to racemization of 10 mol of phosphine per mol of TCNQ; this must involve an equilibrium process. The best explanation of this observation is a slow dissociation of the ion pair to free-radical ions.

The reaction of I with TCNE has been reported to give 1,1,1-triphenyl-2,3,4,5-octacyanophosphole (VIII),[12] and we confirm that in anhydrous medium the reaction proceeds with a 2:1 stoichiometry.[13] However, in CH$_3$CN in the presence of aqueous HCl, I reacts with TCNE in a 1:1 molar ratio to give a quantitative yield of II and 1,1,2,2-tetracyanoethane. In 30% CH$_3$CN–70% CHCl$_3$, containing 5% concentrated HCl, optically active III reacted with TCNE to give *racemic* IV (49%) and 1,1,2,2-tetracyanoethane (43%), the remaining TCNE being recovered as the 2:1 adduct with III identical with that obtained under anhydrous conditions. It is clear that the formation of racemic oxide may also be explained in terms of an intermediate phosphinium radical cation.

Since Ramirez[2] suggested that V was a possible intermediate in the reactions of triarylphosphines with chloranil we attempted to verify this by using optically active III. Racemic IV was obtained on hydrolysis of the phosphine–chloranil adduct, but the experiment was frustrated by the observation that optically active IV racemized in the presence of tetrachloroquinol probably *via* formation of a five-covalent phosphorus structure in solution.

There was no evidence for any complex formation between TCNEH$_2$ or TCNQH$_2$ and IV, and solutions of optically active IV did not racemize in the presence of TCNEH$_2$ or TCNQH$_2$.

Acknowledgment. We are grateful to the Science Research Council for the award of a Research Studentship (to R. L. P.)

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[12] G. S. Reddy and C. D. Weiss, *J. Org. Chem.*, **28**, 1822 (1963).

[13] A recent publication[14] suggested that the structure proposed for VIII was probably incorrect. The ^{31}P chemical shift (−22 ppm from H$_3$PO$_4$) is not consistent with a pentacovalent structure and we find that, under anhydrous conditions, optically active III gives a similar product which retains optical activity, thus providing further evidence against the phosphole structure.

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Received May 12, 1969

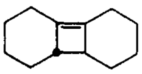
Stereospecific Photochemical Fragmentation of Cyclobutenes in Solution

Sir:

Orbital-symmetry considerations predict that formation of four-membered rings by concerted *cis,cis* cycloaddition has a prohibitively large activation energy for ground-state reactants, but is favored when one of the reactants is electronically excited.[1,2] In accord with these expectations thermal "1,2" cycloadditions have been shown to involve diradical intermediates,[3] whereas complete stereospecificity in the photochemical dimerization of the 2-butenes strongly suggests a concerted process.[4] For the reverse reactions, the same orbital-symmetry considerations predict that concerted *cis,cis* cleavage of four-membered rings is the favored path photochemically but not thermally. Recent observations on the thermal cleavage of cyclobutanes indicate a diradical intermediate, substantiating, in part, these predictions.[5]

Photochemical fragmentation of cyclobutenes to ethylene and acetylenes has been reported,[6,7] but no information has been available concerning the stereochemistry of the reaction. The following deals with the photochemical cleavage of cyclobutenes **1** and **2**.

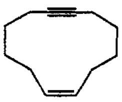
1



2

cis-Cyclobutene (**1**) was prepared from 1,1′-bicyclohexenyl (**3**) using 2-acetonaphthone as photosensitizer,[8] and *trans*-cyclobutene (**2**) was prepared using Moore and Moser's procedure.[9] Pentane solutions (0.03–0.06 *M*) of **1** and **2** were irradiated under nitrogen using a 550-W Hanovia mercury lamp and a Hanovia quartz immersion probe. Reaction mixtures were analyzed by glpc using a 15 ft × 1/8 in. column packed with 15% Carbowax 20M on Chromosorb W.

Direct irradiation of **1** gives 1,1′-bicyclohexenyl (**3**) as the major initial photoproduct. Formation of **3** was kept to less than 1% of the product mixture by irradiating **1** in the presence of triphenylene ($\sim 10^{-5}$ *M*). It was shown that triphenylene functions as photosensitizer for the conversion of **3** to **1**, but does not sensitize reactions of **1**. Prolonged irradiation of **1** in the presence of triphenylene yields one major photoproduct (**4**) which was isolated in 25% yield by chromatography on alumina impregnated with 33% silver nitrate. The nmr spectrum of **4** in CCl$_4$ with TMS as reference consists of two broad peaks centered at 1.51 and 2.15 ppm and a symmetrical multiplet centered at 5.29 ppm (relative areas 4:4:1, respectively). The ir spectrum shows bands of interest at 1450 (m) and 710 cm^{-1} (m). The Raman spectrum of the neat product shows bands at 2290, 2240, and 1656 cm^{-1}. The mass spectrum has a parent ion peak at *m/e* 162. The observations indicate that **4** is *cis*-cyclododeca-1-en-7-yne. Chemical confirmation of this assignment was obtained by partial reduction of the triple bond in methanol using 5% Pd on BaSO$_4$ poisoned with quinoline as catalyst.[10] The nmr of the hydrogenation product in CCl$_4$ is very similar



4

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[1] R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968), and references cited therein.

[2] L. Salem, *J. Amer. Chem. Soc.*, **90**, 543, 553 (1968).

[3] P. D. Bartlett and G. E. H. Wallbillich, *ibid.*, **91**, 409 (1969), and previous papers in this series.

[4] Y. Yamazaki and R. J. Cvetanović, *ibid.*, **91**, 520 (1969).

[5] A. T. Cocks and H. M. Frey, *Chem. Commun.*, 458 (1969).

[6] E. H. White and J. P. Anhalt, *Tetrahedron Lett.*, 3937 (1965).

[7] I. Haller and R. Srinivasan, *J. Amer. Chem. Soc.*, **88**, 3694 (1966).

[8] W. G. Dauben, R. L. Cargill, R. M. Coates, and J. Saltiel, *ibid.*, **88**, 2742 (1966).

[9] We thank Professor W. R. Moore for sending us a detailed description of the synthesis. *Cf.* W. Moser, Ph.D. Thesis, Massachusetts Institute of Technology, 1963.

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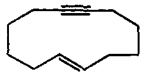
to that of **4** with the exception that the relative peak areas are 2:2:1. The splitting pattern of the symmetrical multiplet centered at 5.30 ppm is identical with that found in *cis,cis*-1,6-cyclodecadienes.[11] In the presence of Adams catalyst in acetic acid **4** consumed 3 molar equiv of hydrogen. Cyclododecane was isolated in 87% yield, mp 61–62°.[12] The nmr spectrum of the cyclododecane shows a single peak at 1.32 ppm, and its mass spectrum shows a parent ion at *m/e* 168.

Direct irradiation of **2** gives only one major product (**5**). This product was isolated as the silver nitrate adduct by treatment with aqueous silver nitrate. Treatment of this adduct with ammonia liberated **5** which was isolated in 42% yield. The nmr spectrum of **5** shows two overlapping broad signals centered at 1.70 and 2.02 ppm and a multiplet centered at 5.70 ppm (relative areas 4:4:1, respectively). The ir spectrum shows a sharp peak at 960 cm^{-1} (s) which is absent in the spectrum of **4**. The Raman spectrum of neat **5** shows bands at 2285, 2232, and 1667 cm^{-1}. The parent ion peak in the mass spectrum is at *m/e* 162.[13] Reduction of **5** over Adams catalyst gave cyclododecane, isolated in 90% yield, which was identical in all respects with the cyclododecane obtained from **4**, mmp 61–62°. On the basis of the above spectral and chemical observations it is concluded that **5** is *trans*-cyclododeca-1-en-7-yne.



5

The photochemistry of **1** and **2** is summarized in eq 1 and 2. In the absence of triphenylene the initial

$$1 \xrightarrow{h\nu} 3 + 4 \qquad (1)$$

$$2 \xrightarrow{h\nu} 5 \qquad (2)$$

rate of formation of **3** from **1** is at least three times faster than the formation of **4**. No photochemical interconversion of **1** and **2** was detected. Completely stereospecific formation of **4** and **5** from **1** and **2**, respectively, is in accord with the Hoffmann–Woodward selection rule for a concerted photochemical four-electron $2\sigma \rightarrow 2\pi$ process.[14] This result is revealing with respect to a related mechanistic aspect of the reactions. Concerted cleavage of the two σ bonds of the electronically excited cyclobutenes could produce electronically excited **4** and **5**. Since electronic excitation in the double bonds of these products would have led to their interconversion,[4] either the electronic excitation is retained exclusively in the triple bonds, or, more likely, the reactions involve direct reorganization from excited cyclobutenes to ground-state products.[15,16]

According to orbital symmetry considerations disrotatory ring opening of electronically excited cyclobutenes to dienes is an allowed process.[1] Formation of *cis,cis*-1,1′-bicyclohexenyl (**3**) from **1** was therefore expected. The reverse reaction is known[8] and its disrotatory course has been established experimentally in the case of 2,4-hexadiene.[18] Disrotatory diene formation from excited **2** would lead to the highly strained *cis,trans*-1,1′-bicyclohexenyl (**6**) which has been proposed as the intermediate in the photosensitized conversion of **3** to **1**.[19] If **6** → **1** is a facile thermal reaction, the fact that **1** is not a product of the irradiation of **2** rules out transient formation of **6** in our system. We note that in accord with orbital symmetry considerations which predict conrotatory ring opening of ground-state cyclobutenes to dienes, thermal diene formation is energetically easier from **2** than from **1**.[20] The effect of ring size on reactions 1 and 2 is under investigation.

Acknowledgment. This research was supported in part by National Science Foundation Grant GP-7941 and by the University Science Development Program of the National Science Foundation, Grant GU-2612.

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Received June 19, 1969

Peripheral Attack in the Reduction and Oxidation of Iron Porphyrins

Sir:

As a part of our study of the electron–transfer chemistry of hemes and hemoproteins we wish to report direct evidence for peripheral attack upon the porphyrin ring during the chemical reduction and oxidation of chloroiron(III) octaethylporphyrin. The system employed is indicated in eq 1. The salient feature of the process is that it is accompanied by hydrogen exchange at the *meso* position.

Thus, dilute solutions of octaethylhemin (I), λ_{max} 628, 532, 504 mμ, were reduced with iron powder in 1:1 N-methylpyrrolidone–CH_3CO_2D under nitrogen[1] to the corresponding heme (II), λ_{max} 566, 532 mμ. The latter was oxidized to the iron(III) state with air or hydrogen peroxide. After removal of iron[2] the purified porphyrin, λ_{max} 611, 560, 529, 495 mμ, was subjected to nmr analysis as the dication in CF_3CO_2D. The spectra of octaethylporphyrin and the porphyrin obtained from Hemin blank runs, that were not subjected to reduction or oxidation, were identical and showed a CH_3 resonance at δ 1.4 (triplet, 24 H), CH_2 at 3.8 (quartet, 16 H), and the vinylic *meso* proton at 10.7 (singlet, 4 H). Hence, neither the hemin nor the porphyrin undergoes skeletal C–H exchange in the reaction solution or upon work-up, and the porphyrin

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[1] The method is an adaptation of that previously reported: D. G. Whitten, E. W. Baker, and A. H. Corwin, *J. Org. Chem.*, **28**, 2363 (1963); C. E. Castro, *J. Amer. Chem. Soc.*, **86**, 2310 (1964).

[2] J. E. Falk, "Porphyrins and Metalloporphyrins," Elsevier Publishing Co., New York, N. Y., 1964, p 135.