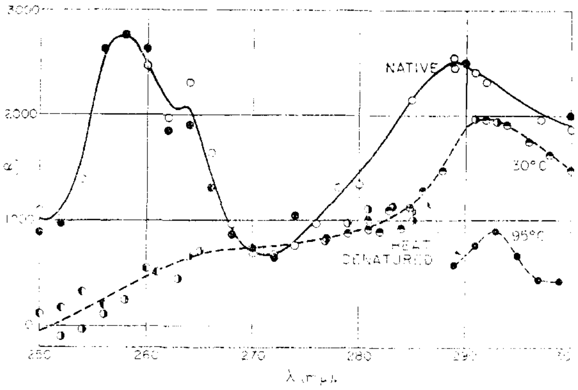

Fig. 1.—Ultraviolet rotatory dispersion of DNA (calf thymus) in 0.15 M NaCl + 0.015 M Na Citrate, pH 7; DNA was denatured at 95°, then cooled to 30°.

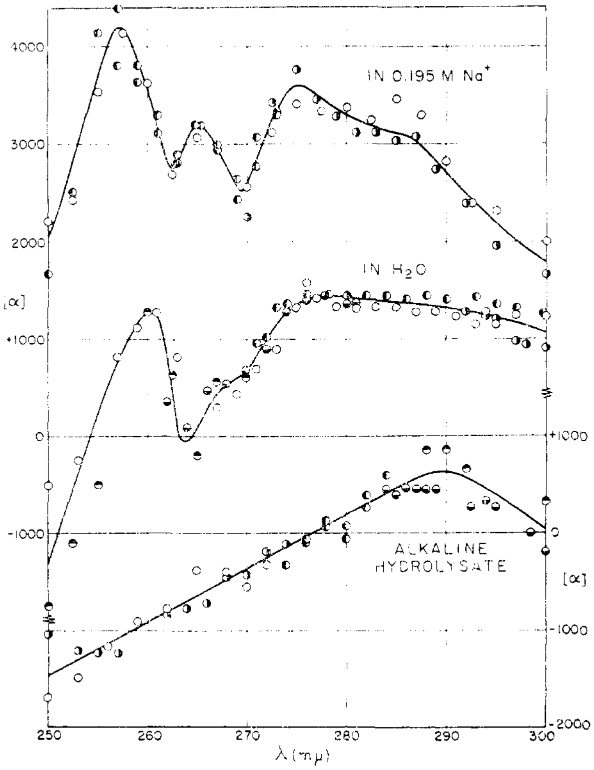

Fig. 2.—Ultraviolet rotatory dispersion of microsomal RNA (calf liver) and its alkaline hydrolysate in 0.15 M NaCl + 0.015 M Na Citrate, pH 7, T 22°.

strength results in a loss of detail and diminished rotatory power (Fig. 2). Completely denatured RNA can be expected to show a profile approaching that of its constituent mononucleotides.

These first observations contain considerable detail not evident in the corresponding absorption spectra, and demonstrate that ultraviolet rotatory dispersion is a promising approach to the investigation of the microstructure in nucleic acids. It is in studies with homopolynucleotides and pairs that we can expect to sharpen detail no doubt obscured in natural nucleic acids containing a multiplicity of bases and base sequences.

We are grateful to Mr. Peter Urnes for assistance in the instrumental work, and to Professor Michael Kasha for helpful discussions. This work was supported by grants from the United States Public Health Service, C-2170, the National Science Foundation and the American Heart Association.

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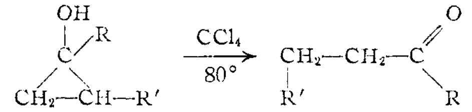
RECEIVED MAY 29, 1961

A FREE-RADICAL CATALYZED REARRANGEMENT OF CYCLOPROPANOLS

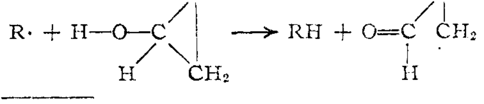
Sir:

We wish to report that in carbon tetrachloride or chloroform solution at 80° cyclopropanols undergo a rapid ring-opening rearrangement reaction, apparently proceeding by a free radical mechanism. For cyclopropanol itself the product, in very high yield, is propionaldehyde, and analogous products, methyl ethyl ketone and γ-phenylpropionaldehyde, are formed from 1-methyl- and *trans*-2-phenylcyclopropanol,[1] respectively.



In a typical experiment 0.5 ml. samples of 0.5 M cyclopropanol in carbon tetrachloride were sealed in 2-ml. tubes, under air or oxygen, and heated at 80°. The progress of the reaction was followed by gas chromatography and infrared and nuclear magnetic resonance spectroscopy. Cyclopropanol disappeared with a half-life of approximately thirty minutes and the only detectable product was propionaldehyde. If the samples were sealed with the exclusion of oxygen, or if di-*t*-butyl-*p*-cresol were added to samples sealed in the presence of air, little reaction occurred even after long periods of heating. Cyclopropanol samples sealed in the absence of oxygen but containing added peroxides again were converted rapidly to propionaldehyde. The rate was not slowed by the addition of triethylamine, nor appreciably enhanced by the addition of acid. 1-Methylcyclopropanol and *trans*-2-phenylcyclopropanol, in preliminary studies, appear to react in a similar manner.

These rearrangements appear remarkable to us for several reasons. In the first place cyclopropyl acetate and methyl cyclopropyl ketone are completely inert under the conditions of the reaction This observation together with the fact that radical abstractions from cyclopropanes are known to be difficult,[2] suggests that the reaction may involve an attack on the O–H bond of the alcohol, probably with simultaneous ring opening. If the reaction



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[1] C. H. DePuy, L. R. Mahoney and K. L. Eilers, *J. Org. Chem.*, in press.

[2] J. R. McNesby and A. S. Gordon, *ibid.*, **79**, 825 (1957).

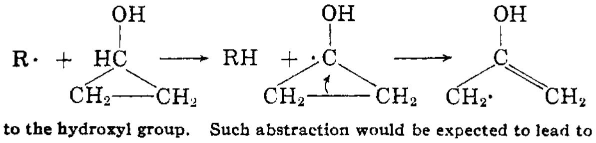
does indeed take this course, it would be without precedent.[3]

Secondly, the reaction is remarkably solvent dependent, occurring rapidly in carbon tetrachloride and chloroform but not in benzene, methylene chloride, cyclohexane, water or several other solvents. In the third place the reaction is not catalyzed by azobisisobutyronitrile, although several peroxides and hydroperoxides are effective. Finally the complete inhibition of the reaction by di-*t*-butyl-*p*-cresol, an inhibitor which has been demonstrated to be effective against peroxyradicals but never to be effective against alkyl radicals, makes the nature of the chain-carrying radical problematical.

The results so far at hand also permit a mechanism based on the radical catalyzed build up of some electrophilic species which is especially reactive toward cyclopropanols. Kinetic, stereochemical and tracer studies are being made.

We are indebted to the Alfred P. Sloan Foundation for support and to Professor G. A. Russell for helpful discussions. This work was supported in part by the Office of Naval Research. Also, acknowledgement is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society.

(3) It might be pointed out that abstraction of a hydrogen atom from the cyclopropane ring, if it occurred, would be easiest adjacent



to the hydroxyl group. Such abstraction would be expected to lead to acetone, rather than propionaldehyde, as a product.

(4) Ohio Oil Co. Fellow, 1960–61.

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J. W. HAUSSER

RECEIVED JUNE 2, 1961

TETRAKIS-(*p*-DIMETHYLAMINOPHENYL)-ETHYLENE DIIODIDE AND ITS FREE RADICAL BEHAVIOR

Sir:

In connection with biological studies of derivatives of tetrakis-(*p*-dimethylaminophenyl)-ethylene (I)[1] we have synthesized the dinitrate (II) and the diiodide (III) of I. Compound I was shaken with silver nitrate in water for 12 hours and afforded II, green crystals from water. *Anal.* Calcd. for $C_{34}H_{40}O_6N_6$: NO_3^-, 19.74. Found: NO_3^-, 19.62, 19.47. In the presence of excess I, the above oxidation conforms to the stoichiometric equation $I + 2AgNO_3 \rightarrow II + 2Ag$. Addition of potassium iodide to II in water gave III, brilliant green crystals from water. *Anal.* Calcd. for $C_{34}H_{40}N_4I_2 \cdot H_2O$: I^-, 32.73; H_2O, 2.33. Found: I^-, 32.88; H_2O, 2.29. The *green* diiodide was heated in air at 75° to constant weight. The color changed to *black* and there was no detectable loss of iodine. *Anal.* Calcd. for $C_{34}H_{40}N_4I_2$: I, 33.50. Found: I(Carius), 33.34, 33.30. Solutions of II and III in water are purple and their optical spectra are the same.[2]

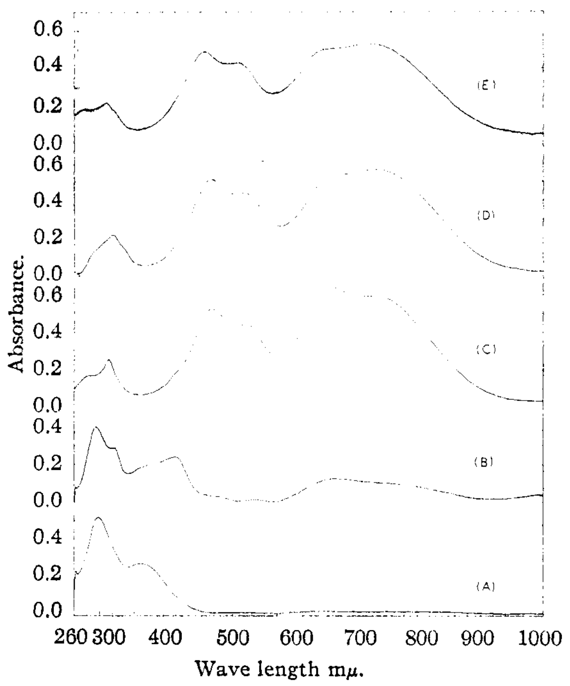
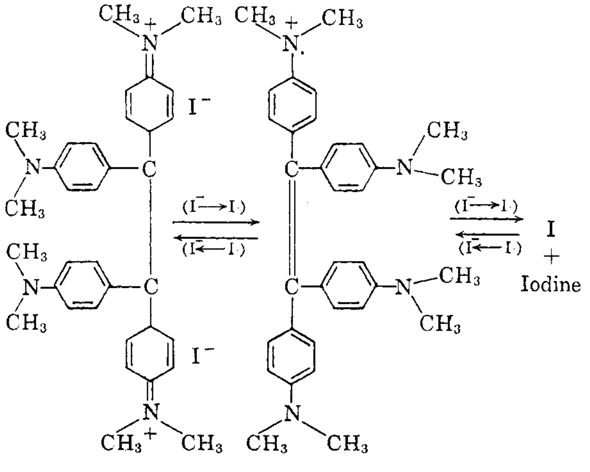


Fig. 1.—Absorption spectra: curve A, compound I, 1.22 × 10^{-5} *M* in ethylene chloride; curve B, compound III, 1.22 × 10^{-5} *M* in ethylene chloride; curve C, compound II, 1.12 × 10^{-5} *M* in ethylene chloride; curve D, compound III, 1.2 × 10^{-5} in water; curve E, compound II, 1.12 × 10^{-5} in water

Water solutions of II and III show no e.p.r. signal. However, in ethylene chloride there is a marked difference between the optical and e.p.r. spectra of II and III. Solutions of II are purple and show no radical activity, whereas solutions of III are green and give an intense e.p.r. signal. This cor-

$$\text{ion-pair (IIIa)} \rightleftarrows \text{cation-}$$
$$\text{radical (IIIb) (Wurster salts)}^3 \rightleftarrows \text{compound I} + \text{iodine}^4$$



IIIa IIIb

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(1) R. Willstätter and M. Goldman, *Ber.*, **39**, 3775 (1906).

(2) The ionic character of halogen arylated ethylene complexes has been established and stable carbonium ion structures have been suggested; see R. E. Buckles and N. A. Meinhardt, *J. Am. Chem. Soc.*, **74**, 1171 (1952), and R. Wizinger and J. Fontaine, *Ber.*, **60**, 1377 (1927). Because the dimethylamino group is capable of assuming a positive charge, II and III are envisioned as having cationic structures which are largely *p*-quinoidal.

(3) E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3267 (1958).

(4) The detailed nature of the iodine moiety has been omitted from the discussion. It was realized that the equilibrium $2I\cdot + I^- \rightleftarrows I_3^-$ might be involved and this has been pointed out by the referee.