$CH{=}C(CH_3)CH_2$- and ring -CH_3; 8.46 (32) m, -$CH_2CH{=}C(CH_3)CH_2$-.

The methoxy groups in coenzyme Q_{10} readily undergo alcoholysis in basic media.[5,6] The two methoxy groups in coenzyme Q_{10} appear to have comparable reactivity in such displacements since the monoethoxy homolog was shown to be a mixture of the two possible isomers.[5] It appeared that ammonolysis of coenzyme Q_{10} to give synthetic rhodoquinone was possible. This was accomplished by treating coenzyme Q_{10} with ammonium hydroxide in a solvent of diethyl ether–ethanol (1:1). The reaction gave a mixture of several unidentified products in addition to a purple quinone, m.p. 39–45°, which gave the same R_f values as natural rhodoquinone on alumina (0.37) and silica gel G (0.33) thin layer plates in 40% ether in *n*-hexane and in reverse-phase paper chromatography on silicon-impregnated paper (0.75) in a solvent of water–1-propanol (1:4). The paper chromatographic comparison of synthetic and natural rhodoquinone, which was carried out under conditions used to distinguish side-chain lengths,[7] in conjunction with the nuclear magnetic resonance spectrum of natural rhodoquinone (showing ten vinyl protons), suggests that the natural product contains a side chain of ten isoprene units. Comparison of the melting points of the synthetic and natural rhodoquinone (39–45° *vs.* 69–70°) suggests that the synthetic material is a mixture of the two isomeric aminoquinones and that rhodoquinone is formed enzymatically within the bacteria rather than artifactually by the ammonium ion in the growth medium. The infrared, ultraviolet, and nuclear magnetic resonance spectra of synthetic and natural rhodoquinone are indistinguishable.

These data, in conjunction with the observation by Rudney[8] that coenzyme Q_{10} is a biosynthetic intermediate to rhodoquinone in *R. rubrum*, show that the structure of natural rhodoquinone is either 2-amino-3-methoxy- or 2-methoxy-3-amino-5-methyl-6-[3′-methyl-2′-butenylenakis-(3′-methyl-2′-butenylene)]-1,4-benzoquinone.

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(5) B. O. Linn, N. R. Trenner, B. H. Arison, R. G. Weston, C. H. Shunk, and K. Folkers, *J. Am. Chem. Soc.*, **82**, 1647 (1960).

(6) C. H. Shunk, D. E. Wolf, J. F. McPherson, B. O. Linn, and K. Folkers, *ibid.*, **82**, 5914 (1960).

(7) R. L. Lester and T. Ramasarma, *J. Biol. Chem.*, **234**, 672 (1959).

(8) H. Rudney and W. Parson, *Proc. Natl. Acad. Sci. U. S.*, in press.

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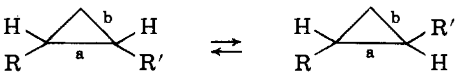
Photoisomerization of Cyclopropane Derivatives. Photointerconversion of Propenes and Cyclopropanes

Sir:

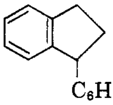
Since our initial discovery that *cis*- and *trans*-1,2-dibenzoylcyclopropane (Ia, IIa) undergo reversible photoisomerization,[1] we have extended the study to the *cis* and *trans* isomers of 1-benzoyl-2-phenylcyclopropane (Ib, IIb) and 1,2-diphenylcyclopropane (Ic, IIc). In view of the current interest in such transformations[2,3] we present a further report.

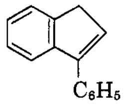


Ia, $R = R' = C_6H_5CO$ II
b, $R = C_6H_5CO$, $R' = C_6H_5$
c, $R = R' = C_6H_5$

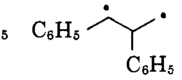
Irradiation of a benzene solution of IIb[4] resulted in partial conversion to the previously unreported *cis* isomer Ib, m.p. 69.5–71° (cyclohexane); λ_{max}^{hexane} 240 mμ (ϵ 14,100); $\nu_{max}^{Nujol\ mull}$ (cm.$^{-1}$) 764 s, 748 w, 721 s, 700 s, 694 s, 681 s, and 648 m. A solution of IIb and Ib (0.026 and 0.025 *M*, respectively, in benzene) reached an apparent photostationary state (IIb:Ib = 1.2, determined by gas chromatography on column 1 at 210°[5a]) after 6 hr.[6] All components were found to be stable under the conditions of analysis.

Photointerconversion of Ic and IIc could also be effected by direct irradiation, but the conditions had to be altered and side reactions became significant. Irradiation of 0.1 *M* benzene or cyclohexane solutions of *cis*- or *trans*-1,2-diphenylcyclopropane[7] in quartz vessels with 2537 Å. light[8] at 40° induced photoisomerization. The ratio IIc:Ic was approximately 0.65, determined after brief irradiation of mixtures approaching this composition. The products, after prolonged irradiation (8.5 hr.) of IIc in benzene, were Ic (22%),[5b] IIc (20%), III (7%), IV (16%), V (7%), and VI (trace). All were isolated by gas chromatography (column 3,[5a] 180°) and identified by their infrared spectra and retention volumes. A trace of 1,3-diphenylpropane could have escaped detection since its retention time and infrared spectrum resembled those of V.


V


VI


VII


VIII

The isomerization and the formation of compounds III–VI may be rationalized on the assumption that bond a in Ic or IIc cleaves to form a species resembling a diradical, represented here by VII.[9] Scisson of bond b to give the much less stable VIII apparently does not occur as no trace of *cis*- or *trans*-1,2-diphenylpropene or 1,2-diphenylpropane could be detected.[10]

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(1) G. W. Griffin, E. J. O'Connell, and H. A. Hammond, *J. Am. Chem. Soc.*, **85**, 1001 (1963). The ratio of IIa to Ia at equilibrium has since been found to be 2.5. This photoisomerization was quenched efficiently by piperylene, naphthalene, and benzophenone, suggesting that a triplet mechanism is operative.

(2) R. C. Cookson, M. J. Nye, and G. Subrahmanyam, *Proc. Chem. Soc.*, 144 (1964).

(3) G. S. Hammond, P. Wyatt, C. D. DeBoer, and N. J. Turro, *J. Am. Chem. Soc.*, **86**, 2532 (1964).

(4) R. J. Mohrbacher and N. H. Cromwell, *ibid.*, **79**, 401 (1957). A General Electric 275-w. cosmetic sunlamp was used. Satisfactory elemental analyses have been obtained for all new compounds described.

(5) (a) Gas chromatographic columns: (1) 305 × 0.4 cm. i.d., copper, packed with 30% SE-30 on Chromosorb W; (2) 157 × 0.6 cm. i.d., glass containing 30% silicone gum SE-30 on 60/80 mesh Chromosorb P; (3) 213 × 1 cm. i.d. version of (2). (b) Yields were determined by gas chromatography on column 2 at 175° using an internal standard.

(6) The ratio was not noticeably affected by further irradiation (6 hr.); however, small amounts of at least two by-products were formed, and these may act as selective sensitizers or quenchers. Thus we cannot be certain of the accuracy of this equilibrium measurement.

(7) R. M. Dodson and G. Klose, *Chem. Ind.* (London) 450 (1963).

(8) A Rayonet Chamber Reactor (Southern New England Ultraviolet Co., Middletown, Conn.) equipped with low-pressure mercury lamps was employed.

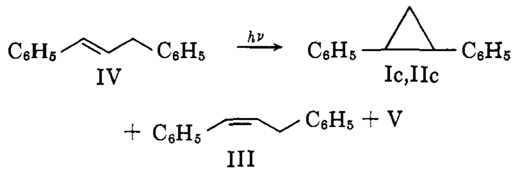
(9) The thermal equilibration of Ic and IIc has just been described by L. B. Rodewald and C. H. DePuy, *Tetrahedron Letters*, **No. 40**, 2951 (1964). The olefins III and IV were conspicuously absent from the products, which indicates that the intermediates in the photo and thermal reactions differ significantly.

(10) Authentic samples of these compounds were prepared for comparison.

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), $\nu_{\max}^{\text{neat}}$ (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.

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[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

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[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