

Figure 1.

independently from the n.m.r. spectrum of the cyclobutane ring protons of anemonin.

As expected, an A_2B_2 type spectrum was observed for the $-\text{CH}_2-\text{CH}_2-$ portion of the cyclobutane ring (Figure 2). This pattern requires the presence of two-fold symmetry. The parameters of the spectrum are: $\delta = 0.1716$ p.p.m., $J_a = 10.72$ c.p.s., $J_b = 2.24$ c.p.s., $J_1 = 10.19$ c.p.s., and $J_2 = -12.15$ c.p.s. J_a and J_b are coupling constants between equivalent protons and J_1 and J_2 are coupling constants between nonequivalent protons. J_a and J_b will then be either the two vicinal *cis* coupling constants in the case of the *cis* isomer, or the two *trans* coupling constants in the case of the *trans* isomer. Vicinal coupling constants are a function of dihedral angles.² In the *cis* compound where the members of each pair of equivalent protons are very nearly eclipsed ($\vartheta_a \approx \vartheta_b \approx 0$), J_a and J_b will be of similar magnitude, but in a *trans* compound, where the dihedral angles ϑ_+ and ϑ_- (Figure 1) need not be equal, J_a and J_b , which are now *trans* coupling constants, can be quite different. In fact, in the present case they differ by about 8 c.p.s.; a difference of this magnitude has not been reported as yet for vicinal proton coupling constants in cyclobutanes.

This immediately suggested a *trans* configuration for anemonin, as indeed was found to be the case.¹ Furthermore, a comparison of the two *trans* coupling constants J_a and J_b allows one to estimate the angle of twist, α , of the cyclobutane ring. For this purpose we assume that the cyclobutane ring is very nearly a (twisted) square, which is borne out by the X-ray data,³ and that the $H_a' C' H_b'$ and the $H_a'' C'' H_b''$ planes bisect the $CC' C''$ and $CC'' C'$ angles, respectively; that is, that C_{2v} symmetry prevails about the carbon atoms C' and C'' . Then the two dihedral angles ϑ_+ and ϑ_- can be related with the $H_a' C' H_b'$ and $H_a'' C'' H_b''$ angle and the angle of twist by

$$\cos \vartheta_{\pm} = \frac{1/2 - \tan^2 (1/2 \varphi \pm \alpha)}{1/2 + \tan^2 (1/2 \varphi \pm \alpha)}$$

A simplified Karplus relation $J = A \cos^2 \vartheta$ can now be used to estimate the angle of twist for a reasonable range of φ values between 110 and 114° (also suggested by the X-ray data³). The inherent uncertainty of A is eliminated by using the ratio of J_a and J_b . This procedure is justified because we are dealing with dihedral angles in the same molecule which both lie between 90 and 180° .

(2) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); cf. also M. Karplus, *J. Am. Chem. Soc.*, **85**, 2870 (1963), and references therein.

(3) I. L. Karle and J. Karle, private communication.

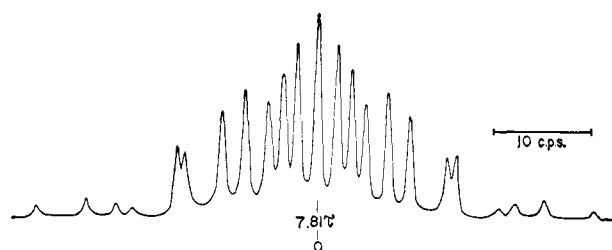


Figure 2. N.m.r. spectrum (100 Mc.) of $-\text{CH}_2-\text{CH}_2-$ protons of anemonin (concentrated CH_2Cl_2 solution).

From the above considerations we estimate the angle of twist to be between 9 and 11° . This is in excellent agreement with the figure of $9.9 \pm 0.3^\circ$ derived from X-ray data.³ Encouraged by this agreement, we are investigating similar cyclobutane systems in order to test the general validity of this method.

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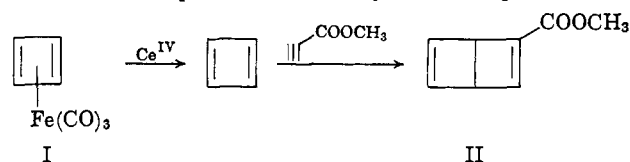
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Cyclobutadiene

Sir:

Although diene-iron tricarbonyl complexes are usually thermally stable and relatively inert chemically, nonetheless they can be readily decomposed at low temperatures, with liberation of the free diene, upon treatment with such oxidizing agents as ferric or ceric ions. We have previously taken advantage of this feature for the preparation of dienes not readily available by more standard procedures.¹ The purpose of this note is to present evidence that this same reaction sequence allows for the preparation of cyclobutadiene.²

Initial studies showed that cyclobutadieneiron tricarbonyl (I) decomposed in the presence of ceric ions to give, together with other materials, a dimer of cyclobutadiene.³ It has now been shown that, when conducted in the presence of acetylenic compounds, the



(1) J. D. Holmes and R. Pettit, *J. Am. Chem. Soc.*, **85**, 2531 (1963); D. H. Gibson and R. Pettit, *ibid.*, **87**, 2620 (1965).

(2) For leading reference to recent attempts to prepare cyclobutadiene see M. A. Avram, I. G. Dinulescu, E. Marica, G. Mateescu, E. Sliam, and C. D. Nenitzescu, *Ber.*, **97**, 382 (1964). Reference to the pertinent earlier work is given by E. Vogel, *Angew. Chem.*, **72**, 4 (1960); W. Baker and J. F. W. McOmie in "Non-Benzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience Publishers, Inc., New York, N. Y., 1959, p. 43.

(3) G. F. Emerson, L. Watts, and R. Pettit, *J. Am. Chem. Soc.*, **87**, 133 (1965).

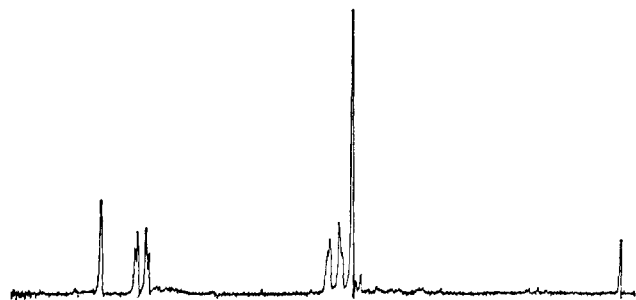


Figure 1. N.m.r. spectrum of 2-carbomethoxybicyclo[2.2.0]hexa-2,5-diene.

decomposition leads to the formation of the Dewar benzene derivatives expected from the addition of an acetylene to cyclobutadiene.

Addition of ceric ammonium nitrate to a cold solution of cyclobutadieneiron tricarbonyl and methyl propiolate in alcohol affords 2-carbomethoxybicyclo[2.2.0]hexa-2,5-diene (II); the product is readily purified by liquid chromatography on silica gel.

The n.m.r. spectrum of the adduct is shown in Figure 1. The six absorption bands, occurring at τ 2.90, 3.37, 3.51, 6.00, 6.16, and 6.32 (with relative areas of 1:1:1:1:1:3), can be clearly assigned to the protons on carbon atoms 3, 6, 5, 1, 4, and the ester group, respectively. The positions of the olefinic and bridgehead protons in II are in close proximity with those reported for the corresponding hydrogens in bicyclo[2.2.0]hexa-2,5-diene (τ 3.45 and 6.16, respectively).⁴ Upon heating to 90° for 30 min. compound II is completely isomerized to methyl benzoate.

Similar decomposition of the complex I in the presence of dimethyl acetylenedicarboxylate yields 2,3-dicarbomethoxybicyclo[2.2.0]hexa-2,5-diene. This compound, which is also purified by chromatography on silica gel, exhibits absorption bands in the n.m.r. spectrum at τ 3.39, 6.02, and 6.25 (relative areas 1:1:3); the first two of these being rather broad, indicating weak coupling between the two. The material is completely isomerized to dimethyl phthalate upon heating to 90° for 0.5 hr.

Apart from its intrinsic interest as far as cyclobutadiene is concerned, the trapping of cyclobutadiene with acetylenes promises to provide a method of general utility for the synthesis of "Dewar benzene" derivatives. For example, we have identified *o*-xylene, benzoic acid, benzyl alcohol, benzaldehyde, and benzene as being produced upon thermal isomerization of the initial products of the reaction of cyclobutadiene with 2-butyne, propiolic acid, propargyl alcohol, propargyl aldehyde, and acetylene, respectively. The utility of this reaction is being studied further, and the results will be reported later.⁵

Of critical importance in the present problem is the question as to whether free cyclobutadiene is involved in these reactions or whether they proceed *via* some organometallic intermediate which reacts with the acetylene and subsequently undergoes oxidative decomposition with liberation of the bicyclohexadiene

(4) E. E. van Tamelen and S. P. Pappas, *J. Am. Chem. Soc.*, **85**, 3297 (1963).

(5) Analogous attempts to prepare Dewar benzene derivatives through the dehalogenation of dichlorotetramethylcyclobutene with zinc in the presence of acetylenes were unsuccessful, although low yields of the corresponding benzene derivatives were obtained: C. E. Berkoff, R. C. Cookson, J. Hudec, D. W. Jones, and R. O. Williams, *J. Chem. Soc.*, 194 (1965).

derivative.⁶ In order to provide an answer to this question the following experiment was devised.

A solution of the complex I in alcohol was slowly added to a flask containing a stirred aqueous solution of ceric ammonium nitrate maintained at 0°. The gases which evolved were passed through a short tube and led into a second flask immersed in liquid nitrogen. A water aspirator was attached to the second flask and a pressure of 100 mm. was maintained in the system. After completion of the addition, the apparatus was disconnected and a cold ethereal solution of methyl propiolate was added to the material which had collected in the receiver flask. The ether solution was then heated and analyzed by vapor phase chromatography. The experiment was repeated several times, and in each case small amounts of methyl benzoate were detected in the product.

We interpret this to mean that free cyclobutadiene is liberated in the reaction between the complex and ceric ions and that this hydrocarbon, although obviously extremely reactive, nonetheless possesses a finite lifetime.

Further reactions of cyclobutadiene, especially those which might indicate the nature of the spin multiplicity of the ground state of the molecule, are being studied; the results of these will be presented subsequently.⁷

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(6) A summary of the analogous difficulties involved in the attempted preparation of tetramethylcyclobutadiene are summarized by P. S. Skell and R. J. Peterson, *J. Am. Chem. Soc.*, **86**, 2530 (1964).

(7) On the basis of the type of products produced upon the dehalogenation of dichlorotetramethylcyclobutene by sodium-potassium vapors at 250° Skell and Peterson concluded that tetramethylcyclobutadiene possessed a triplet ground state.⁶ However, the severity of the experimental conditions is such that these experiments may possibly not reflect the true nature of the ground state.

(8) University of Texas Socony-Mobil Fellow, 1964-1965.

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Cyclobutadieneiron Tricarbonyl. A New Aromatic System¹

Sir:

The preparation of a stable metal complex of cyclobutadiene, the iron tricarbonyl complex I, was recently described.² We now wish to report data which indicate that this complex is aromatic in the sense that it undergoes electrophilic substitution reactions to yield a series of new cyclobutadiene complexes. These reactions, which find a close parallel in the well-known substitution reactions of ferrocene, are summarized below.

Reaction of cyclobutadieneiron tricarbonyl (I) with acetyl chloride and aluminum chloride in carbon

(1) This paper was reported at the Florida sectional meeting of the American Chemical Society, Gainesville, Fla., May 1965.

(2) G. F. Emerson, L. Watts, and R. Pettit, *J. Am. Chem. Soc.*, **87**, 131 (1965).