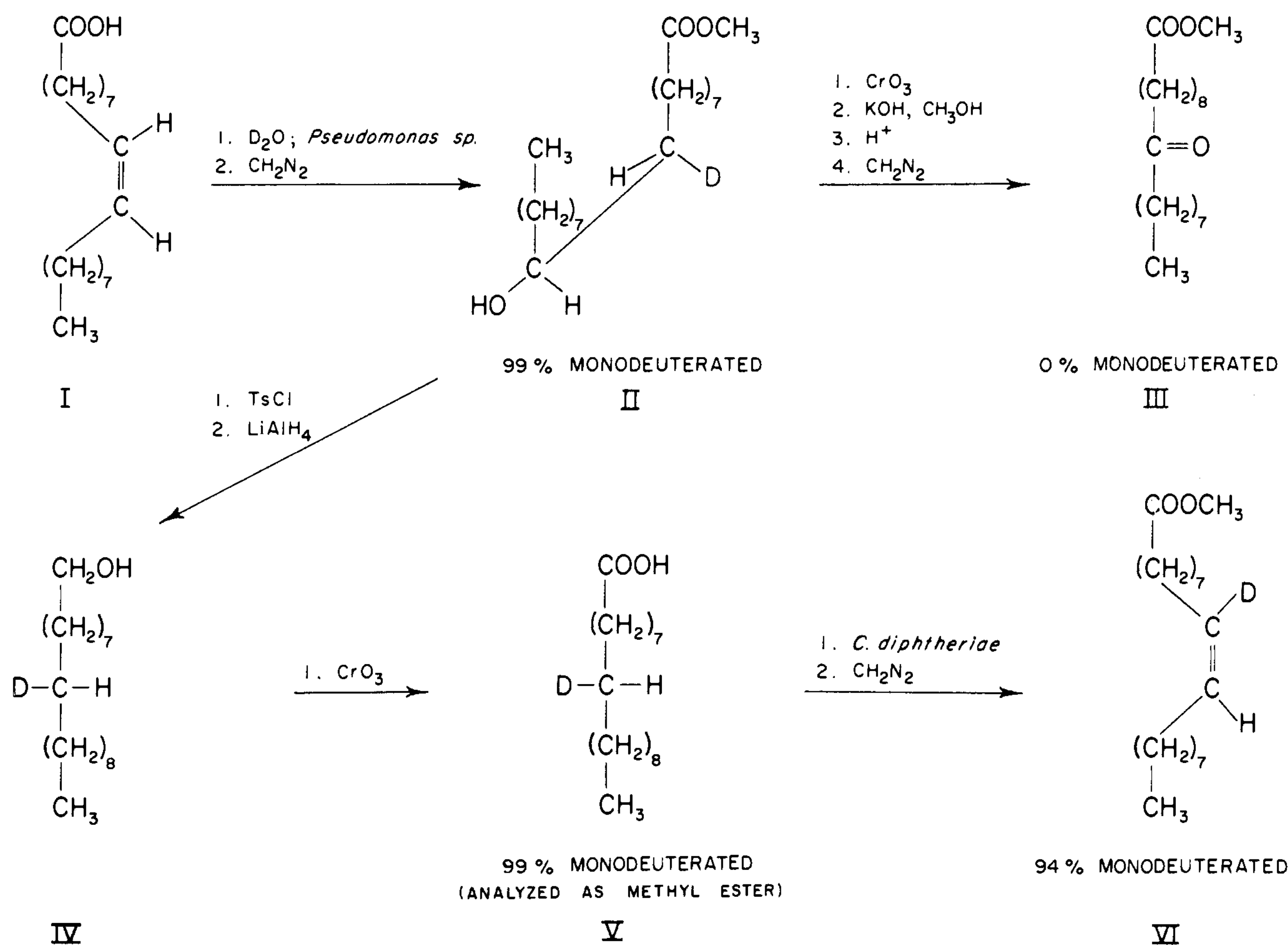
(2) L. L. Wallen, R. G. Benedict, and R. W. Jackson, *Arch. Biochem. Biophys.*, **99**, 249 (1962). We are indebted to Dr. Wallen for a gift of a culture of this organism.

(3) G. J. Schroepfer, Jr., and K. Bloch, *J. Am. Chem. Soc.*, **85**, 3310 (1963).

(4) G. J. Schroepfer, Jr., and K. Bloch, *J. Biol. Chem.*, 240, 54 (1965).

(5) R. Ryhage and E. Stenhagen, *Arkiv Kemi*, **15**, 545 (1960).

(6) Since the origin of the "extra" hydrogen atom in this fragment has not been established, there remains the extremely remote possibility that the deuterium was located on C-10 of the hydroxystearate and that



peak at m/e 143 representing $^{+}(CH_2)_6COOCH_3$[5] is not shifted in the spectrum of the deuterated sample, the deuterium is not on carbon atoms 2 through 7. Localization of the deuterium to carbon atom 9, rather than 8, was established in the following manner: Chromic acid oxidation[7] of the monodeuterated methyl 10-hydroxystearate yielded the 10-keto ester. To remove enolizable deuterium (C-9) the methyl ester was heated with methanolic KOH. Virtually complete loss of deuterium was indicated by the lack of absorption at 4.70 μ in the infrared spectra of 10-ketostearic acid (m.p. 81.0–81.5°) and of methyl 10-ketostearate (III; m.p. 44°) and by mass spectral analysis of III.

the "extra" hydrogen atom had its exclusive origin from this position. Definitive evidence that the deuterium was not on C-10 of the hydroxystearate was obtained by analysis of the mass spectrum of the monodeuterated methyl stearate (V). The peak at m/e 127 in the spectrum of methyl stearate has been assigned to the fragment $CH_3(CH_2)_8^+$, representing carbon atoms 10 through 18: R. Ryhage and E. Stenhagen, *J. Lipid Res.*, 1, 361 (1960). This peak was not shifted in the spectrum of the monodeuterated methyl stearate. Moreover, the results obtained in the studies of the microbiological conversion of the monodeuterated stearic acid to oleic acid are incompatible with location of the deuterium on C-10. This statement arises from the following considerations: Deuterium at C-10 of 10(D)-hydroxystearate would have to be in the L-configuration. Hydrogenolysis of the tosylate of 10(D)-hydroxy-10(L)-$^2H_1$-stearate with lithium aluminum hydride would yield 10(D)-$^2H_1$-stearic acid[4] (after oxidation of the resulting octadecanol). Since the enzymatic desaturation reaction involves stereospecific removal of the 10(D)-hydrogen,[4] the observed complete retention of deuterium on conversion of stearate to oleate (*vide infra*) is incompatible with location of the deuterium in the D-configuration of stearate (or the L-configuration of 10(D)-hydroxystearate). Therefore, the deuterium was not located at C-10.

(7) J. Ross, A. I. Gebhardt, and J. F. Gerecht, *J. Am. Chem. Soc.*, 71, 282 (1949).

The absolute configuration of the deuterium at C-9 was determined in the following manner. Hydrogenolysis of the tosylate of II with lithium aluminum hydride yielded 9-$^2H_1$-octadecanol (IV; m.p. 57.5–58.0°). Chromic acid oxidation of IV yielded 9-$^2H_1$-stearic acid (V; 99% monodeuterated; m.p. 68–69°). The deuterium-labeled stearic acid was incubated with a growing culture of *Corynebacterium diphtheriae*, a source of an enzyme which stereospecifically removes hydrogen in the D-configuration from C-9 upon conversion of stearic acid to oleic acid.[4] The methyl oleate (VI) isolated from the incubation contained 94% monodeuterated species (corrected for dilution with endogenous oleate of the bacterium), indicating that the configuration of the deuterium at C-9 of stearate was L. Since the asymmetry at C-9 is not affected by hydrogenolysis of the tosylate of the 10-hydroxystearate, it follows that the deuterium at C-9 of the 10-hydroxystearate is also of the L-configuration.

The enzymatic formation of 10-hydroxystearic acid from oleic acid is characterized by notable stereospecificity. The absolute configuration of the hydroxyl function at C-10 is D. During the course of the reaction solvent hydrogen is introduced at C-9 in the L-configuration.

George J. Schroepfer, Jr.
Division of Biochemistry
Department of Chemistry and Chemical Engineering
University of Illinois, Urbana, Illinois
Received January 15, 1965