The mass spectrum of 2,6-diacetamido-2,6-dideoxy-L-idose diethyl dithioacetal[7] (VII) can be recognized as that of a 2-acetamido compound by the fragments involving the loss of a molecule of acetamide. A peak at *m/e* 177 shows it is not a 3-acetamido compound. Peaks at *m/e* 132, 102, and 72 are characteristic of the terminal acetamido function. A molecular ion peak and peaks at *m/e* 135 and M − 135 are present.

The mass spectrum of 3,6-diacetamido-3,6-dideoxy-D-altrose diethyl dithioacetal (VIII)[15] is recognized as that of a diethyl dithioacetal by the peak at *m/e* 135, and as that of a 3-acetamido compound by the peak at *m/e* 218, the small molecular ion peak of intensity 0.02% of the base peak, and the peak at M − H_2O. Fragments 132, 102, and 72 are characteristic of the 6-acetamido-6-deoxy function.

A detailed study of these amino sugars as well as 4-amino-, 5-amino-, and diaminoaldoses, by mass spectrometry, will be the subject of a forthcoming publication.

(15) M. L. Wolfrom, D. Horton, and Y.-L. Hung, Abstracts, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964, p. 3D. The stereochemistry was communicated privately by Dr. D. Horton.

(16) The support of Grant GM 12328-01 from the National Institutes of Health, U. S. Public Health Service, is acknowledged.

Don C. DeJongh,[16] Stephen Hanessian
Wayne State University, Department of Chemistry
Detroit, Michigan 48202
Research Laboratories, Parke, Davis and Company
Ann Arbor, Michigan 48106
Received January 6, 1965

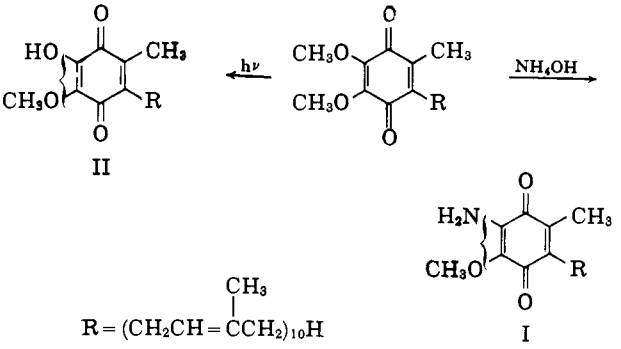
Coenzyme Q. LXII. Structure and Synthesis of Rhodoquinone, a Natural Aminoquinone of the Coenzyme Q Group[1]

Sir:

Rhodoquinone (I), a naturally occurring quinone from *Rhodospirillum rubrum*, and *Athiorhodaceae*, has now been shown by structural and synthetic studies to be an aminoquinone belonging to the coenzyme Q group. The apparent enzymic formation of rhodoquinone from coenzyme Q_{10} may indicate that the aminoquinone has a photosynthetic function.

It was previously reported[2] that the structure of rhodoquinone is a hydroxyquinone (II), based on C–H analysis, molecular weight measurement, micro hydrogenation data, and ultraviolet and infrared spectra, with particular significance attached to absorptions at 3495 and 3370 cm.$^{-1}$ in the infrared spectrum. The assignment of the hydroxyquinone function was based essentially upon the above two bands in the infrared spectrum; however, primary amines also show two bands in this region.[3]

That rhodoquinone is not a hydroxyquinone was apparent from its ultraviolet and visible spectra in neutral and basic ethanol solutions. Acidic hydroxyl groups of hydroxyquinones react with base to give resonance-stabilized anions which absorb at longer wave length, but rhodoquinone shows no change in the ultraviolet or visible regions of the absorption spectrum in ethanolic potassium hydroxide as compared to ethanol (λ_{max} 283 mμ ($E^{1\%}_{1cm}$ 121), 512 mμ ($E^{1\%}_{1cm}$ 14)). For comparison, the hydroxyquinone from coenzyme Q_{10} (II) was newly prepared by the technique used by Imada[4] for converting coenzyme Q_7 to its O-demethylated analog. The spectral and chromatographic properties of II are quite different from those of rhodoquinone; a marked change in the visible region of the ultraviolet absorption spectrum of II was observed when the spectrum of an ethanolic solution was compared to that of an ethanolic potassium hydroxide solution (λ_{max} 277 mμ ($E^{1\%}_{1cm}$ 44), 428 mμ ($E^{1\%}_{1cm}$ 5.7), as compared to λ_{max} 281 mμ ($E^{1\%}_{1cm}$ 28), 536 mμ ($E^{1\%}_{1cm}$ 15.4)). The infrared spectrum of a carbon tetrachloride solution of II showed only one peak in the O–H stretching region at 3350 cm.$^{-1}$, and the nuclear magnetic resonance spectrum is definitive for the hydroxyquinone structure II; τ 4.96 (10) m, CH=; 6.04 (3) s, $-OCH_3$; 6.88 (2) d, ring $-CH_2-$; 8.07 (38) m, $-CH_2CH=C(CH_3)CH_2-$ and ring $-CH_3$; 8.45 (32) m, $-CH_2CH=C(CH_3)CH_2-$.



The R_f values (t.l.c.) of the hydroxyquinone II and rhodoquinone on silica gel G plates in 40% ether in *n*-hexane are 0.1 and 0.33, respectively. Nitrogen determinations in natural and synthetic rhodoquinone gave high values averaging about 2.7%; all spectral data were consistent with the presence of one methoxyl and one amino group.

The nuclear magnetic resonance spectrum of a carbon tetrachloride solution of rhodoquinone is in agreement with structure I; τ 4.94 (10) m, CH=; 5.50 (2) b, $-NH_2$; 6.13 (3) s, $-OCH_3$; 6.88 (2), ring $-CH_2-$; 8.04 (38) m, $-CH_2CH=C(CH_3)CH_2-$ and ring $-CH_3$; 8.42 (32) m, $-CH_2CH=C(CH_3)CH_2-$. The assignment of the peak at τ 5.50 to the two amino protons was substantiated by taking the spectrum of a carbon tetrachloride solution of rhodoquinone containing a catalytic amount of formic acid. Under these conditions the only change in the spectrum was the disappearance of the peak due to the exchangeable amino protons at τ 5.50.

Rhodoquinone gives a monoacetate (amide) derivative when treated with acetic anhydride. The amide functional group was confirmed by spectral methods; infrared (smear) 3250 cm.$^{-1}$ (N–H stretching), 1655 and 1618 cm.$^{-1}$ (amide I band and quinone carbonyl); ultraviolet (C_2H_5OH) λ_{max} 275 mμ ($E^{1\%}_{1cm}$ 178), and 400 mμ (sh) ($E^{1\%}_{1cm}$ 8); n.m.r. (CCl_4) τ, 3.15 (1) s, –NH; 4.96 (10) m, CH=; 5.96 (3) s, $-OCH_3$; 6.88 (2) d, ring $-CH_2-$; 7.94 (3) s, CH_3CO-; 8.08 (38) m, $-CH_2-$

(1) This research was partially supported by funds from the Merck Sharp and Dohme Research Laboratories and we express our appreciation to Dr. Max Tishler. We are grateful to Dr. Harry Rudney of Western Reserve University for a sample of rhodoquinone.

(2) J. Glover and D. R. Threlfall, *Biochem. J.*, **85**, 14P (1962).

(3) L. J. Bellamy in "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1959, p. 248.

(4) I. Imada, *Chem. Pharm. Bull.* (Tokyo), **11** (6), 815 (1963).

$CH{=}C(CH_3)CH_2{-}$ 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.

(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.

Harold W. Moore, Karl Folkers
Stanford Research Institute
Menlo Park, California

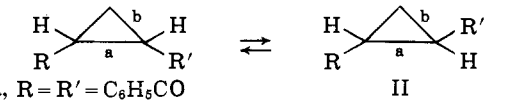
Received January 16, 1965

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.

(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.

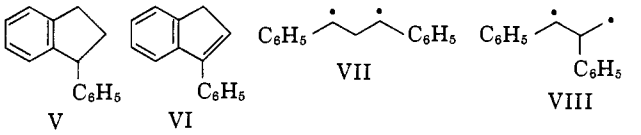


Ia, R = R′ = C_6H_5CO
b, R = C_6H_5CO, R′ = C_6H_5
c, R = R′ = C_6H_5

II

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



V VI VII VIII

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.

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]

(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.