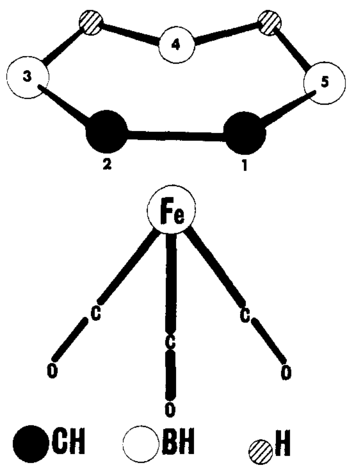

Figure 2. Proposed structure of (π-$C_2B_3H_7$)$Fe(CO)_3$.

100-MHz proton nmr spectrum of I in CCl_4 contains a sharp C–H singlet of area 2 at δ -5.58 ppm relative to $(CH_3)_4Si$, as well as partially overlapped quartets at δ -6.30, J = 152, area 2; δ -4.87, J = 152, area 1; and δ -0.24, J = 160, area 1, assigned to H–B(4,6), H–B(5), and H–B(1), respectively.

The ir spectrum of I (CCl_4 solution *vs.* CCl_4) contains two very strong CO stretching bands at 2076 and 2017 cm^{-1}, in agreement with the proposed structure; the only other well-defined absorptions are at 3090 (m), 2960 (w), 2590 (vvs, BH stretch), 1270 (vs), and 1188 (s) cm^{-1}. No significant bands are present in the B–H–B stretching region.

The more volatile complex is a pale yellow liquid, identified as (π-$C_2B_3H_7$)$Fe(CO)_3$ (II), for which the structure in Figure 2 is proposed. The mass spectrum exhibits a sharp cutoff at *m/e* 204, corresponding to the parent ion, and the observed relative intensities in the parent region are in very close agreement with those calculated for the indicated composition.[7] Most importantly, the presence of three boron atoms is unequivocally established. As with complex I, the presence of three CO groups in the mass spectrum is shown by intense peak groupings at *m/e* 176, 148, and 120.

The ^{11}B nmr spectrum of a CCl_4 solution of II consists of one broad, slightly asymmetric doublet at δ -4.90, $J \approx 135$, indicating that all three boron atoms are in similar electronic environments. Significantly, no other peaks were found, in agreement with a structure having no apex boron atoms. The 100-MHz proton nmr of II in CCl_4 contains a sharp C–H resonance of area 2 at δ -5.38, as well as quartets at δ -7.42, J = 126, area 1, and δ -3.70, J = 135, area 2, assigned to H–B(4) and H–B(3,5) respectively. In addition, a broad hump of area 2 centered at δ $+3.7$ is attributed to the bridge proton resonance. The ir spectrum of II (CCl_4 solution *vs.* CCl_4) exhibits very strong CO stretching bands at 2068 and 2007 cm^{-1} and other principal absorptions at 3008 (m), 2569 (vvs, BH stretch), 1888 (ms, B–H–B stretch), 1700 (m), 1600 (m), 1350 (m), and 1050 (m) cm^{-1}.

Somewhat surprisingly, complex I is less thermally stable than II, the former decomposing at 230° while II is unchanged at that temperature. Solutions of the complexes in CCl_4 appear to be unaffected by exposure to air for several hours, as monitored by ir spectra. Investigations of these compounds and related species are continuing.

Acknowledgments. This work was supported by the Office of Naval Research.

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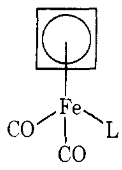
Received October 10, 1970

Cycloaddition Reactions between Cyclobutadiene and Unsaturated Molecules Coordinated to Iron

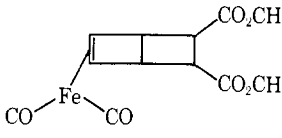
Sir:

We wish to report on some novel cycloaddition reactions between cyclobutadiene and other olefinic systems while both components are coordinated to a transition metal and to demonstrate the potential of these reactions in organic synthesis.

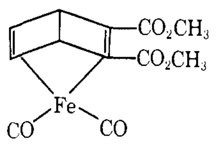
We had previously shown[1] that cyclobutadieneiron tricarbonyl, upon irradiation in the presence of dimethyl maleate, afforded cyclobutadiene(dimethyl maleate)iron dicarbonyl (I, L = dimethyl maleate). An analogous compound (I, L = dimethyl fumarate) was obtained when the irradiation was conducted in the presence of dimethyl fumarate.[1] Both complexes were of normal stability. In particular, they displayed no tendency to undergo cycloaddition reactions leading to the complex II; this is in strong contrast to the very facile addition which occurs between cyclobutadiene and dimethyl maleate and dimethyl fumarate when neither of the reagents is coordinated to a metal.[2] However, irradiation of cyclobutadieneiron tricarbonyl in the presence of dimethyl acetylenedicarboxylate affords only dimethyl phthalate and no intermediate complex analogous to I can be isolated.



I



II



III

A rational explanation for the difference in behavior of the acetylenic and olefinic dienophiles is that in both instances the light acts on the iron–carbonyl complex to eject a molecule of carbon monoxide; the resultant cyclobutadieneiron dicarbonyl then reacts with both the acetylene and olefin derivatives to form complexes of the type I. In the case where L is the acetylenic ligand, the molecule undergoes intramolecular cycloaddition to generate the Dewar benzene complex III which suffers further degradation to dimethyl phthalate. The formation of such a Dewar benzene complex would involve loss of only one of the five coordinate bonds about the iron atom in I whereas a similar cycloaddition reaction with the maleate ligand, leading to the complex II, would require loss of two coordinating bonds and would be energetically less favorable.

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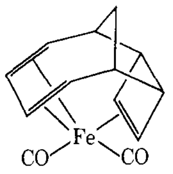
(10) R. N. Grimes, *J. Amer. Chem. Soc.*, **88**, 1895 (1966).

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

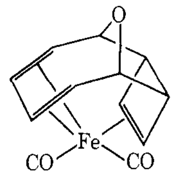
(2) L. Watts, J. D. Fitzpatrick, and R. Pettit, *ibid.*, **88**, 623 (1966).

These observations prompted the present investigation involving other olefinic systems capable of undergoing cycloaddition reactions.

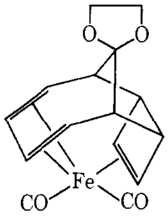
Irradiation of cyclobutadieneiron tricarbonyl in ether containing cycloheptatriene afforded an orange crystalline solid (mp 102°; yield 20%) having the molecular formula $C_{11}H_{12}Fe(CO)_2$.[3] The material displayed two metal carbonyl absorptions in the ir spectrum at 1990 and 1929 cm^{-1} and showed absorptions in the pmr spectrum at δ 1.05 (m, 1 H), 1.4 (d, 1 H), 2.6 (m, 2 H), 3.45 (m, 2 H), 4.55 (m, 2 H), 5.7 (m, 2 H), and 6.45 (t, 2 H).[4] The structure of the complex which has been confirmed by X-ray analysis is given in formula IV.[5]



IV



V



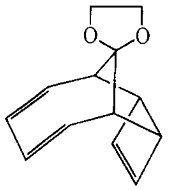
VI

We consider that the complex IV arises through photolytic loss of carbon monoxide from cyclobutadieneiron tricarbonyl followed by complexation of cycloheptatriene (I, L = C_7H_8) and intramolecular cycloaddition of the two hydrocarbon ligands. It is to be noted that the formation of IV from the intermediate cyclobutadiene–(cycloheptatriene) complex I involves no loss of coordination number for the iron atom. The stereochemistry of the ligand in the complex IV and the analogous reactions with other triene systems (*vide infra*) support this proposed sequence of events.

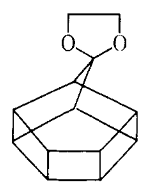
Irradiation of cyclobutadieneiron tricarbonyl with oxepin[6] afforded, in low yield (2%), the analogous complex V as an orange crystalline solid (mp 177°). The ir and pmr spectra of the oxepin adduct V very closely resembled that of the complex IV; the two ir metal–carbonyl absorptions appeared at 1995 and 1930 cm^{-1}, while pmr absorptions were observed at δ 2.95 (m, 1 H), 4.0 (m, 2 H), 5.35 (m, 1 H), and 5.95 (t, 1 H).

With tropone as the coreactant the irradiation of cyclobutadieneiron tricarbonyl afforded only polymeric material; however with the ethylene ketal of tropone[7] the reaction proceeded normally to yield the complex VI as an orange crystalline solid (mp 135° dec; yield 10%). The complex VI displayed metal–carbonyl ir absorptions at 1995 and 1934 cm^{-1} and pmr absorptions at δ 2.3 (m, 1 H), 3.3 (m, 1 H), 3.55 (t, 2 H), 4.25 (m, 1 H), 5.75 (m, 1 H), and 6.35 (t, 1 H).

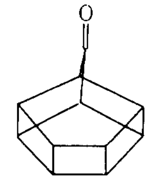
Degradation of the complex VI with ceric ion produced the free ligand VII[8] (yield, 80%) which upon irradiation for 1 hr in ether[3] gave the saturated cage ketal VIII (yield, 20%).[9] Hydrolysis of VIII afforded homopentaprismanone (IX) as a white crystalline solid (mp 154°; yield 84%); the ketone displayed an ir carbonyl absorption at 1775 cm^{-1} and pmr absorptions at δ 2.18 (m, 1 H) and 3.3 (m, 4 H).



VII



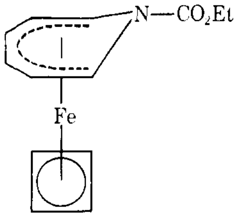
VIII



IX

The irradiation of cyclobutadieneiron tricarbonyl with *N*-carboethoxyazepine[10] yielded an orange crystalline organo–iron complex (mp ~130° dec; yield 30%) which contained no absorptions in the metal–carbonyl region of its ir spectrum. The material possessed pmr absorptions at δ 1.1 (t, 3 H), 3.7 (s, 4 H), 3.9 (m, 2 H), 4.55 (m, 2 H), 5.2 (m, 2 H), and 6.2 (m, 2 H), and the elemental analysis indicated the substance to be a cyclobutadiene–(azepine) iron derivative. The detailed structure of the substance was determined by X-ray analysis which revealed the material to have the sandwich formulation X.[5]

The novel sandwich compound X presumably arises *via* the replacement of one carbon monoxide ligand by the azepine derivative in a manner common to the reactions described above. However, for unknown reasons, the major part of the reaction prefers to proceed *via* further displacement of carbon monoxide ligands by olefinic bonds rather than by intramolecular cycloaddition as with the other triene systems mentioned.



X

Although cyclobutadiene can be detected by mass spectrometric means upon gas-phase photolysis of its iron–carbonyl complex,[11] it would seem from the present work that it does not necessarily follow that metal free products obtained upon irradiation of cyclobutadieneiron tricarbonyl with various substrates result from reactions of free cyclobutadiene.[12]

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(3) This, and each of the other irradiation experiments reported in this paper, was performed using anhydrous ether as the solvent and a 450-W Hanovia ultraviolet lamp equipped with a Vycor filter as the lamp source. For the reactions between cyclobutadieneiron tricarbonyl and a triene derivative the photolyses were conducted in 4 hr and the products purified by chromatography over alumina; except in the case of the oxepin reaction no significant amounts of organo–iron complexes other than the product indicated and unreacted cyclobutadieneiron tricarbonyl were detected.

(4) The elemental analyses of this and the other new compounds listed are in agreement with the proposed formula.

(5) R. E. Davis and H. D. Simpson, personal communication, The University of Texas, Austin, Tex. The details of the structural determination are to be published.

(6) E. Vogel, W. A. Böll, and H. Günther, *Tetrahedron Lett.*, 609 (1965).

(7) H. E. Simmons and T. Fukunaga, *J. Amer. Chem. Soc.*, **89**, 5208 (1967).

(8) The pmr spectrum of the ketal VII exhibited absorptions at δ 2.35 (m, 1 H), 3.45 (d, 1 H), 3.85 (s, 2 H), 5.5 (m, 2 H), and 6.0 (s, 1 H). The white crystalline compound polymerizes on heating.

(9) The pmr spectrum of the cage ketal VIII exhibited absorptions at δ 2.25 (m, 1 H), 3.17 (m, 4 H), 3.95 (s, 2 H). The compound melted at 105° and gave a parent molecular ion in its mass spectrum at *m/e* 202.

(10) W. Lwowski and J. J. Maricich, *J. Amer. Chem. Soc.*, **87**, 3630 (1965).

(11) W. Tyerman, M. Kato, P. Kebarle, S. Masamune, D. Strausz, and H. Gunning, *Chem. Commun.*, 497 (1967).

(12) Thus the recent data presented by Font, Barton, and Strausz[13] could possibly proceed *via* a reaction path involving an intermediate cyclobutadieneiron dicarbonyl derivative and its subsequent decomposition and not one involving free cyclobutadiene.

(13) J. Font, S. C. Barton, and O. P. Strausz, *Chem. Commun.*, 499 (1970).

Further reactions of coordinated cyclobutadiene and their utility in the synthesis of strained molecules of interest will be discussed in subsequent papers.

Acknowledgment. The authors thank the National Science Foundation, the Petroleum Research Fund (administered by the American Chemical Society), and the Robert A. Welch Foundation for financial support.

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Received August 12, 1970

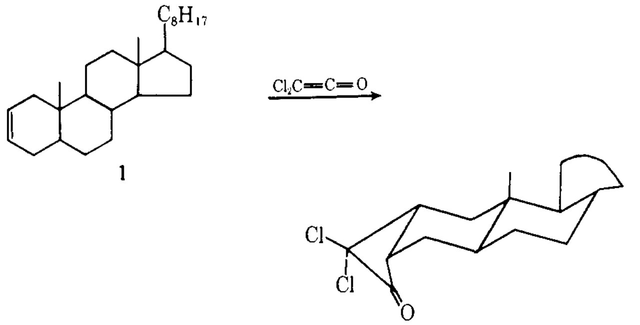
Stereoelectronic Effects in the Cycloaddition of Dichloroketene to Cyclohexenes[1]

Sir:

Recently cycloadditions of ketenes to olefins have attracted considerable interest,[2] and the high stereoselectivity of the process has been explained in terms of orbital symmetry.[3] A communication[4] from this laboratory has reported that the addition of dichloroketene to 2-cholestene (**1**) also exhibited an unusually high degree of regioselectivity[5] (Scheme I).

The preferred formation of **2** can be rationalized by considering the conformation of the possible products **2** and **3** as related to the transition state and the orbital overlap involved during the symmetry-allowed $2_s + 2_a$ process.

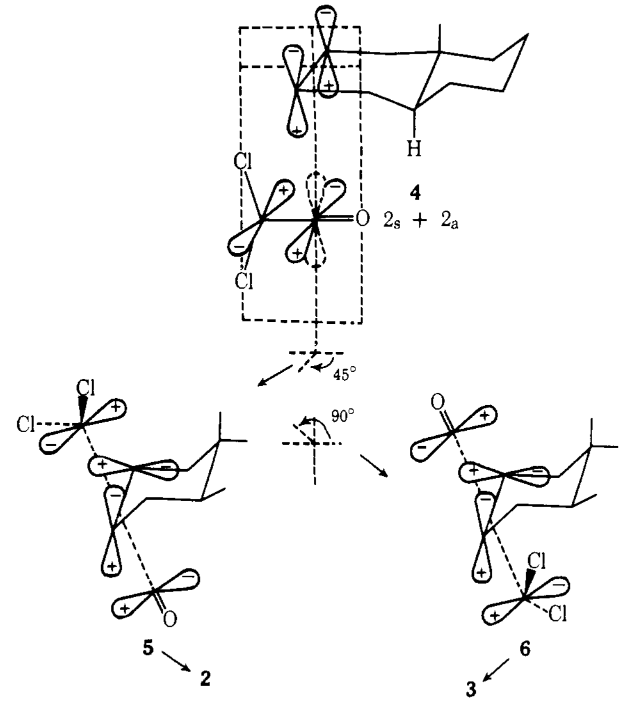
Scheme I

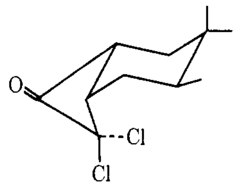


1

2
>80%

To complete orbital overlap (bond formation) from the orthogonal complex **4**,[6] rotation of the ketene is required. If the transition state (**5** or **6**) is geometrically similar to the product, which we assume to be somewhat puckered,[7] a rotation of *ca.* 45° is required to afford isomer **2** (*via* transition state **5**). On the other hand, a rotation of the ketene between 90 and 135° is necessary to produce isomer **3** (*via* **6**). Following the principle of least motion,[8] transition state **5** should be favored, leading to the regioisomer **2**. This is equivalent to considering stereoelectronic control[9] in this cycloaddition (preferential axial orbital overlap in a chair conformer of the cyclohexane ring).





3

In order to determine the generality of this effect we have studied the addition of dichloroketene to 4-*tert*-butylcyclohexene (**7**), where either side of the molecule is accessible to reagents (epoxidation gives a 3:2 ratio of cis:trans isomers).[10] If the cycloaddition to this olefin follows the selectivity shown by 2-cholestene, then one would expect predominantly two products (**8** and **9**, R = Cl), resulting from axial bond formation between the carbonyl carbon and the six-membered ring. If the reaction were not regioselective an equal distribution of four isomers (**8**–**11**, R = Cl) is expected.

Reaction of trichloroacetyl bromide with activated zinc[11] in the presence of **7** gave a product (ir 1800 cm^{-1}) which on reduction (Zn–HOAc, 100°) afforded a mixture of cyclobutanones A and B, free from chlorine,

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[1] Cycloadditions. V. Support of this work by the National Science Foundation is gratefully acknowledged.

[2] See, for instance, (a) H. C. Stevens, D. A. Reich, D. R. Brandt, R. R. Fountain, and E. J. Goughan, *J. Amer. Chem. Soc.*, **87**, 5257 (1965); (b) L. Ghosez, R. Montaigue, and P. Mollet, *Tetrahedron Lett.*, 135 (1966); (c) R. Huisgen, L. A. Feiler, and P. Otto, *ibid.*, 4485 (1968); (d) M. Rey, S. Roberts, A. Dieffenbacher, and A. S. Dreiding, *Helv. Chim. Acta*, **53**, 417 (1970); (e) W. T. Brady, E. F. Hoff, R. Roe, Jr., and F. H. Parry, Jr., *J. Amer. Chem. Soc.*, **91**, 5679 (1969); (f) J. E. Baldwin and J. A. Kapecki, *ibid.*, **92**, 4874 (1970).

[3] R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

[4] V. R. Fletcher and A. Hassner, *Tetrahedron Lett.*, 1071 (1970).

[5] Regio is used to describe directional selectivity in bond making or breaking: A. Hassner, *J. Org. Chem.*, **33**, 2686 (1968).

[6] Such a complex formation or transition state has been postulated for cycloadditions: T. Do Minh and O. P. Strausz, *J. Amer. Chem. Soc.*, **92**, 1768 (1970); P. R. Brook, J. M. Harrison, and A. J. Duke, *Chem. Commun.*, 589 (1970).

[7] Evidence for the nonplanar conformation of cyclobutanones is available: J. M. Conia and J. Gore, *Bull. Soc. Chim. Fr.*, 1968 (1964); A. Hassner and V. R. Fletcher, *Tetrahedron Lett.*, in press.

[8] J. Hine, *J. Org. Chem.*, **31**, 1236 (1966).

[9] E. J. Corey and R. A. Sneen, *J. Amer. Chem. Soc.*, **78**, 6269 (1956), see footnote 3.

[10] B. Rickborn and J. Quartucci, *J. Org. Chem.*, **29**, 2476 (1964).

[11] W. T. Brady, H. G. Liddell, and W. L. Vaughn, *ibid.*, **31**, 626 (1966).