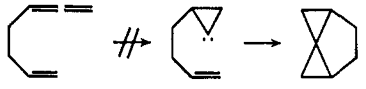
numerous minor products and a considerable amount of polymer.

The photochemistry of III is less complex and less efficient. Both the benzene-sensitized and the vacuum ultraviolet photolyses yield IV[11] as a primary product.[6] Compound IV can itself be photoisomerized, but does not revert to III. The quantum yield for the benzene-sensitized conversion of III → IV is 0.02.

We recently reported[12] that the benzene-sensitized photolysis of 1,2-cyclononadiene yields tricyclo-$[2.2.0.0^{2,9}]$nonane. A mechanism involving the closing of the allene to a cyclopropylidene and subsequent transannular insertion into a C–H bond was proposed. If triene I followed the same reaction pathway, the expected product, resulting from the addition of the cyclopropylidene to the terminal double bond, would be tricyclo$[4.1.0.0^{4,6}]$heptane (V). By comparison of the spectra and chromatographic properties of an authentic sample[13] of V with those of the photoproducts, we have established that V is not formed in either the benzene-sensitized or the vacuum ultraviolet photolyses of I. Clearly the photo-Cope rearrangement of the 1,5-diene system takes precedence over the allene → cyclopropylidene mutation when both are possible.



I V

The most reasonable mechanism for these photochemical rearrangements is the concerted intramolecular process by which the thermal Cope rearrangements are known to proceed. A four-center chair-like transition state for the thermal Cope has been demonstrated by a classic experiment[14] and ratified by orbital symmetry considerations.[15] The six-center boat-like transition state should be preferred by an excited-state reactant and may also be available to sterically stressed systems in thermal rearrangements.[15] Both conformations are available to I, while III can comfortably assume the six-center transition state, but appears from models to be severely strained in the four-center arrangement.[16] However, the ease of reaching the thermally preferred four-center conformation does not fully control the reaction rates in this system. Vapor-phase pyrolyses in a flow system with short contact time show that III → IV is more facile than I → II, at least at temperatures above 300°. (At 340°, (III → IV)/(I → II) = 1.5.)

Although it is not yet possible to choose between the reasonable alternatives for the electronic state of the triene leading to rearrangement (the first excited singlet, the lowest triplet, or a vibrationally excited ground electronic state), it is interesting to note that the photochemical isomerization shows the reverse proclivity ((III → IV)/(I → II) = 0.1) of the thermal process.

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Received October 30, 1968

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[11] Retention times relative to benzene: 10% Carbowax 20M (70°), 2.7, 15% squalane (80°), 6.0, 15% TCEP (80°), 1.6.

[12] H. R. Ward and E. Karafiath, *J. Amer. Chem. Soc.*, 90, 2193 (1968).

[13] L. Skattebøl, *Chem. Ind.* (London), 2146 (1962).

[14] W. von E. Doering and W. R. Roth, *Tetrahedron*, 10, 67 (1962).

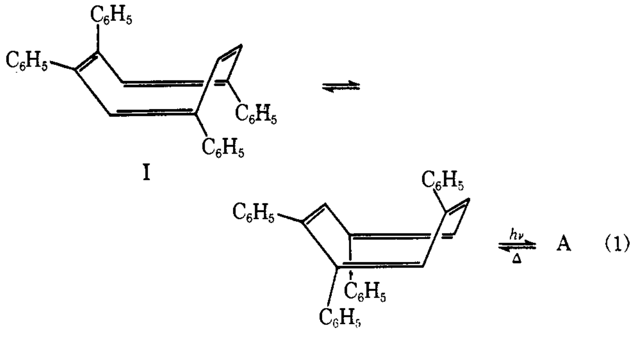
[15] R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, 87, 4389 (1965).

[16] If III could be obtained as a single enantiomeric form whose configuration could be related to that of the product IV, then it would be possible to distinguish between the two reaction routes (provided that neither III or IV racemizes prior to or after the rearrangement). The formidable difficulties inherent in meeting these conditions have discouraged us from attempting these experiments.

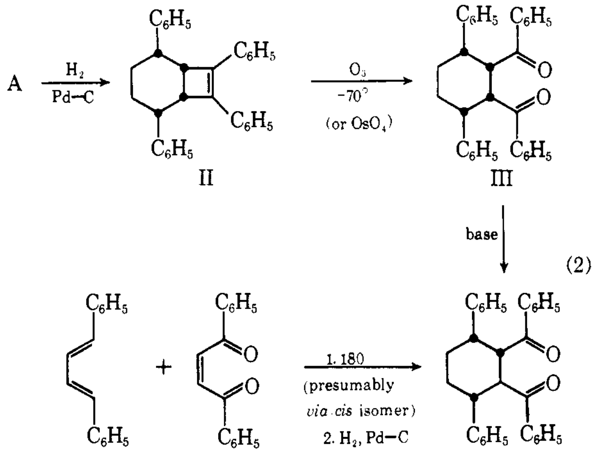
A Probable *trans*-Cyclooctatetraene

Sir:

The irradiation of 1,2,4,7-tetraphenylcyclooctatetraene (I)[1] in hexane yields a photoisomer (A), mp 121–122° dec, to which we assign structure VII.[2] The photoisomer reverts quantitatively to cyclooctatetraene (I) very slowly in the solid state and with a half-life of 18 hr in solution at 25° (first-order rate constant).



Hydrogenation of isomer A yielded only a tetrahydro derivative, assigned structure II. The ultraviolet spec-



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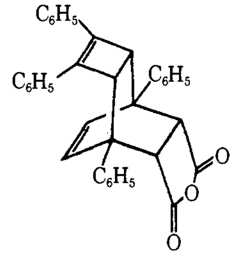
[1] (a) E. H. White and H. C. Dunathan, *J. Am. Chem. Soc.*, 86, 453 (1964); (b) E. H. White and R. L. Stern, *Tetrahedron Letters*, 193 (1964).

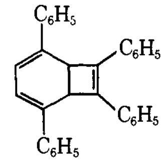
[2] Because of its lability, the photoisomer could not be freed of solvent; *e.g.*, when recrystallized from a toluene–hexane mixture, analysis gave C 93.46, and H 6.19 (*Anal.* calcd for $C_{32}H_{24}$: C, 94.08; H, 5.92); when recrystallized from ethyl ether, C 92.82, H 6.19 (*Anal.* calcd for $C_{32}H_{24} \cdot 0.25C_4H_{10}O$: C, 92.81; H, 6.25). The molecular weight by two methods on four trials averaged 450 (theory 408). Correct analyses were obtained for all other compounds, and molecular weights were determined for key compounds.

trum of II ($\lambda_{max}^{C_6H_{14}}$ 228 nm sh (log ϵ 4.36), 288 (4.13)) and the fluorescence spectrum ($\lambda_{max}^{C_6H_{14}}$ 405 nm) are in agreement with values for model compounds (λ_{max}^{ether} 228 nm sh (log ϵ 4.28), 290 (4.12) for 1,2-diphenyl-3,4-bis(acetoxymethyl)cyclobutene; λ_{max}^{ether} (fluorescence) 382 nm).[3]

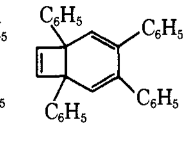
Isomer A forms an adduct with maleic anhydride; structure IV (or a geometrical isomer) is assigned to it on the basis of the physical data which require the presence of a 1,2-diphenylcyclobutene group ($\lambda_{max}^{CH_3OH}$ 292 nm (log ϵ 4.11)).[3] Thus, the *chemical* data are in apparent agreement with structure V for the photoisomer.[4]



IV



V



VI

The fluorescence spectrum of isomer A ($\lambda_{max}^{C_6H_{14}}$ 445 nm), furthermore, is the same as that of dimethyl 1,4-diphenylcyclohexa-1,3-diene-5,6-*trans*-dicarboxylate.[5]

Structure V is ruled out, however, by the nmr spectrum of photoisomer A (Figure 1) and by the absence of an absorption maximum at 290 nm.[3] The nmr spectrum of V would be expected to show two equally weighted nonaromatic signals.[6] The spectrum found for isomer A consists of a complex aromatic multiplet (20 H) and four sharp singlets (one proton each at 6.79, 6.58, 6.31, and 4.69 ppm). The spectrum was unchanged from −40 to +40°, and double-resonance experiments at 100 MHz resulted in no further sharpening of the four singlets.[7]

The data *could* be accounted for by a mixture of V and VI in mobile equilibrium (but slow on an nmr time scale) with selective hydrogenation and derivatization of only form V for steric reasons. However, this hypothesis requires an equilibrium constant of 1 and an enthalpy change of zero for the isomerization.

We prefer, therefore, the view that the photoisomer possesses the unique structure VII. This mono-*trans*-cyclooctatetraene is a rigid structure as judged by molecular models and it exists in a single form, unlike the all-*cis* isomer[8] (eq 1). The rigidity presumably accounts for the high fluorescence of photoisomer A (I is nonfluorescent). The models show, further, that the $C_{2,3}$ double bond of VII is orientated such that the hydrogen at C-3 is in the shielding region of the π bonds ($C_{4,5}$, $C_{1,8}$); thus its nmr signal is shifted upfield from the vinyl region (6.8–6.3 ppm) to 4.69 ppm.[9]

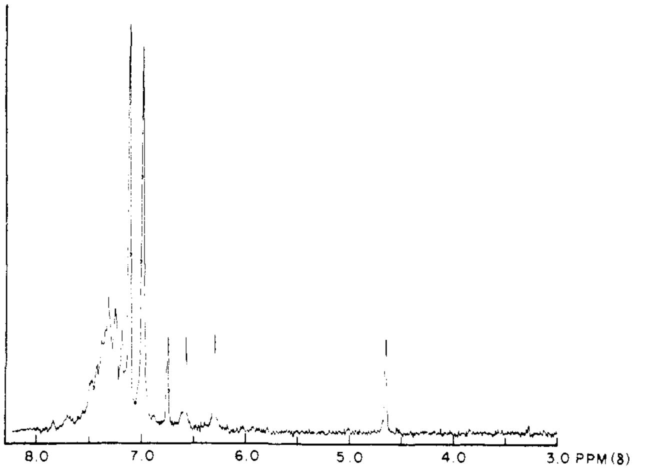
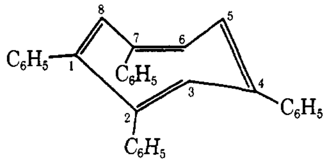
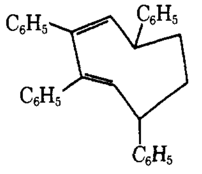


Figure 1. Spectrum (60 MHz) of isomer A in $CDCl_3$ (relative to TMS at 0).



VII



VIII

In addition, the dihedral angles between $H_{1,2}$ and $H_{1,3}$ are sufficiently removed from 0 and 90°, respectively, that their coupling constants appear to be zero (also found for I[1a]). Structure VII for the isomer is also consistent with the fact that the infrared and ultraviolet spectra of I[1a] and photoisomer A (=VII; $\lambda_{max}^{C_6H_{14}}$ 255 nm (log ϵ 4.38), 350 (4.05)) are quite similar.

None of the other four *cis,cis,cis,trans* forms related to VII nor the three forms with two *trans* double bonds account as satisfactorily for the properties of the photoisomer. In addition, other ring systems such as tricyclo[5.1.0.$0^{4,8}$]octa-2,5-diene (semibullvalene), tricyclo[3.3.0.$0^{2,6}$]octa-3,7-diene, tricyclo[4.1.1.$0^{7,8}$]octa-2,4-diene, tricyclo[4.2.0.$0^{2,5}$]octa-3,7-diene, and dihydrophenanthrene (from *ortho,ortho* bridging of the 1,2 phenyl groups) can be ruled out by one or more of the experimental facts.

Using this model (VII) for the photoisomer, we interpret the hydrogenation (eq 2) in terms of saturation of the most exposed double bonds to form VIII as a transient intermediate, followed by conrotatory cycliza-

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(3) Other uv models were reported by E. H. White and J. P. Anhalt, *Tetrahedron Letters*, 3937 (1965), and A. T. Blomquist and Y. C. Meinwald, *J. Am. Chem. Soc.*, **81**, 667 (1959).

(4) Irradiation of cyclooctatetraene has been reported to yield bicyclo[4.2.0]octatriene absorbing in the ultraviolet at 283 nm (G. J. Fonken, *Chem. Ind.* (London), 1625 (1963)). The same compound (uv absorption at 273 and 277 nm) has been reported from a chemical synthesis by E. Vogel, H. Kiefer, and W. R. Roth, *Angew. Chem.*, **76**, 432 (1964). In our hands, only impure cyclooctatetraene led to a photoproduct above *ca.* −120°. Irradiation of the impure cyclooctatetraene at 2537 Å led to a new absorption maximum at 281 nm, which disappeared on warming the sample to 100°.

(5) L. F. Fieser and M. J. Haddadin, *J. Am. Chem. Soc.*, **86**, 2392 (1964).

(6) N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964.

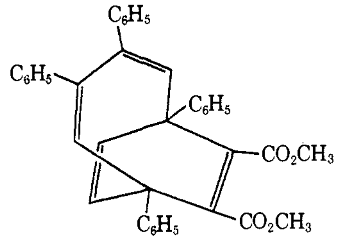
(7) Attempts to measure the ^{13}C–H satellite spectrum have failed because of the thermal instability of the photoisomer and its low solubility.

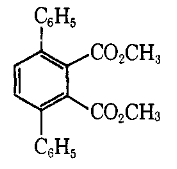
(8) F. A. L. Anet, A. J. R. Bourn, and Y. S. Lin, *J. Am. Chem. Soc.*, **86**, 3576 (1964).

(9) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959, p 129; W. A. Ayer, C. E. McDonald, and J. B. Stokes, *Can. J. Chem.*, 41, 1113 (1963); W. L. Meyer and R. W. Huffman, *Tetrahedron Letters*, 691 (1962).

tion[10,11] to give II. The formation of adduct IV is accounted for similarly by 1,4 bonding with the exposed C-4,5,6,7 diene system or by interception of species V.

The adduct of VII with dimethyl acetylenedicarboxylate did not contain a 1,2-diphenylcyclobutene chromophore ($\lambda_{\max}^{\mathrm{CH_3OH}}$ 272 nm (log ϵ 3.96); $\lambda_{\max}^{\mathrm{C_6H_{14}}}$(fluorescence) 385 nm) and on irradiation it yielded dimethyl 3,6-diphenylphthalate (X). These and other data lead to structure IX for this adduct and confirm the position of attack of the dienophile at carbons 4 and 7 of photoisomer VII.


IX


X

Acknowledgment. We thank the Petroleum Research Fund of the American Chemical Society (PRF 328-A) for its support of this work.

(10) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965); R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).

(11) Cyclization of a *cis,trans*-1,3-cyclooctadiene has been reported (K. M. Schumate, P. N. Neuman, and G. J. Fonken, *J. Am. Chem. Soc.*, **87**, 3996 (1965); R. S. H. Liu, *ibid.*, **89**, 112 (1967)).

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Received October 19, 1968

The Mechanism of Hydrolysis of Diethyl 2-Carboxyphenylphosphonate[1]

Sir:

The hydrolysis of diethyl 2-carboxyphenylphosphonate, I, has been estimated[2] to proceed some 8 × 10^7 times faster than that of the *para* isomer. A mechanism involving general acid catalysis was suggested[2] similar to that advocated by Bender and Lawlor[3] for salicyl phosphate. We have investigated the reaction in detail with the following results and conclusions.

The rate of hydrolysis of the first ester function[4] of I, followed by pH-stat titration, is expressed by eq 1, giving the pH profile shown in Figure 1. The rate of hydrolysis of diethyl 2-carboxymethylphenylphosphonate,[5] VII, $pK_a = 4.2$, was found to be 5.4×10^{-5} min^{-1} at pH 3.0 and 79.5° which is some *10⁵ times slower* than that of the diester I. The final hydrolysis product of I is the acid III.

Partial hydrolyses of I in D_2O at pD 3.5 were halted by the addition of alkali to pD 10 and shown to contain an intermediate not present in the products of complete hydrolysis and having the same nmr spectrum as the monoester II, which is best obtained by controlled alkaline hydrolysis of the ester anhydride V. The pH profile for the hydrolysis of the monoester II, which can be followed by change in optical density[6] at 252 nm, is well expressed by eq 2 (Figure 1).

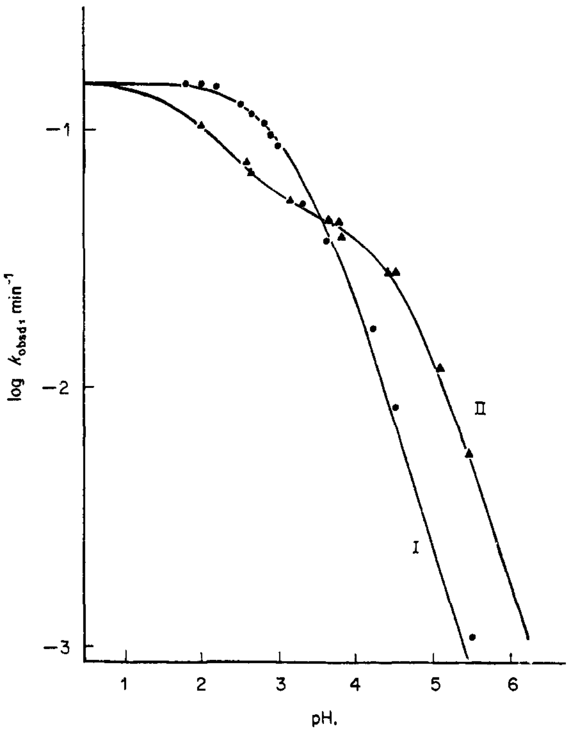
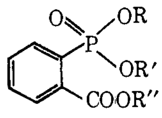
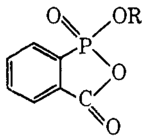


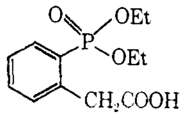
Figure 1. Dependence of k_{hydr} on pH. Solid lines calculated from rate constants given in text. Experimental values: diester I, ●; monoester II, ▲.

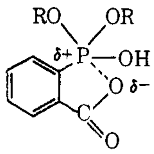


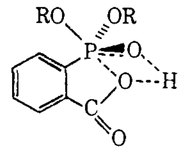
I, R = R′ = Et; R″ = H
II, R = Et ; R′ = R″ = H
III, R = R′ = R″ = H
IV, R = Et; R′ = Me; R″ = H



V, R = Et
VI, R = H


VII


A


B

$$k_{\mathrm{I}}^{\mathrm{obsd}} = 0.156a_{\mathrm{H}}/(a_{\mathrm{H}} + K_1)\ \mathrm{min}^{-1} \qquad (1)$$

$$k_{\mathrm{II}}^{\mathrm{obsd}} = \frac{0.15a_{\mathrm{H}}^2 + 0.0637K_2a_{\mathrm{H}}}{K_2K_3 + K_2a_{\mathrm{H}} + a_{\mathrm{H}}^2}\ \mathrm{min}^{-1} \qquad (2)$$

$K_1 = 7.08 \times 10^{-4}$, $K_2 = 7.94 \times 10^{-3}$, and $K_3 = 3.98 \times 10^{-5}\ M$.

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[1] This research was supported in part by a scholarship (to M. J. B.) from the United Coke and Chemical Co.

[2] M. Gordon, V. A. Notaro, and C. E. Griffin, *J. Am. Chem. Soc.*, **86**, 1898 (1964).

[3] M. L. Bender and J. M. Lawlor, *ibid.*, **85**, 3010 (1963).

[4] All kinetic experiments were performed in aqueous solution, ionic strength 0.1 at 25 ± 0.1°, except where otherwise indicated.

[5] All new compounds described have been adequately characterized by analytical and spectroscopic data.

[6] Although hydrolysis of II produces a second phosphorus acid function, $pK_a = 9.17$, II is fully protonated in the pH range studied for the hydrolysis of I and does not interfere with the first-order kinetic form of k^{obsd}.