

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  $\tau$  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 ( $\tau$  3.45 and 6.16, respectively).<sup>4</sup> 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  $\tau$  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.<sup>5</sup>

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.<sup>6</sup> 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.<sup>7</sup>

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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.<sup>6</sup> 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 System<sup>1</sup>

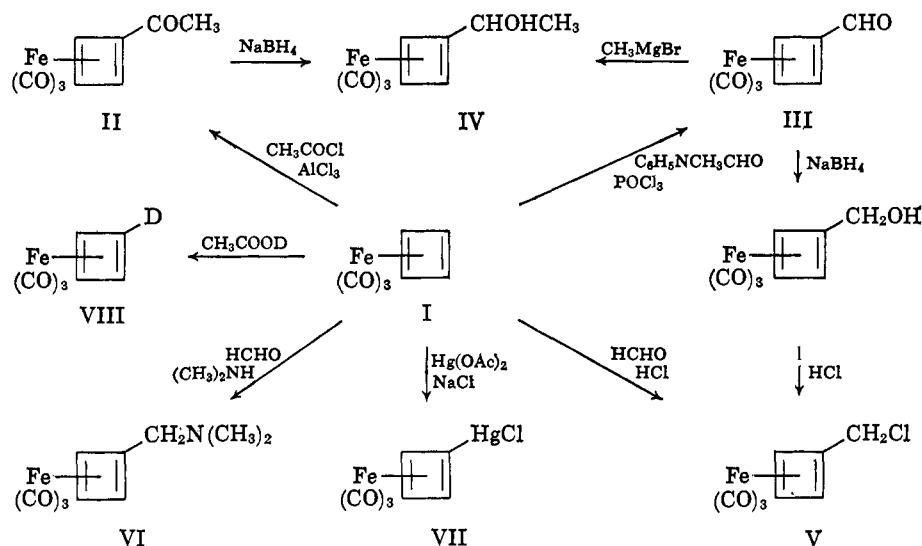
Sir:

The preparation of a stable metal complex of cyclobutadiene, the iron tricarbonyl complex I, was recently described.<sup>2</sup> 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).



disulfide for 45 min. at 20° affords the acetyl complex II in 60% yield.<sup>3</sup> The analogous benzoyl complex is similarly prepared using benzoyl chloride and AlCl<sub>3</sub>.

Formylation of the complex I with POCl<sub>3</sub> and N-methylformanilide affords the iron tricarbonyl complex of cyclobutadienecarboxaldehyde (III). The aldehyde III reacts with methylmagnesium bromide to give the secondary alcohol IV; the alcohol complex IV is also produced upon reaction of the ketone II with NaBH<sub>4</sub>. (Cyclobutadienecarboxylic acid)iron tricarbonyl is obtained from the oxidation of the aldehyde with silver oxide.

Chloromethylation of the complex I leads to the formation of chloromethylcyclobutadieneiron tricarbonyl (V). This same material is rapidly formed in quantitative yield when the primary alcohol complex, obtained by reduction of the aldehyde III with NaBH<sub>4</sub>, is treated with concentrated aqueous HCl.<sup>4</sup>

Reaction of the complex I with HCHO and dimethylamine in acetic acid affords the N-dimethylamino methyl derivative VI. Treatment of I with Hg(OAc)<sub>2</sub> and NaCl gives rise to the chloromercury derivative VII.

The monodeuterio complex VIII is rapidly formed, together with higher deuterated derivatives, when solutions of the complex I in CF<sub>3</sub>COOD are allowed to stand for several minutes. Qualitatively the reactivity of cyclobutadieneiron tricarbonyl toward electrophilic reagents appears to be comparable to that of ferrocene.

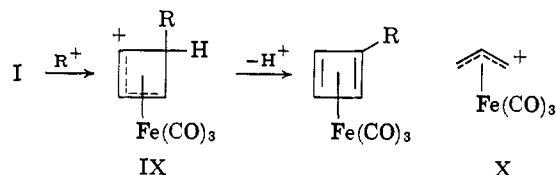
The n.m.r. spectra of these complexes are in complete accord with their assigned structures. The full details of these will be reported later, but it is important to point out that in each monosubstituted derivative of I the n.m.r. spectrum clearly demonstrates the equivalency of the two hydrogens adjacent to the substituent. This indicates that when complexed to the metal atom the cyclobutadiene ring adopts a square arrangement of the carbon atoms<sup>5</sup>; in free cyclobutadiene itself recent calculations suggest that the four carbon atoms lie at the corners of a rectangle.<sup>6</sup>

(3) The C, H, and Fe analytical data for this complex, its 2,4-dinitrophenylhydrazone, and each of the other substituted cyclobutadiene complexes reported in this paper agree within 0.3% of the calculated values. Details of the physical properties of these compounds will be reported in the full paper.

(4) The structure of the stable cationic species which are presumably involved in this facile substitution process is the subject of a forthcoming publication.

(5) The four carbon atoms of the cyclobutadiene ring in the tetraphenylcyclobutadiene-iron tricarbonyl complex have been shown to

Although it is in marked contrast to the notorious instability of cyclobutadiene, the aromatic character of the complex I is readily rationalized in terms of the conventional mechanism for electrophilic substitution of other aromatic systems. Addition of an electrophilic species, R<sup>+</sup>, to the complex I would generate the π-allyl-iron tricarbonyl cationic complex IX. We have previously isolated stable salts of the π-allyl-iron tricarbonyl cation X,<sup>7</sup> and systems of the type IX would therefore be expected to afford a low energy pathway for the substitution process.



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possess a square-planar configuration: R. P. Dodge and V. Schomaker, *Nature*, **186**, 798 (1960).

(6) M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.*, **87**, 3255 (1965).

(7) G. F. Emerson and R. Pettit, *ibid.*, **84**, 4591 (1962). G. F. Emerson, J. E. Mahler, and R. Pettit, *Chem. Ind. (London)*, 836 (1964).

(8) National Institutes of Health Predoctoral Fellow, 1964-1965.

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### Self-Consistent Field Molecular Orbital Calculations for Cyclobutadiene<sup>1</sup>

Sir:

Since cyclobutadiene has at last been synthesized,<sup>2</sup> we thought it of interest to study this molecule in more

(1) This work was supported by the National Institutes of Health, U. S. Public Health Service, through Grant No. GM-11531-02.

(2) L. Watts, J. D. Fitzpatrick, and R. Pettit, *J. Am. Chem. Soc.*, **87**, 3253 (1965).