

enes are present when ketene is irradiated at an average wave length of about 3200 Å. Dissociation of an excited ketene molecule would be expected to give singlet methylenes if the state is singlet and to give triplet methylenes if the state is triplet. It has been suggested¹¹ that some of the anomalies in methylene behavior may be due to varying ratios of singlet to triplet radicals. We wish to report data which bear on this point.

Earlier work¹² has indicated a marked difference in photochemical behavior of ketene at wave lengths around 2700 Å. from that at wave lengths around 3700 Å. The behavior at 3200 Å. is intermediate between the two cases. At 2700 Å. the quantum yield of carbon monoxide formation is 2 within experimental error. At 3700 Å. it is both pressure and temperature dependent. Also oxygen reduces the ethylene yield at 2700 Å. from about 0.91 to about 0.64. This yield, however, is not dependent on oxygen pressure. At 3650 Å. the ethylene yield is strongly dependent on oxygen pressure and is reduced to less than one-third of its oxygen-free value. Yields at 3700 Å. are temperature dependent and the apparent activation energy for dissociation of excited ketene is roughly 4 kcal.

Frey⁹ and Simons and Rabinovitch¹⁰ have used *cis*-butene-2 to distinguish between singlet and triplet methylenes, and this device has been used in the present work. Let α be the fraction of methylenes in the singlet state and $1 - \alpha$ the fraction in the triplet state. Then the ratio of "singlet type" products to "triplet type" products will be

$$R = \frac{\alpha + \frac{1}{2}(1 - \alpha)}{\frac{1}{2}(1 - \alpha)} = \frac{1 + \alpha}{1 - \alpha}$$

This equation assumes that $\text{CH}_2(\text{T})$ gives only *cis*- and *trans*-dimethylcyclopropane and that these do not isomerize. Thus the value of α calculated in this way may be slightly low. In the present instance this ratio will be equal to (*cis*-1,2-dimethylcyclopropane + *cis*-pentene-2 + 2methylbutene-2)/*trans*-1,2-dimethylcyclopropane = R .

The products were analyzed by gas chromatography. The light source was an Osram 500-w. lamp. Emission from this lamp is nearly a continuum. By color filters one region extending from 2650 to 2950 Å. (A) was isolated and another from 3460 to 3820 Å. (B) was also used. The following average results in the absence of foreign gas were obtained: region A, $R = 14 \pm 3$; region B, $R = 4 \pm 1$. Hence $\alpha = \sim 0.88 \pm 0.04$ for region A and 0.6 ± 0.1 for region B if the data are taken at face value. However "hot" molecules are formed by reaction of methylenes with the butene,^{13,14} and these may isomerize before they lose vibration energy. In the limit this phenomenon would give an apparent value of 0.5 for α . The effect can be minimized by adding an inert gas such as nitrogen and at moderate pressures the complication of inducing the singlet to triplet transition of methylenes will be unimportant. If nitrogen is added, the data indicate that in the region from 2650 to 2950 Å. the fraction of sin-

(11) W. A. Noyes, Jr., *Proc. Acad. Sci. Lisbon*, 3 (1964); W. A. Noyes, Jr., and I. Unger, *Pure Appl. Chem.*, 9, 461 (1964).

(12) A. N. Strachan and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, 76, 3258 (1954).

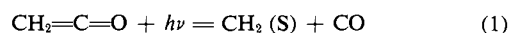
(13) H. M. Frey and G. B. Kistiakowsky, *ibid.*, 79, 6373 (1957).

(14) G. B. Kistiakowsky and K. Sauer, *ibid.*, 78, 5699 (1956).

glet methylenes is over 0.98. In the longer wave region the true value of α is undoubtedly well below 0.5. It is interesting to note that the fraction of triplet methylenes in the long wave region agrees well with that found by Simons and Rabinovitch.¹⁰

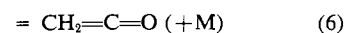
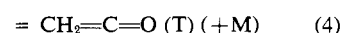
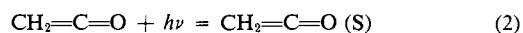
Tentatively one can suggest that triplet methylenes react more rapidly with oxygen than do the singlet methylenes. This will explain at least partially the effect of oxygen on ethylene yields.^{12,15}

It is suggested, therefore, that at short wave lengths the primary photochemical process in ketene is



The data do not show whether or not (1) occurs immediately or after a time lag, but since there is no effect of pressure at 2700 Å. presumably dissociation at this wave length is very rapid.

At the longer wave lengths the primary process should be



where (S) denotes a singlet state and (T) triplet state.^{12,16}

The data do not permit conclusions to be drawn about the role of collisions in (3)-(6) inclusive. The data of Simons and Rabinovitch¹⁰ require (4) to be bimolecular. Possibly (4) is a quasi-unimolecular reaction.¹¹ For the time being we prefer to reserve judgment on this point. Further details will be published later.

Acknowledgment. The authors wish to thank the Robert E. Welch Foundation and the Office of Aerospace Research, Air Force Office of Scientific Research, United States Air Force for grants which aided in support of this research.

(15) G. B. Porter, *ibid.*, 79, 1878 (1957).

(16) Cf. G. A. Taylor and G. B. Porter, *J. Chem. Phys.*, 36, 1353 (1962).

Shih-yeng Ho, I. Unger, W. Albert Noyes, Jr.
Department of Chemistry, University of Texas
Austin, Texas 78712

Received March 20, 1965

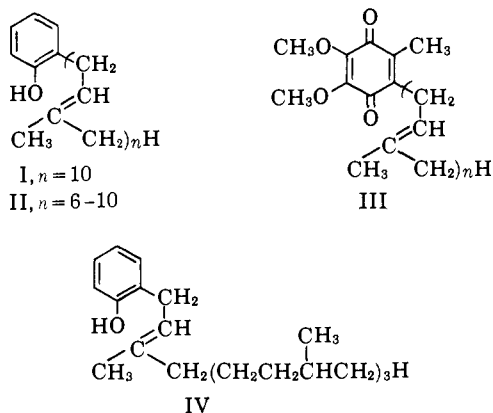
2-Decaprenylphenol, Biosynthetic Precursor of Ubiquinone-10^{1a}

Sir:

A biosynthetic precursor of ubiquinone has now been isolated in pure form, and its structure has been established as 2-decaprenylphenol^{1b} or 2-[3'-methyl-2-butenylenakis(3'-methyl-2'-butenylen)]phenol (I), a new substance. It is very likely that 2-decaprenylphenol is a member of a new group of 2-multiprenylphenols (II) which are in the biosynthetic pathways of the corresponding members of the ubiquinone¹ group (III). Also, it is plausible that such 2-multiprenylphenols, including lower (*i.e.*, $n = 3, 4,$ and 9) homologs and 2-phytylphenol (IV), are precursors by other path-

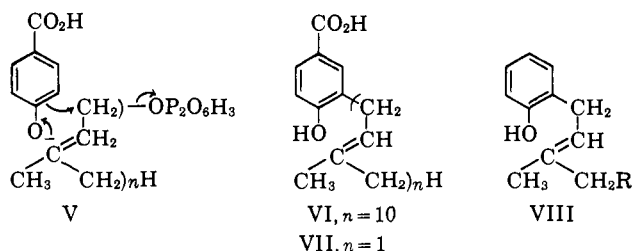
(1) (a) Coenzyme Q. LXV. (b) Nomenclature is based on a recommendation of an IUPAC-IUB Commission of Biochemical Nomenclature.

ways to the plastoquinones-3,² -4,³ and -9,^{4,5} and the tocopherols. Biological activities, *in vivo* as well as *in vitro*, may be presaged for these isoprenoidphenols.



p-Hydroxybenzaldehyde and *p*-hydroxybenzoic acid (HBA) are converted to the benzoquinone nucleus of Q in *Rhodospirillum rubrum*.⁶⁻⁹ The conversion of HBA to Q also occurs in mammalian species such as the rat.^{7,10} It has recently been shown¹¹ that shikimic acid is incorporated into Q by *E. coli*, but as a precursor to HBA. It was found that HBA was converted into a new substance,⁹ recognized chromatographically and of unknown structure, which in turn was converted to Q. We have now isolated this substance in pure form and determined its structure as 2-decaprenylphenol (I).

It is presumed that HBA is biosynthetically alkylated by a decaprenyl pyrophosphate (V, $n = 10$) to give the 3-decaprenyl-4-hydroxybenzoic acid (VI, $n = 10$) which by enzymic decarboxylation yields I. Initial decarboxylation of HBA to phenol, followed by alkylation, is probably not the pathway since uniformly labeled phenol was not incorporated into Q.^{6,8} Support for the biosynthetic existence of VI is evident



in the knowledge that VII is incorporated in the antibiotic novobiocin by *Streptomyces spheroides*.¹² The

occurrence of *p*-hydroxybenzoic acid in nature has been recognized for years. It is notable that it has a high order of growth activity for microorganisms and was considered a bacterial vitamin¹³; however, the mechanism of its growth activity has remained obscure in comparison to the elucidation of the roles of *p*-aminobenzoic acid and folic acid in growth. Clearly, the mechanism of the role of HBA in growth systems can be *via* VI and VIII to a variety of isoprenoid quinones and related natural products.

The isoprenylation of HBA in the natural biosynthetic pathway to Q is contrary to the concept^{14,15} that isoprenylation is the final reaction in the biosynthesis of ubiquinone; however, the reaction of isoprenyl pyrophosphates with 2,3-dimethoxy-5-methyl-1,4-benzoquinone can be quite valid for a laboratory, but unnatural, system. The isoprenylation of phenols by diphenyl phosphate esters is a new advance^{16,17} in organic chemistry, but not necessarily an analogy for the biosynthesis of Q and vitamin E.

The lipid fraction⁸ obtained from *R. rubrum* was chromatographed on a column of silica gel. Elution with ether-hexane yielded the purified precursor I as a clear colorless oil. Further purification was accomplished by thin layer chromatography on silica gel G plates which were developed in benzene. This material and a sample of radioactive material prepared from a labeling experiment⁹ with *p*-hydroxybenzoic acid-U-C¹⁴ migrated with the same R_f values on silica gel G plates in both benzene (R_f 0.32) and 10% ether in hexane (R_f 0.13).

The ultraviolet absorption spectrum of the precursor I ($\lambda_{\max}^{\text{hexane}}$ 272 and 279 $m\mu$; $\lambda_{\max}^{95\% \text{ EtOH}}$ 273 $m\mu$; in ethanol and sodium hydroxide λ_{\max} 291 $m\mu$) is in good agreement for either an *ortho*- or *meta*-substituted phenol. For example, 2-allylphenol,¹⁸ *o*-cresol,¹⁹ and *m*-cresol¹⁹ have maxima at 272 and 279 $m\mu$; *p*-cresol¹⁹ shows maxima at 279 and 286 $m\mu$. The infrared absorption spectrum of I has a band at 3400 cm^{-1} due to the hydroxyl group; no carbonyl absorption was present.

The nuclear magnetic resonance spectrum²⁰ is most definitive in establishing the structure: τ 2.94-3.51 (complex multiplet, aromatic), 4.99 (multiplet, vinyl), 5.30 (singlet, hydroxyl), 6.65 (doublet, benzyl), and 8.0-8.4 (multiplet, alkyl hydrogens), with the intensity ratios being 4.0:10.0:1.0:2.0:71, respectively. The aromatic region of the n.m.r. spectrum of I is nearly superimposable upon the corresponding region of *o*-cresol, but differs significantly from those of *p*- and *m*-cresol. The fact that the n.m.r. spectrum is in agreement for 10 vinyl protons characterizes the phenol I as having a 10-unit isoprenoid chain. Previously, it had been shown⁹ that the labeled precursor

(2) D. Misiti, H. W. Moore, and K. Folkers, *J. Am. Chem. Soc.*, **87**, 1402 (1965).

(3) N. Eck and A. Trebst, *Z. Naturforsch.*, **18b**, 446 (1963).

(4) N. R. Trenner, B. H. Arison, R. E. Erickson, C. H. Shunk, D. E. Wolf, and K. Folkers, *J. Am. Chem. Soc.*, **81**, 2026 (1959).

(5) M. Kofler, A. Langemann, R. Rüegg, L. H. Chopard-dit-Jean, A. Rayroud, and O. Isler, *Helv. Chim. Acta*, **42**, 1283 (1959).

(6) H. Rudney and W. W. Parson, *J. Biol. Chem.*, **238**, PC 3137 (1963).

(7) W. W. Parson and H. Rudney, *Proc. Natl. Acad. Sci. U. S.*, **51**, 444 (1964).

(8) W. W. Parson and H. Rudney, *J. Biol. Chem.*, in press.

(9) W. W. Parson and H. Rudney, *Proc. Natl. Acad. Sci. U. S.*, **53**, 599 (1965).

(10) A. S. Aiyer and R. E. Olson, *Federation Proc.*, **23**, 425 (1964).

(11) G. B. Cox and F. Gibson, *Biochim. Biophys. Acta*, **93**, 204 (1964).

(12) C. H. Shunk, C. H. Stammer, E. A. Kaczka, E. Walton, C. F. Spencer, A. N. Wilson, J. W. Richter, F. W. Holly, and K. Folkers, *J. Am. Chem. Soc.*, **78**, 1770 (1956).

(13) B. D. Davis, *Nature*, **166**, 1120 (1950).

(14) W. Stoffel and C. Martius, *Biochem. Z.*, **333**, 440 (1960).

(15) H. G. Schieffer and C. Martius, *ibid.*, **333**, 454 (1960).

(16) J. A. Miller and H. C. S. Wood, *Chem. Commun. (London)*, No. 3, 39 (1965).

(17) J. A. Miller and H. C. S. Wood, *ibid.*, No. 3, 40 (1965).

(18) T. J. Webb, L. I. Smith, W. A. Bastedo, Jr., H. E. Ungnade, W. W. Prichard, H. H. Hoehn, S. Wawzonek, J. W. Opie, and F. L. Austin, *J. Org. Chem.*, **4**, 389 (1939).

(19) L. Lang, "Absorption Spectra in the Ultraviolet and Visible Region," Vol. II, Academic Press Inc., New York, N. Y., 1961, pp. 139-144.

(20) N.m.r. spectra were taken with a Varian HR 60 spectrometer in CCl_4 solutions; chemical shifts are in τ units relative to tetramethylsilane as an internal standard.

is converted stepwise into labeled ubiquinone-10 and rhodoquinone-10 (newly identified as an amino derivative of Q-10²¹), indicating a 10-unit side chain.

Treatment of I with 3,5-dinitrobenzoyl chloride yielded a monobenzoate derivative: ν_{\max}^{film} no OH absorption, 1755 cm.⁻¹ (carbonyl), 1540 and 1340 cm.⁻¹ (nitro); n.m.r., τ 0.79 (nitro aromatic, 3 H), 2.69–2.85 (phenol aromatic, 4 H), 5.0 (vinyl, 10 H), 6.80 (benzyl, 2 H), and 7.95 and 8.36 (alkyl, ca. 65 H).

2-Decaprenylphenol is the first known precursor to ubiquinone which possesses both the aromatic nucleus and isoprenoid side chain. Studies are in progress on subsequent biosynthetic steps to ubiquinone, and on the syntheses of these new isoprenoid phenols.

Acknowledgment. Appreciation is expressed (K. F.) to Dr. Leo P. Vernon of the Charles F. Kettering Research Laboratory, Yellow Springs, Ohio, for a research grant, and to the Muscular Dystrophy Associations of America, Inc., for a research grant.

(21) H. W. Moore and K. Folkers, *J. Am. Chem. Soc.*, **87**, 1409 (1965).

(22) Post-Doctoral Fellow of the Muscular Dystrophy Associations of America, Inc.

(23) Research Career Awardee GMK6993 of the U. S. Public Health Service.

Richard K. Olsen, Jack L. Smith²²

G. Doyle Daves, Harold W. Moore, Karl Folkers

Stanford Research Institute
Menlo Park, California

William W. Parson, Harry Rudney²³

Department of Biochemistry, Western Reserve University
Cleveland, Ohio

Received March 29, 1965

The Magnitudes and Relative Signs of Long-Range Silicon-Proton Coupling Constants¹

Sir:

A knowledge of the signs of spin-spin coupling constants is of considerable importance in checking the theory for these parameters and in sorting out the magnitudes of the terms contributing to the coupling interaction. Sign determinations are of particular interest for couplings extending over more than two intervening bonds where a cancellation of contributing terms can occur.² Most of the relative sign determinations reported thus far³ have been for proton-proton couplings, and these have been related in turn to an assumed positive value for a directly bonded C¹³-H coupling constant.⁴ Correlations of this type have been extended recently to P³¹-H and Si²⁹-H coupling constants.^{5,6} In this communication we wish to report the relative signs for long-range silicon-proton coupling constants in substituted vinylsilanes.

The proton spectra were recorded on a Varian DP-60 spectrometer and H¹-{H¹} decoupling measurements were carried out following the procedure of Freeman.⁷

(1) This work was carried out while the author was guest worker at the National Physical Laboratory, Basic Physics Division, Teddington, England, July-Aug. 1964.

(2) M. Karplus, *J. Chem. Phys.*, **33**, 1842 (1960).

(3) D. M. Grant, *Ann. Rev. Phys. Chem.*, **15**, 489 (1964).

(4) M. Karplus, *J. Am. Chem. Soc.*, **84**, 2458 (1962).

(5) (a) S. L. Manatt, G. L. Juvinall, and D. D. Elleman, *ibid.*, **85**, 2664 (1963); (b) G. M. Whitesides, J. L. Beauchamp, and J. D. Roberts, **85**, *ibid.*, 2665 (1963).

(6) S. S. Danyluk, *ibid.*, **86**, 4504 (1964).

(7) R. Freeman, *Mol. Phys.*, **4**, 385 (1961).

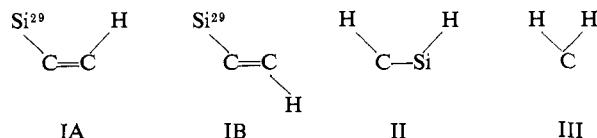
The H¹-{Si²⁹} decoupled spectra were obtained by procedures described previously.⁶ A summary of the magnitudes and relative signs for proton-proton and silicon-proton coupling constants for a variety of silicon derivatives is given in Table I. The directly bonded Si²⁹-H coupling constants were obtained from the respective Si²⁹ decoupling frequencies and are somewhat less accurate than the Si²⁹C=CH (I) couplings, obtained by an analysis of the Si²⁹ satellite spectra.

Table I

Compound	Type of coupling	Magnitude, c.p.s.	Sign of J	Sign of K ^a
CH ₃ SiHCl ₂	Si ²⁹ -H	285 ± 10	-	+
	H-C-Si-H	3.7 ± 0.1	+	+
CH ₃ SiHBr ₂	Si ²⁹ -H	275 ± 10	-	+
	H-C-Si-H	3.6 ± 0.1	+	+
(CH ₃) ₂ SiHCl ^b	Si ²⁹ -H	227 ± 5	-	+
	H-C-Si-H	3.3 ± 0.1	+	+
(CH ₃) ₂ SiHBr	Si ²⁹ -H	211 ± 10	-	+
	H-C-Si-H	3.5 ± 0.1	+	+
(CH ₃) ₂ SiHI	Si ²⁹ -H	225 ± 5	-	+
	H-C-Si-H	3.6 ± 0.1	+	+
(CH ₃) ₂ Si >C=C<H Cl	H-C-H	1.02 ± 0.03	-	-
	Si ²⁹ -C=C-H (cis)	4.36 ± 0.05	-	+
	Si ²⁹ -C=C-H (trans)	10.51 ± 0.05	-	+
Cl ₂ Si >C=C<H Cl	H-C-H	2.04 ± 0.03	-	-
	Si ²⁹ -C=C-H (cis)	7.48 ± 0.05	-	+
	Si ²⁹ -C=C-H (trans)	21.20 ± 0.05	-	+

^a K_{IJ} = (2π/hγ_Iγ_J)J_{IJ}. ^b See ref. 6.

The signs of the reduced coupling constants, K_{Si²⁹-H} and K_{II}, are the same in both the monomethyl- and dimethylsilyl halide derivatives. If K_{II} is assumed to be positive, in conformity with the signs for other vicinal couplings,^{5,8,9} then the absolute sign of the Si²⁹-H



coupling constant is also positive in agreement with earlier results.⁶ The magnitudes of J_{Si²⁹-H} for the dimethylsilyl derivatives are slightly less than the values reported for corresponding monomethylsilyl halides by Ebsworth and Frankiss.¹⁰ No significant change of J_{Si²⁹-H} with halogen substituent (Cl, Br, I) is noted for the dimethylsilyl halides. On the other hand, replacement of a CH₃ group by a halogen leads to an appreciable increase (more positive) of K_{Si²⁹-H} (~55 c.p.s.). It is likely that similar observations for corresponding

(8) P. C. Lauterbur and R. J. Kurland, *J. Am. Chem. Soc.*, **84**, 3406 (1962).

(9) D. P. Evans, S. L. Manatt, and D. D. Elleman, *ibid.*, **85**, 238 (1963).

(10) E. A. V. Ebsworth and S. G. Frankiss, *Trans. Faraday Soc.*, **59**, 1518 (1963).