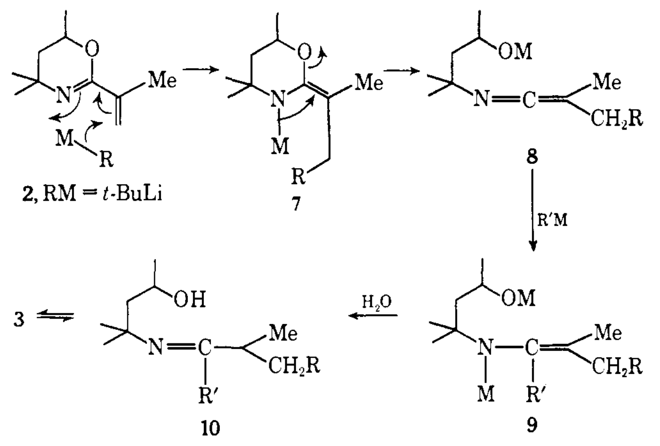

produced the aldehyde **6** in 80% over-all yield (Table I).[6] Although the cyclohexyl group adds but once, it does not deter the use of a second equivalent of a less bulky reagent to form the ketone (entry 8, Table I).

This process does not involve a simple addition to the C=N link of the oxazine **2** since treatment of **5** with RMgX or RLi failed to produce **3** even under forcing conditions.[7] The mechanism of the double alkylation of **2** leading to **3** was shown to involve a subtle *alkylation–ring cleavage–alkylation–ring closure* sequence (**7**–**8**–**9**–**10**–**3**). Confirmation of this pathway was gathered when 1.0 equiv of *t*-butyllithium was added to **2** and the solvent evaporated leaving a hygroscopic salt, which proved to be **8** (M = Li, R = *t*-Bu), ir (mull) 2010 cm^{-1} (very intense).[8] Addition of **8** to water converted it to the *t*-butyl analog of **5**. It, therefore, becomes clear how Grignards and organometallics add to the "oxazine" producing **9**,[9] which upon hydrolysis forms the imine **10**, the tautomer of the cyclic tetrahydro-1,3-oxazine **3**. Further studies on this novel ketone synthesis are in progress with an aim toward preparing cyclic, additional α-alkyl, and optically active ketones.[10]

Acknowledgments. Financial assistance from the Petroleum Research Fund, administered by the American Chemical Society, Ciba Pharmaceutical Co., Hoffman-LaRoche, and Warner-Lambert Research Institute is gratefully acknowledged.

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(6) This product, as well as others prepared in this report containing related structures, complements nicely the aldehyde and ketone synthesis described by H. C. Brown *Accounts Chem. Res.*, **2**, 65 (1969). The products obtained *via* the oxazine route are those which the Brown synthesis would form with difficulty due to the complexity of the olefins required.

(7) The dihydro-1,3-oxazine ring **1**, **2**, or **5** has been found to be totally inert to the Grignard reagent after heating to reflux in ether, benzene, and THF for prolonged periods. This, therefore, represents a new carboxylic acid derivative stable to the Grignard reagent and may be employed as a unique protecting group (A. I. Meyers, I. R. Politzer, B. K. Bandlish, and G. R. Malone, *J. Amer. Chem. Soc.*, **91**, 5886 (1969)).

(8) C. L. Stevens and J. C. French, *ibid.*, **76**, 4401 (1954) reported that a completely aliphatic-substituted ketenimine showed strong absorption at 2045 cm^{-1}.

(9) Ketenimines are well known to react in the above fashion with Grignards and organolithium reagents (C. L. Stevens and R. J. Gasser, *ibid.*, **79**, 6057 (1959)).

(10) Complete experimental details will be sent to anyone upon request.

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Received July 3, 1969

Further Experiments Pertaining to the Ground State of Cyclobutadiene

Sir:

Theoretical calculations continue to offer conflicting results as to the nature of the ground state of cyclobutadiene.[1-3] While there appears to be general agreement that a structure having a square arrangement of carbon atoms would be more stable in its triplet rather than singlet electronic state, calculations differ as to whether this triplet state is more[1] or less stable[2,3] than a singlet state having a rectangular configuration. There is evidence that cyclobutadiene can be liberated from its iron tricarbonyl complex and although the amounts which have been collected and detected separately are extremely small, nonetheless these experiments indicate that the molecule is at least thermodynamically stable, though of course extremely reactive.[4] It has been previously shown that oxidative decomposition of cyclobutadieneiron tricarbonyl in the presence of reagents with which cyclobutadiene would be expected to add does indeed lead to these adducts and frequently in high yield. Thus decomposition of the complex in the presence of such dienophiles as dimethyl maleate,[5] dimethyl fumarate,[5] benzoquinone,[6] dibromobenzoquinone,[6] cyclobutadiene,[5] or benzocyclobutadiene[7] or with dienes such as cyclopentadiene,[5] diethoxycyclopentadiene,[8] or thiapyrone dioxide[9] leads to adducts which have the stereochemistry that would be expected on the basis of normal Diels–Alder rules of addition. On the basis of these results we have suggested that cyclobutadiene possesses a singlet ground state. In the present paper we offer further evidence that these *in situ* experiments give products resulting from the reaction of cyclobutadiene itself and provide added data pointing to a singlet nature for the ground state.

Although other diene–iron tricarbonyl complexes, *e.g.*, butadieneiron tricarbonyl, readily shed the ligands upon oxidation of the Fe^0 in the complex to Fe^{2+},[10] nonetheless in the present instance there would seem to be several possible modes of reaction which could proceed prior to the liberation of *free* cyclobutadiene which should be considered. In our opinion the four most serious alternatives are (a) direct reaction between the reagent, *e.g.*, dimethyl maleate, and the cyclobutadiene complex, (b) replacement of a CO ligand by maleate followed by intramolecular addition to the coordinated cyclobutadiene ligand, (c) replacement of CO by maleate and then addition to the coordinated cyclobutadiene during the oxidation, and (d) external attack by maleate on some oxidized form of the complex having the cyclobutadiene ligand still attached to the iron atom.

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(1) N. L. Allinger, C. Gilardeau, and L. W. Chow, *Tetrahedron*, **24**, 2401 (1968).

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

(3) R. J. Buenker and S. D. Peyerimhoff, *J. Chem. Phys.*, **48**, 354 (1968).

(4) L. Watts, J. D. Fitzpatrick, and R. Pettit, *J. Amer. Chem. Soc.*, **87**, 3253 (1965); W. Tyerman, M. Kato, P. Kebarle, S. Masamune, O. Strausz, and H. Gunning, *Chem. Commun.*, 497 (1967).

(5) L. Watts, J. D. Fitzpatrick, and R. Pettit, *J. Amer. Chem. Soc.*, **88**, 623 (1966).

(6) J. C. Barborak, L. Watts, and R. Pettit, *ibid.*, **88**, 1328 (1966).

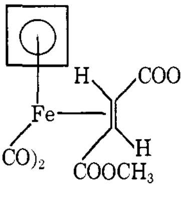
(7) W. Merk and R. Pettit, *ibid.*, in press.

(8) J. C. Barborak and R. Pettit, *ibid.*, **89**, 3080 (1967).

(9) L. A. Paquette and L. D. Wise, *ibid.*, **89**, 6659 (1967).

(10) R. Pettit and G. F. Emerson, *Advan. Organometal. Chem.*, **1**, 31 (1964).

The first of these possibilities is readily eliminated by noting that cyclobutadieneiron tricarbonyl is unreactive toward dimethyl maleate in the absence of oxidizing agents over extended periods. The second possibility is eliminated in the following way. Irradiation of cyclobutadieneiron tricarbonyl in the presence of dimethyl fumarate is found to produce cyclobutadieneiron dicarbonyl–dimethyl fumarate, I. Compound I (yellow crystals, mp 26–27°) displays three singlet absorptions in its nmr spectrum at τ 6.6 (area 6), 6.54 (area 4), and 5.78 (area 2) and in the ir spectrum two metal carbonyl bands are observed at 2065 and 1990 cm^{-1}.[11] Similarly, irradiation in the presence of dimethyl maleate gives rise to the analogous dimethyl maleate complex II, a yellow liquid having three singlet nmr absorptions at τ 6.65 (4), 6.63 (2), and 6.53 (6) and two ir metal carbonyl absorptions at 2038 and 1980 cm^{-1}. Both complexes I and II are stable at 25° over extended periods; in particular, they display no tendency to undergo intramolecular Diels–Alder additions.



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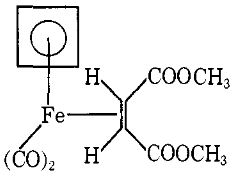
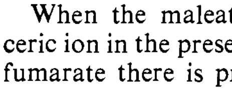
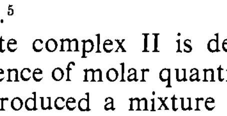


II

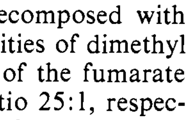
Decomposition of complex I with ceric ammonium nitrate produces the single bicyclohexene dicarboxylic acid derivative III which is also the sole adduct formed when cyclobutadieneiron tricarbonyl is decomposed with ceric ion in the presence of dimethyl fumarate.[5]



III



IV



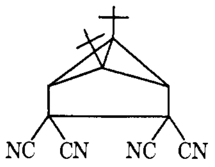
V

Similar oxidative decomposition of complex II produces only the *endo-cis*-bicyclohexenedicarboxylic acid ester IV which is also produced exclusively when cyclobutadieneiron tricarbonyl is decomposed in the presence of dimethyl maleate.[5]

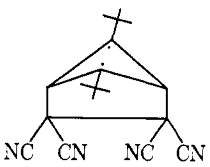
When the maleate complex II is decomposed with ceric ion in the presence of molar quantities of dimethyl fumarate there is produced a mixture of the fumarate adduct III and the isomer IV in the ratio 25:1, respectively. Similar decomposition of the fumarate complex II in the presence of molar quantities of dimethyl maleate produces a mixture of the adducts III and IV, in a ratio of approximately 50:1, respectively. Decomposition of cyclobutadieneiron tricarbonyl in the presence of equimolar amounts of dimethyl fumarate and dimethyl maleate indicates that dimethyl fumarate is the much more reactive reagent as would be expected from the reactivity scale of dienophiles.[12] Furthermore, examination of the nmr spectrum of a mixture of the fumarate complex II and a large excess of dimethyl maleate indicates no ligand exchange of the esters. These data then eliminate the possibility (c) in which intramolecular addition of the cyclobutadiene and dienophilic ligands is supposed to occur during the oxidative decomposition.

Returning to the question as to the ground-state nature of cyclobutadiene, it seems reasonable to expect that a triplet state could exhibit radical type reactivity while a singlet state would behave as a diene in a Diels–Alder manner. A comparison of 1,1-diphenylethylene and dimethyl maleate reveals that the former is more reactive as a radical trapping reagent;[13] whereas the latter is more reactive as a dienophile in a Diels–Alder reaction. Decomposition of cyclobutadieneiron tricarbonyl in the presence of equimolar quantities of 1,1-diphenylethylene and dimethyl maleate yields only the adduct IV and no product corresponding to structure V can be detected. Similarly, in competition between dimethyl fumarate and diphenylethylene, compound III is the only adduct observed. This result is consistent with the hypothesis that cyclobutadiene has a singlet rather than a triplet ground state. These latter experiments at the same time negate possibility d outlined above; any suggested reactive intermediate in the oxidative decomposition of the complex must be either a cation or a cation radical, either of which would be more reactive to diphenylethylene than dimethyl maleate.

VI



VII



VIII

Evidence along separate lines is provided through reactions of 1,3-di-*t*-butylcyclobutadiene (VI). Decomposition of the iron tricarbonyl complex of VI in the presence of tetracyanoethylene affords the dihydrobenzvalene derivative VII in high yield.[14] The appearance of VII is readily explicable in terms of orbital-symmetry arguments provided VI possesses a singlet ground state; in its simplest form the reaction leading to VII is a *cis,trans,trans*-2 + 2 + 2 cycloaddition which is an allowed process according to the Woodward–Hoffmann rules for concerted reactions. However, irrespective of the question of electron spin, if VI possessed a triplet state then the concerted addition leading to VII would not be an allowed process on the basis of orbital symmetry arguments[15,16] and would be required to proceed

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[11] At −78° the two olefinic protons of the fumarate ligand appear as separate absorptions indicating restricted rotation about the Fe-olefinic bond at these temperatures. The elemental analysis of this and the other new compounds listed are in agreement with the proposed formula.

[12] J. Sauer, H. Wiest, and A. Mielert, *Chem. Ber.*, **97**, 3183 (1964).

[13] W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, p 223.

[14] We are grateful to Dr. R. Davis for determining the structure of compound VII by means of X-ray studies. The nmr spectrum of the total crude reaction product yielding VII contained no significant absorptions other than those arising from VII itself (τ 8.77 (s, 18) and 6.35 (s, 2)).

[15] R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 2046 (1965).

[16] Consider the disposition of atoms as shown in formula VI and that the ring lies in the *xy* plane. Then classify the orbitals involved with respect to the *xz* and *yz* symmetry planes, respectively. The ground state of triplet cyclobutadiene with respect to these planes is ψ_1^2(S,S), ψ_2^1(A,S), and ψ_3^1(S,A) and that of tetracyanoethylene is π^2(S,S). Similar classification of the σ orbitals generated in VII is $(\sigma_1 + \sigma_2)^2$(S,S), $(\sigma_1 - \sigma_2)^2$(S,A), and σ_3^2(S,S). Thus the concerted conversion is a symmetry-forbidden process. Similar arguments show that the concerted addition of triplet cyclobutadiene to double bonds leading to bicyclohexene derivatives is also forbidden; however, the intermediate radicals or ions involved in a nonconcerted reaction would have greater stability than would VIII.

via a diradical intermediate such as VIII or some dipolar intermediate. The reaction proceeds very fast at 0° which seems more consistent with a concerted process rather than a two-step process, at least one involving some high-energy radical intermediate such as VIII.

The above data, together with those obtained earlier, all point to a singlet ground state for cyclobutadiene and, since there is general agreement among the various theoretical treatments recently produced that the most stable state of a square configuration should be a triplet state, we consider then that the data also point to a rectangular configuration for the ground state of the molecule.

(17) The authors thank the National Science Foundation, the Petroleum Research Foundation, administered by the American Chemical Society, the U. S. Army (Durham, N. C.), and the Robert A. Welch Foundation for financial assistance. We also thank Badische Anilin und Soda Fabrik for a generous gift of cyclooctatetraene.

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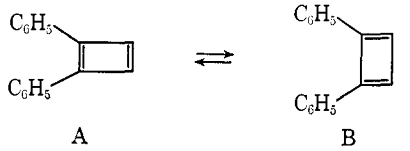
Received April 18, 1969

On the Possible Rectangular Nature of Cyclobutadiene

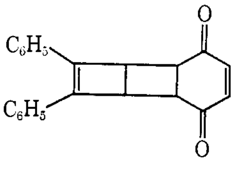
Sir:

The majority of experimental evidence available to date indicates that cyclobutadiene possesses a singlet electronic ground state.[1] This is in agreement with the calculations of Dewar and Gleicher[2] whose theoretical treatment also predicts that the singlet state has the four carbon atoms disposed at the corners of a rectangle, rather than a square, with the molecule having alternating short double bonds and long single bonds. If this geometry is correct, it follows that two isomers of *ortho*-disubstituted cyclobutadienes could exist. The present paper presents data which are consistent with the postulate that two isomeric and interconvertible *o*-diphenylcyclobutadienes exist as indicated in eq 1.



A B (1)

Assuming for the moment that the equilibrium 1 does exist, then because of the sensitivity of Diels–Alder additions to steric effects it would be expected that isomer B (1,4-diphenylcyclobutadiene) would be more reactive as a diene than isomer A (1,2-diphenylcyclobutadiene). In agreement with this we find that liberation of *o*-diphenylcyclobutadiene, through oxidative degradation of its iron tricarbonyl complex,[3] in the presence of benzoquinone yields only the Diels–Alder adduct I and in high yield.[4] The structure of compound I (yellow crystals, mp 173°) follows from its nmr spectrum which consists of absorptions at τ 2.62 (multiplet, area 10), 3.50 (singlet, area 2), 5.82 (complex, area 2), and 6.23 (complex, area 2).[5] Using N-phenylmaleimide which, like benzoquinone, is rated as a moderately active dienophile[6] again gives rise only to the symmetrical adduct II. Compound II (white crystals, mp 203°) exhibits absorptions centered at τ 2.70 (complex, area 15), 5.91 (area 2), and 6.25 (area 2), the latter absorptions appearing as an A_2B_2 system. Compounds I and II would result from Diels–Alder addition to the isomeric form B and inspection of the nmr spectrum of the total crude reaction product in each case fails to reveal the presence of any adduct which would follow from addition of the dienophiles with isomer A.



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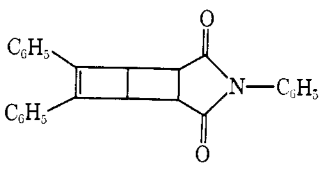
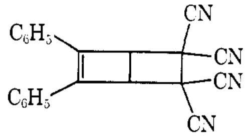
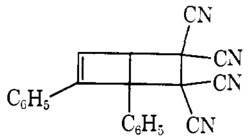


II

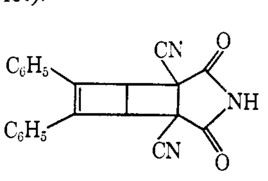
The reaction however takes a different course when extremely reactive dienophiles are employed. With tetracyanoethylene[6] *o*-diphenylcyclobutadiene cleanly yields the two adducts III and IV in the ratio 1:7, respectively.[4] The major isomer, IV (white crystals, mp 112°), apart from the ten aromatic protons at τ 2.48, exhibits one olefinic proton at τ 2.84 (doublet, J = 1.0 cps) and one allylic proton at τ 5.12 (doublet). The isomeric adduct III (white crystals, mp 202°) displays nmr absorptions at τ 2.55 (complex multiplet, area 10) and 5.13 (singlet, area 2). Almost identical behavior is seen with dicyanomaleimide which is an even more reactive dienophile than tetracyanoethylene.[7] Addition of dicyanomaleimide to *o*-diphenylcyclobutadiene produces the two isomeric adducts V and VI again in a ratio of 1:7, respectively. Compound V (white crystals, mp 248°) has absorptions at τ 2.6 (multiplet, area 10) and 5.31 (singlet, area 2) while compound VI (white crystals, mp 115°) displays nmr absorptions at τ 3.10 (area 1, doublet), 5.20 (area 1, doublet), and 2.80 (area 10, multiplet).



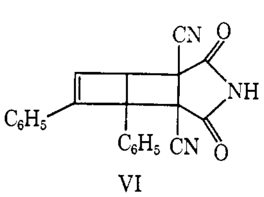
III



IV



V



VI

The most direct explanation of the above results is that *o*-diphenylcyclobutadiene exists as an equilibrium mixture of the two isomers A and B. With moderately active dienophiles the rate of interconversion of A and B is fast compared to the Diels–Alder addition and the

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(1) P. Reeves, J. Henery, and R. Pettit, *J. Amer. Chem. Soc.*, **91**, 5888 (1969).

(2) M. J. S. Dewar and G. J. Gleicher, *ibid.*, **87**, 3255 (1965).

(3) G. G. Emerson, L. Watts, and R. Pettit, *ibid.*, **87**, 131 (1965).

(4) The nmr spectrum of the total crude reaction product reveals no significant absorptions other than those due to the indicated product.

(5) The elemental analysis of this and each of the other new compounds reported are in agreement with those expected from the proposed structure. The stereochemistry of the Diels–Alder adducts reported has not been determined.

(6) J. Sauer, H. Wiest, and A. Mielert, *Chem. Ber.*, **97**, 3183 (1964).

(7) J. Sauer and B. Schroder, *Angew. Chem. Intern. Ed. Engl.*, **4**, 711 (1965).