(1976), and references therein.

(28) Equation 1 is a modification of eq 5 in F. W. Baker, R. C. Parish, and L. M. Stock, *J. Am. Chem. Soc.*, **89**, 5677 (1967).

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(33) D. Bellus, H.-C. Mez, and G. Rihs, *J. Chem. Soc., Perkin Trans. 2*, 884 (1974).

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(35) G. C. Pimentel and A. I. McClellan, "The Hydrogen Bond", W. H. Freeman, San Francisco, Calif., 1960.

(36) For discussions of the coupling constant–hybridization relationship see ref 13, footnote *a* in Table VIII, and ref 37a and 38. That such "equations may break down in highly strained small ring systems" was pointed out in ref 37b.

(37) (a) R. D. Bertrand, D. M. Grant, E. L. Allred, J. C. Hinshaw, and A. B. Strong, *J. Am. Chem. Soc.*, **94**, 997 (1972); (b) M. Pomerantz and D. F. Hillenbrand, *Tetrahedron*, **31**, 217 (1975).

(38) For reviews of the chemistry of bicyclo[1.1.0]butane see ref 13 and K. B. Wiberg, *Adv. Alicyclic Chem.*, **2** (1968). Although the involvement of the zero-bridge bond in the reactions and spectroscopy of such [1.1.0] derivatives deals with activated complexes and excited states, we believe that it is also involved in ground-state properties, such as the acid pK_a values discussed in this paper.

(39) The terms perpendicular and bisected are italicized when applied to the [1.1.0] system to differentiate them from their use in cyclopropylcarbinyl systems.

(40) D. A. Dobash, Quantum Chemistry Program Exchange, University of Indiana, Bloomington, Ind., No. 141.

(41) Related INDO calculations on cyclopropanecarboxylic acid and its anion (H–C–X (X = H or CO_2H), 116°; ring C–C–C, 60°; ring C–C, 1.515 Å; C–H, 1.082 Å)[30] show the bisected conformations are favored over the perpendicular conformers by 4.9 and 2.7 kcal/mol, respectively.

(42) E. M. Arnett, *Prog. Phys. Org. Chem.*, **1**, 223 (1963). Also see J. March, "Advanced Organic Chemistry", McGraw-Hill, New York, N.Y., 1968, pp 219–221.

(43) Melting points were determined on a Kofler hot-stage and are uncorrected. Spectra were recorded on commercial instruments (IR, Perkin-Elmer 137 or 457; NMR, Varian A-60 or T-60; mass, AEI MS-9). Temperatures given for short-path distillations were pot temperatures.

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(45) L. L. McCoy, *J. Am. Chem. Soc.*, **80**, 6568 (1958).

(46) A. A. Pavia, J. Wylde, R. Wylde, and E. Arnal, *Bull. Soc. Chim. Fr.*, 2709 (1965).

(47) See J. S. Meek and D. T. Osuga, *Org. Syn.*, **43**, 9 (1963).

(48) R. N. McDonald and R. R. Reitz, *J. Org. Chem.*, **37**, 2703 (1972).

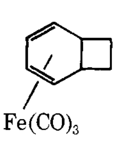
Synthesis and Reactions of the Tautomeric Complexes η-2,3,4,5-Cyclooctatrienoneiron Tricarbonyl and Bicyclo[4.2.0]octa-2,4-dien-7-oneiron Tricarbonyl. Generation of Bicyclo[4.2.0]octa-2,4-dien-7-one[1]

Maurice S. Brookhart,* George W. Koszalka, Gregory O. Nelson, Gary Scholes, and R. A. Watson

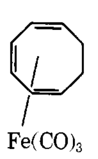
Contribution from the William Rand Kenan, Jr., Laboratories of Chemistry, Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514. Received June 10, 1976

Abstract: Photolytic reaction of 2,4,6-cyclooctatrienone with iron pentacarbonyl in benzene yields η-2,3,4,5-cyclooctatrienoneiron tricarbonyl (XI), whereas thermal reaction of the ketone with benzylideneacetoneiron tricarbonyl or 3-penten-2-one-iron tricarbonyl in benzene at 60 °C results in trapping of the bicyclic diene tautomer of cyclooctatrienone as bicyclo[4.2.0]octa-2,4-dien-7-oneiron tricarbonyl (IX). Detailed ^{1}H and ^{13}C NMR studies have been carried out to elucidate the structures of these complexes. Low temperature (−30 °C) oxidative cleavage of IX gives bicyclo[4.2.0]octa-2,4-dien-7-one which at 0 °C undergoes ring opening to cyclooctatrienone with a first-order rate constant of 5.7×10^{-4} s^{-1}, $\Delta G^{\ddagger} = 20.0$ kcal/mol. The equilibrium ratio of 2,4,6-cyclooctatrienone to bicyclo[4.2.0]octadienone was estimated from ^{1}H FT-NMR studies to be ca. 135. This value agrees with one estimated from the ratio of rate constants for the ring opening and ring closing reactions of the two tautomers. When treated with sodium methoxide–methanol, the bicyclic ketone complex IX undergoes ring opening to yield the monocyclic ((carbomethoxymethyl)cyclohexadiene)iron tricarbonyl XIV; protonation of the intermediate anion was observed to occur stereospecifically exo. Upon treatment with methyllithium the bicyclic ketone complex IX is converted to the tertiary alcohol. This alcohol undergoes base-induced ring cleavage to yield the monocyclic ketone, ((2-oxopropyl)cyclohexadiene)iron tricarbonyl (XVI), again with stereospecific exo protonation of the intermediate anion.

Introduction



I



II

The reactions of cyclooctatriene and its derivatives with iron carbonyl reagents can lead to a variety of mononuclear cyclic polyolefin iron carbonyl complexes, the nature of which depends upon the triene derivative and the iron carbonyl reagent used as well as the reaction conditions. Early work by Stone showed that reaction of 1,3,5-cyclooctatriene with $Fe(CO)_5$ at 140 °C leads only to the complex of the bicyclic tautomer, bicyclo[4.2.0]octa-2,4-dieneiron tricarbonyl (I),[2] while reaction with $Fe_3(CO)_{12}$ at lower temperatures (80–100 °C) leads to mixtures of I plus cyclooctatrieneiron tricarbonyl (II).[3] Pure samples of II can be generated photolytically at room temperature employing cyclooctatriene and $Fe(CO)_5$.[4] In the equilibrium between the uncomplexed cyclooctatriene and bicyclooctadiene tautomers, the triene is favored over the diene by a ratio of 85:15 at 100 °C;[5] however, in contrast for

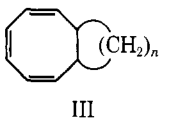
Table I. Proton Chemical Shifts[a] and Coupling Constants for Compounds IX and XI

Compd	Solvent	H_1	H_2	H_3	H_4	H_5	H_6	H_7	$H_{8,8'}$	Coupling constants[b]
XI	CS_2		2.96	6.27	5.56	3.39	6.10	5.52	2.86, 2.29	$J_{23} = 6.9, J_{24} = 1.1$
XI	Benzene-d_6		2.79	5.45	4.72	2.80	5.73	5.31	2.57, 2.20	$J_{34} = 5.8, J_{45} = 8.5$
										$J_{56} = 8.1, J_{67} = 10.5$
										$J_{68} = 0.8, J_{68'} = 2.5$
										$J_{58} = 1.1, J_{78} = 5.6$
										$J_{78'} = 9.7, J_{88'} = 11.3$
										$J_{28} = 2.0$
IX	$CDCl_3$	2.93	3.47	5.47	5.65	3.11	3.47		2.11 (H_{8a})	$J_{12} = 4.6, J_{13} = 1, J_{15} = 0.3$
									2.66 (H_{8b})	$J_{23} = 6.5, J_{24} = 1.6$
										$J_{35} = 1.6, J_{34} = 4.31$
IX-d_3	$CDCl_3$	2.93	3.47	5.47	5.65	3.11	*c*		*c*	$J_{45} = 6.4, J_{8a,8b} = 17$
										$J_{8a,2}$ or $J_{8a,6} = 3.25$
										$J_{18a} = 2.5, J_{18b} = 8.25$

[a] Chemical shifts in δ relative to internal Me_4Si in CS_2, to internal benzene (δ 7.26) in benzene-d_6, and to internal $CHCl_3$ (δ 7.27) in $CDCl_3$. [b] Coupling constants in hertz. [c] Resonances absent.

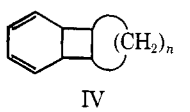
the iron-complexed systems, diene complex I appears to be more stable than triene complex II. We have observed that II undergoes essentially quantitative isomerization to I at 100 °C ($\Delta G^{\ddagger} = 29.3$ kcal/mol) with a minimum ratio of I:II at equilibrium of 100.[4]

The reactions of ring-fused derivatives of cyclooctatriene of general structure III have been examined by Cotton and Deganello[6] and ourselves.[7]



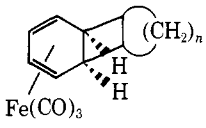
III

a, $n = 1$
b, $n = 2$
c, $n = 3$
d, $n = 4$



IV

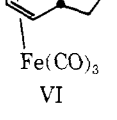
In the case of bicyclo[6.2.0]decatriene (IIIb) Cotton and Deganello showed that even though IIIb was largely favored over its diene tautomer IVb, reaction with $Fe_2(CO)_9$ led to isolation of a low yield of the stable tricyclic dieneiron tricarbonyl complex (Vb), along with a binuclear triene complex (IIIb-$Fe_2(CO)_6$) and other unidentified complexes. In a similar manner iron tricarbonyl complexes Vc and Vd also were isolated.[6]



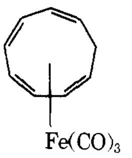
V

a, $n = 1$
b, $n = 2$
c, $n = 3$
d, $n = 4$

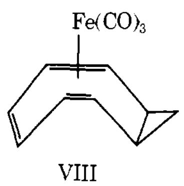
We have shown that benzylideneacetoneiron tricarbonyl (BDA-$Fe(CO)_3$) serves as a remarkably selective reagent for trapping tricyclic diene tautomers IVa and IVb in high yields.[7] Reaction of bicyclo[6.2.0]decatriene (IIIb) with BDA-$Fe(CO)_3$ leads exclusively to tricyclic diene complex Vb (82%) whereas reaction with bicyclo[6.1.0]nonatriene leads to tricyclic diene complex Vb as well as dihydroindeneiron tricarbonyl (VI). We[8] and Deganello[9] have shown that reaction of bicyclo[6.1.0]nonatriene with either $Fe_2(CO)_9$ thermally or $Fe(CO)_5$ photolytically leads to VI, cyclononatetraeneiron tricarbonyl (VII), and the unusual 1,5-bonded bicyclo[6.1.0]-nonatrieneiron tricarbonyl (VIII) as the major mononuclear products.



VI

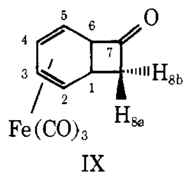


VII

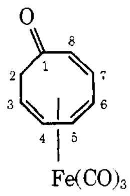


VIII

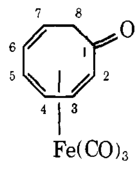
Relatively little work has been reported concerning the reactions of iron carbonyl reagents with substituted cyclooctatriene systems. In this regard a particularly attractive candidate for study is 1,3,5-cyclooctatrienone,[10] in that, unlike the hydrocarbon complexes, the keto functionality potentially allows conversion of isolated complexes into a variety of interesting derivatives. The sole report of the reaction of cyclooctatrienone with iron carbonyl reagents is that by King who showed that reaction of the ketone with $Fe_3(CO)_{12}$ led to a mononuclear C_8H_8O-$Fe(CO)_3$ complex in 13% yield and a binuclear C_8H_8O-$Fe_2(CO)_6$ complex in ca. 3% yield.[11] A bicyclic structure for the mononuclear complex, bicyclo[4.2.0]-octa-2,4-diene-7-oneiron tricarbonyl (IX), was ruled out by King since infrared data showed the absence of a cyclobutanone moiety. The structure was postulated to involve binding of iron tricarbonyl to two double bonds of the monocyclic cyclooctatrienone as in η-3,4,5,6-cyclooctatrienoneiron tricarbonyl (X) or η-2,3,4,5-cyclooctatrienoneiron tricarbonyl (XI); however, the data available did not permit the exact structure to be specified.



IX



X



XI

In this paper we wish to report the synthesis, detailed spectroscopic characterization and selected reactions of the tautomeric complexes η-2,3,4,5-cyclooctatrienoneiron tricarbonyl (XI) and η-2,3,4,5-bicyclo[4.2.0]octa-2,4-dien-7-oneiron tricarbonyl (IX), as well as isolation of bicyclo[4.2.0]octa-2,4-dien-7-one from low-temperature cleavage of IX.

Results and Discussion

η-2,3,4,5-Cyclooctatrienoneiron Tricarbonyl. Irradiation of a benzene solution of iron pentacarbonyl and cyclooctatrienone through Pyrex with a Hanovia medium-pressure lamp led to evolution of carbon monoxide and production of a deep orange solution which on workup afforded an orange crystalline mononuclear complex C_8H_8O-$Fe(CO)_3$ in ca. 40% yield. Reaction of the ketone with $Fe_3(CO)_{12}$ according to the procedure of King[11] led to isolation of a mononuclear complex which proved to be identical with the one produced photolyt-

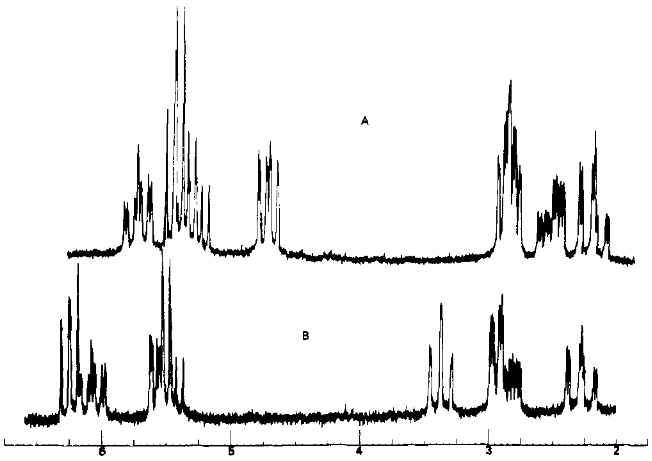


Figure 1. (a) 100-MHz ^1H NMR spectrum of complex XI in benzene-d_6; (b) 100-MHz ^1H NMR spectrum of complex XI in CS_2.

ically with $Fe(CO)_5$. This complex was examined in detail by ^1H and ^{13}C NMR spectroscopy. The ^1H NMR shifts were remarkably sensitive to solvent; spectra recorded in rigorously degassed carbon disulfide and benzene-d_6 are shown in Figure 1. The ability to shift relative peak positions by changing solvents in conjunction with double resonance experiments allowed complete assignments of all coupling constants and chemical shifts. In cases where the same coupling constant could be measured in each solvent system, no solvent dependence of coupling constants was observed. The ^1H NMR chemical shifts and observed coupling constants are summarized in Table I. These data are consistent only with the η-2,3,4,5-cyclooctatrienoneiron tricarbonyl structure, XI.[12] The methylene protons, 8 and 8′ (δ 2.20 and 2.57, benzene), are strongly coupled (J = 9.7, 5.6 Hz) to the proton with a chemical shift of δ 5.31. This chemical shift is clearly consistent with that expected for a vinyl proton attached to an uncomplexed double bond as in structure XI and not with that expected for a proton attached to the external carbon of a bound diene as in X. The chemical shift for H(3) in X would be expected to appear at higher fields in the range of δ 3.0 to 3.5.[13]

The ^{13}C chemical shifts for complex XI are summarized in Table II and are consistent with the assigned structure. At 25 °C the iron carbonyl resonance is somewhat broadened (ca. 15 Hz at half-height) due to incomplete averaging of the three distinct carbonyls in the static structure. As the temperature is lowered this carbonyl resonance rapidly broadens, and at −46 °C three distinct resonances are observed at 212.9, 207.1, and 204.3 ppm. This behavior is consistent with the general fluxional nature of dieneiron tricarbonyl complexes studied in detail previously by Takats[14] although in the present case, the barrier to scrambling appears to be somewhat higher than those observed for simple dieneiron tricarbonyl complexes.[15]

Bicyclo[4.2.0]octa-2,4-dien-7-oneiron Tricarbonyl. As earlier noted we have shown that reaction of BDA-$Fe(CO)_3$ with cyclooctatriene derivatives leads exclusively to trapping of the bicyclic diene tautomer as the iron tricarbonyl complex.[7] Huisgen has reported that 1,3,5-cyclooctatrienone XII is in equilibrium with bicyclo[4.2.0]octa-2,4-dien-7-one XIII, and from tentative ^1H NMR measurements the bicyclic tautomer was estimated to be present to the extent of ca. 5% at 25 °C[5d] (however, see below for a revised estimate). Reaction of this equilibrating pair of tautomers with either BDA-$Fe(CO)_3$ or 3-penten-2-oneiron tricarbonyl in benzene at 45 °C leads exclusively to the bicyclic diene complex IX in ca. 55% yield. Use of the 3-penten-2-oneiron tricarbonyl proved more convenient in that after exchange the volatile pentenone could easily be removed from product complex IX. Use of BDA-$Fe(CO)_3$ necessitates careful chromatographic separation of free benzylideneacetone from IX. The free trienone XII is somewhat unstable, and the moderate yield seems primarily due to degradation of XII under the reaction conditions. The ^1H NMR spectrum of IX is illustrated in Figure 2, and NMR parameters are summarized in Table I. Chemical shifts and coupling constants were assigned on the basis of decoupling experiments on IX and NMR analysis of the deuterated derivative 6,8,8′-trideuteriobicyclo[4.2.0]octa-2,4-dien-7-oneiron tricarbonyl, IX-d_3. The deuterated complex IX-d_3 was synthesized by exchange of cyclooctatrieneone in methanol-d_1/sodium methoxide, followed by reaction of the trideuterated ligand with 3-penten-2-oneiron tricarbonyl. The IX-d_3 complex showed no ^1H NMR signals at δ 2.11, 2.66, and 3.47. Clearly the 2.11 and 2.66 resonances can be assigned to the C(8) methylene protons and the 3.47 band to H(6). Broad band deuterium decoupling led to a first-order spectrum, analysis of which revealed $J_{1,2} = 4.6$, $J_{1,3} = 1.0$, $J_{1,5} = 0.3$, $J_{2,3} = 6.5$, $J_{2,4} = 1.6$, $J_{3,5} = 1.6$, $J_{3,4} = 4.3$, and $J_{4,5} = 6.4$ Hz. Proton decoupling experiments established that $J_{8a,8b} = 17$, $J_{1,8a} = 2.5$, and $J_{1,8b} = 8.25$ Hz. The basis for assignment of protons 8a and 8b is the predicted larger coupling of H(1) with the cis proton at C(8)(H(8b)), where the dihedral angle between H(8b) and H(1) is ca. 0 °C.

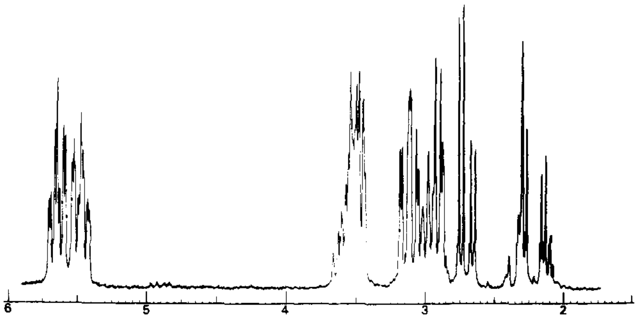
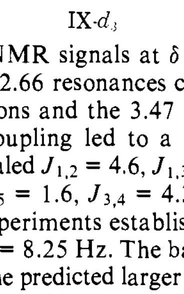


Figure 2. 100-MHz ^1H NMR spectrum of complex IX in $CDCl_3$.

Table II. Carbon Chemical Shifts for Compounds I, IX, and XI

Compd	^{13}C shifts and assignments[a]
I	24.4[b] (C_7,C_8), 37.4[c] (C_1,C_6), 70.1[c] (C_2,C_5), 85.9[c] (C_3,C_4), 212.1 (CO's)
IX	58.0 (C_1), 64.8 (C_2 or C_5), 68.0 (C_2 or C_5), 86.8 (C_3 or C_4), 85.0 (C_3 or C_4), 30.1 (C_6), 48.0 (C_8), 204.7 (C_7), 210.9 (CO's)
XI	42.4 (C_8), 53.5 (C_2 or C_5), 60.1 (C_2 or C_5), 90.9 (C_3 or C_4), 92.1 (C_3 or C_4), 120.9 (C_6 or C_7), 135.5 (C_6 or C_7), 210.7 (25°, C_1), 213.5 (−46°, C_1), 208.2[d] (25°, CO's), 204.3, 207.1, 212.9 (−46°, CO's)

[a] Shifts in ppm downfield from Me_4Si. All samples measured in $CDCl_3$. [b] Triplet in off-resonance spectrum. [c] Doublet in off-resonance spectrum. [d] Line width at half-height ca. 15 Hz.

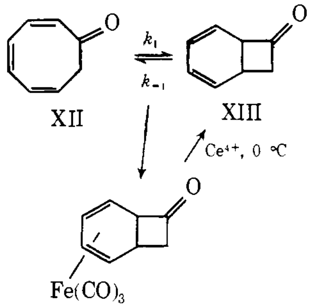


IX-d_3

The ^{13}C NMR data for IX is summarized in Table II and supports the assigned structure. Several shift assignments can be made by comparison of the carbon shifts with those of bicyclo[4.2.0]octadieneiron tricarbonyl (I) also reported in Table

II. Comparing cyclobutane with cyclobutanone,[16] substitution of the keto function shifts the α-carbons resonances downfield by 23 ppm and the β-carbon resonance upfield by 14 ppm. Using these shift increments in comparing I with IX, the following assignments can be made: C(1) (58.0 ppm), C(6) (30.1 ppm), and C(8) (48.0 ppm). Further proof of structure comes from the infrared spectrum which shows the typical iron tricarbonyl bands at 1980 and 2055 cm^{-1} and a band at 1782 cm^{-1} characteristic of the carbonyl stretching frequency of cyclobutanones.[17]

Reactions of Bicyclo[4.2.0]octa-2,4-dien-7-oneiron Tricarbonyl. Although bicyclo[4.2.0]octa-2,4-dien-7-one has been detected by infrared as a minor component in equilibrium with its valence tautomer, 1,3,5-cyclooctatrienone, isolation of a pure sample of XIII has not yet been reported. This can be accomplished by low-temperature oxidative cleavage of IX. Treatment of IX with ceric ammonium nitrate adsorbed an alumina in ether at −30 °C followed by low-temperature workup led to isolation of a pure sample of bicyclo[4.2.0]octa-2,4-dien-7-one. This ketone showed ^{1}H NMR signals (CDCl$_3$) at δ 6.05 (1 H, vinyl), 5.91 (2 H vinyl), 5.56 (1 H, vinyl), 4.23 (H(6)), 3.00–3.81 (H(1), H(8a), H(8b)). Upon warming to 0 °C, XIII undergoes a clean first-order isomerization to the trieneone XII. The rate of isomerization of XIII to XII can be followed at 0 °C by integration of the δ 4.23 band of XIII relative to the δ 6–7 band of XII. From this data we obtain $k_{-1} = 5.7 \times 10^{-4}\ \mathrm{s}^{-1}$ which corresponds to a $\Delta G_{-1}^{\ddagger} = 20.0$ kcal/mole. Huisgen[5d] has measured k_1 from tetracyanoethylene trapping of XIII at 44 °C ($k_1 = 4.9 \times 10^{-4}\ \mathrm{s}^{-1}$), 50 °C ($9.8 \times 10^{-4}\ \mathrm{s}^{-1}$), and 56.7 °C ($19.9 \times 10^{-4}\ \mathrm{s}^{-1}$). Extrapolation of these data to 0 °C yields a value of $k_1 = 2.0 \times 10^{-6}\ \mathrm{s}^{-1}$ and thus an estimated k_{eq} (k_1/k_{-1}) of ca. 0.0035 which corresponds to $\Delta G = 3.1$ kcal/mol. Assuming that $\Delta G = 3.1$ kcal/mol at 25 °C, then $k_{\mathrm{eq}} = 0.0052$ at 25 °C. This value of k_{eq} is substantially lower than the value of 0.05 previously estimated by Huisgen from provisional ^{1}H NMR data.[5d] We have reexamined the equilibrium mixture of tautomers at 25 °C using ^{1}H FT-NMR measurements and find that the relative intensities of the δ 2.98 signal of XII and δ 4.23 signal of XIII are ca. 135:1, indicating a K_{eq} at 25 °C of ca. 0.007, $\Delta G = 2.9$ kcal/mol. These values are in accord with those estimated from the measured values of k_1 and k_{-1}, and we feel that since the two methods are in close agreement, the revised estimate of K_{eq} of ca. 0.007 at 25 °C represents a substantially more accurate determination than previously reported.



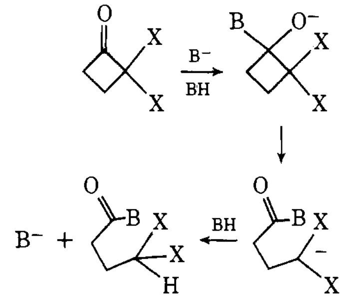
XII XIII

IX

$K_{\mathrm{eq}} = 0.007$, 25 °C
$k_{-1} = 5.7 \times 10^{-4}\ \mathrm{sec}^{-1}$, 0 °C
$\Delta G^{*} = 20.0$ kcal/mol

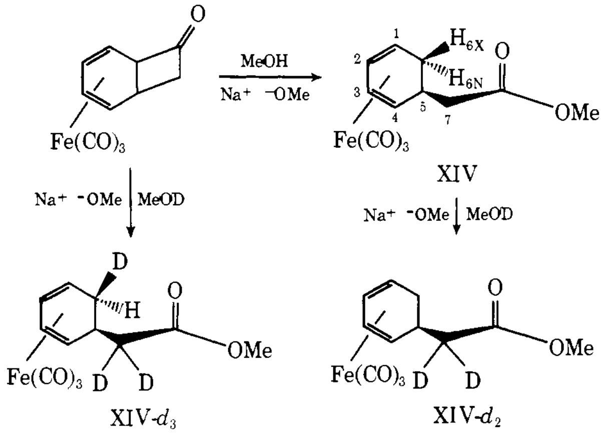
Ring Cleavage of Complex IX and Its Derivatives. Cyclobutanones containing anion-stabilizing groups at the α position have been shown to undergo base-catalyzed ring cleavage reactions via the mechanism shown in Scheme I.[18]

Scheme I



Trost has recently reported a wide variety of substituted cyclobutanones that undergo such cleavage reactions.[18g] Interestingly, bicyclic ketone complex IX also undergoes ring cleavage under similar conditions. When complex IX is stirred in sodium methoxide–methanol for 4 h at 25 °C, it is cleanly converted to the monocyclic ester XIV. Use of sodium methoxide-methanol-d_1 results in production of the trideuterio derivative XIV-d_3 in which deuterium has been incorporated at the C(7) methylene position and stereospecifically exo at the C(6) position as shown in Scheme II. Exchange of the monocyclic ester complex XIV in methanol-d_1 gave the dideuterio ester, XIV-d_2. The ^{1}H NMR spectral data for XIV, XIV-d_2, and XIV-d_3 are summarized in Table III. Chemical shifts and coupling constants were assigned on the basis of specific proton decoupling experiments on XIV at 270 MHz and broad band deuterium decoupled 100-MHz spectra of XIV-d_2 and XIV-d_3.

Scheme II



The ^{1}H NMR data clearly show the anion formed in the base-catalyzed reaction is quenched stereospecifically exo to the iron moiety. In the trideuterio XIV-d_3 generated in methanol-d_1, the AB pattern at δ 2.19 assigned to the diastereotopic C(7) methylene protons and the doublet of triplets at δ 1.25 assigned to H(6X) are absent. The assignment of the exo proton at C(6) (H(6X)) to the resonance at δ 1.25 is based on two features of the coupling patterns. It should be noted that crystal structures of substituted and unsubstituted cyclohexadieneiron(0) complexes indicate a ridged cyclohexadiene geometry with an eclipsed conformation about the C(5)–C(6) bond.[19] On this basis the dihedral angle between H(6N) and H(5N) is expected to be ca. 0° while the H(5N)–H(6X) dihedral angle would be about 120°. Applying the Karplus relation[20] $J_{5\mathrm{N},6\mathrm{N}}$ is expected to be considerably larger than $J_{5\mathrm{N},6\mathrm{X}}$ and is thus consistent with the assignments made ($J_{5\mathrm{N},6\mathrm{N}} = 10.6$ Hz, $J_{5\mathrm{N},6\mathrm{X}} = 3.4$ Hz). Further support for these assignments comes from the fact that the two protons assigned as endo protons show very similar vicinal couplings to the adjacent vinyl protons ($J_{6\mathrm{N},1} = 3.5$ Hz, $J_{5\mathrm{N},4} = 3.9$ Hz) while the

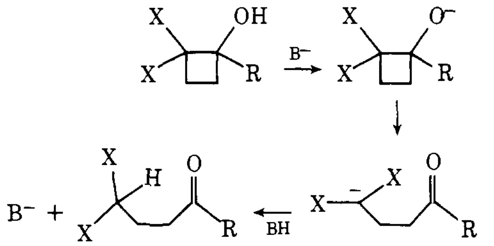
Table III. ^{1}H NMR Chemical Shift Assignments[a] and Coupling Constants for Compounds XIV and XVI

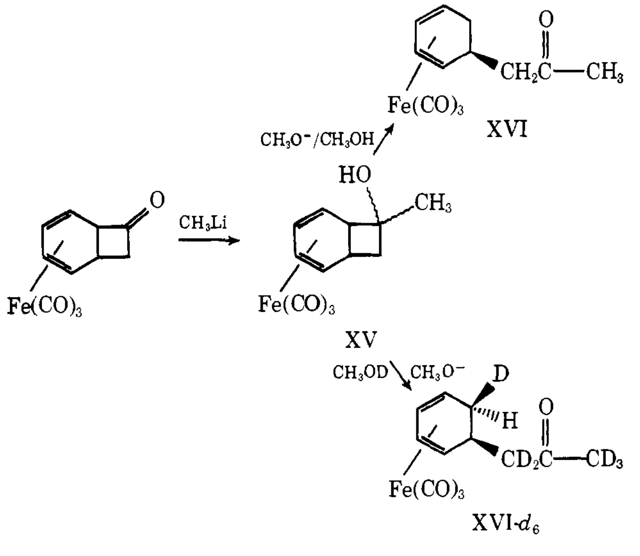
	Chemical shifts									
Compd	H_1	H_2	H_3	H_4	H_{5N}	H_{6N}	H_{6X}	$H_{7,7'}$	Other	Coupling constant[b]
XIV	3.03	5.26	5.37	3.09	2.49	2.09	1.25	2.19	3.67 (OCH_3)	$J_{1,6X} = 1.5 \pm 2$, $J_{1,6N} = 3.9$ $J_{1,2} = 6.5$, $J_{1,3} = 2.0$
XIV-d_2	3.03	5.26	5.37	3.09	2.49	2.09	1.25	*c*	3.67 (OCH_3)	$J_{2,3} = 4.1$, $J_{2,4} = 1.4$
XIV-d_3	3.03	5.26	5.37	3.09	2.49	2.09	*c*	*c*	3.67 (OCH_3)	$J_{3,4} = 6.5$, $J_{4,5N} = 3.5$ $J_{5N,7} = 6.6$, $J_{5N,7'} = 8.1$ $J_{5N,6N} = 10.6$, $J_{5N,6X} = 3.4$ $J_{6N,6X} = 15.1$, $J_{7,7'} = 14.8$
XVI	3.02	5.25	5.29	3.06	2.50	2.07	1.03	2.25	1.96 (CH_3)	$J_{1,3} = 2.2$, $J_{1,2} = 6.2$
XVI-d_6	3.02	5.25	5.29	3.06	2.50	2.07	*c*	*c*	*c*	$J_{1,6X} = 1.8$, $J_{1,6N} = 4.0$ $J_{2,3} = 3.9$, $J_{2,4} = 1.6$ $J_{3,1} = 6.6$, $J_{4,5N} = 3.2$ $J_{5N,6N} = 11$, $J_{5N,6X} = 3.5 \pm 0.5$ $J_{6N,6X} = 15$

[a] Chemical shifts in δ relative to internal $CHCl_3$ (δ 7.27). [b] Coupling constants in hertz. [c] Resonances absent.

exo proton exhibits a somewhat different vicinal coupling ($J_{6X,1} = 1.5$ Hz).

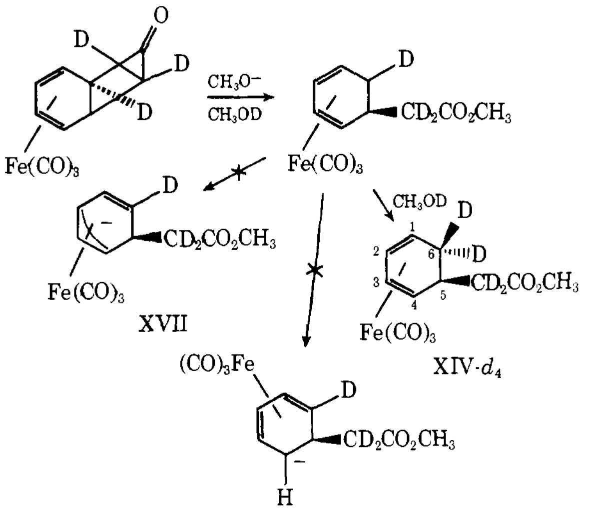
Trost has reported that cyclobutanols with anion-stabilizing groups also undergo base-catalyzed ring cleavage to yield carbonyl derivatives according to the general scheme illustrated below.[16g] Treatment of cyclobutanone complex IX with methyllithium yields a single diastereomeric tertiary alcohol XV whose stereochemistry is unassigned. Treatment of alcohol XV with sodium methoxide-methanol for 12 h at 65 °C results in clean conversion to (5-(2-oxopropyl)cyclohexadiene)iron tricarbonyl (XVI). Use of methanol-d_1 leads to the d_6 ketone XVI-d_6. As for the cleavage of XV, the anionic intermediate is stereospecifically quenched and when carried out in methanol-d_1 leads to exclusive incorporation of deuterium in the 6 exo position. The proton chemical shift assignments are based on the very close analogy of XVI with XIV and are summarized in Table III. Aside from NMR analysis, the structure of XVI was further verified by comparison with an authentic sample of XVI prepared by an independent route.[21] Reduction of cyclobutanone complex IX with sodium borohydride gives a secondary alcohol of undetermined stereochemistry which undergoes cyclobutanol ring cleavage upon treatment with sodium methoxide. The ^{1}H NMR shows that the expected aldehyde is the major product, as evidenced by the characteristic aldehydic proton at δ 9.65, but due to the lability of this complex under the basic conditions employed, other products are formed (most likely condensation products) from which the aldehyde was not separated.





The exact structure of the anionic intermediate in the base-induced cleavage reaction of the bicyclic ketone complex (IX) is of considerable interest. Relatively little is known regarding anionic polyolefinic iron complexes. Maltz[22] has reported that the cycloheptatrienyliron tricarbonyl anion is readily formed from deprotonation of cycloheptatrieneiron tricarbonyl in marked contrast to free cycloheptatriene. However, since the cycloheptatrienyliron tricarbonyl anion is a fluxional molecule and the static structure has not yet been observed by NMR, it is not clear whether the best description of this species is one in which iron is bound to a diene unit leaving a free allylic anion or one in which iron is bound to an allylic anion leaving a free diene moiety.

Some additional information as to the structure of the intermediate anion generated here was derived from the following experiment. The 6,8,8′-trideuteriobicyclo[4.2.0]octa-2,4-dien-7-oneiron tricarbonyl complex IX-d_3 was treated with methanol-d_1-sodium methoxide, and the resulting ester was analyzed by ^{1}H NMR to locate the endo deuterium. It was



found that the product contained deuterium exclusively at the endo-C(6) position with no incorporation at C(4) as shown below. This experiment indicates that protonation occurs exclusively at C(6) and, during the lifetime of the anion, C(4) and C(6) do not equilibrate via iron migration. Furthermore, it seems unlikely that the anionic species isomerizes to the π-allyl anion complex XVII, since protonation of this species would be expected to occur at C(4) and result in incorporation of deuterium at the endo position of C(4).

Experimental Section

General. All ^{1}H and ^{13}C NMR spectra were recorded on a Varian XL100 FT-NMR except the ^{1}H NMR spectra of cyclooctatrienoneiron tricarbonyl which were recorded on a Varian HA-100 NMR spectrometer and the ^{1}H NMR of (5-(carbomethoxymethyl)cyclohexadiene)iron tricarbonyl which were recorded on a Bruker WH-270 NMR spectrometer. All NMR samples of iron complexes were prepared under nitrogen using degassed solvents. Infrared spectra were recorded on a Perkin-Elmer 421 infrared spectrometer.

2,4,6-Cyclooctatrienone (XIII). Cyclooctatrienone was prepared by the procedure reported by Cope and Tiffiny[10] except that butyllithium instead of phenyllithium was used to generate lithium diethyl amide. A viscous yellow liquid was obtained which exhibited an ^{1}H NMR spectrum identical with that reported earlier by Roberts.[20] ^{13}C NMR ($CDCl_3$, in ppm downfield from Me_4Si): 43.65 (C(1)), 126.41, 129.61, 130.04, 133.41, 137.01, 138.01, 191.9 (C=O).

2,7,7′-Trideuteriocyclooctatrienone. Cyclooctatrienone (0.2 g, 1.6 mmol) was treated with 5 ml of 2 M sodium methoxide in methanol-d_1 for 3 h, followed by addition of ether and quenching with deuterium oxide. The ether layer was dryed (K_2CO_3) and concentrated, and the residue was distilled to give 0.130 g (65%) of the deuterated ketone.

Cyclooctatrienone (XII)–Bicyclo[4.2.0]octa-2,4-dienone (XIII) Equilibrium. A 0.03 M solution of chromium acetylacetonate in neat cyclooctatrienone was examined by ^{1}H-FT NMR (100 transients). Integration of the δ 2.98 signal of XII and the δ 4.23 signal of XIII gave a ratio of XII/XIII of 135:1, indicating a K_{eq} of ca. 0.007. The $Cr(acac)_3$ was added to reduce all proton T_1's to equivalent values and thereby insure accurate integration. Examination of this mixture by infrared revealed carbonyl bands at 1660 and 1780 cm^{-1} for XII and XIII in a ratio of 25:1.1, respectively. This ratio does not represent an equilibrium ratio of XII:XIII, and it must be concluded that the extinction coefficient is higher for XIII than for XII.

Cyclooctatrienoneiron Tricarbonyl (XI). A solution of cyclooctatrienone (2.79 g, 23 mmol) and iron pentacarbonyl (4.9 g, 25 mmol) in benzene was photolyzed for 12 h in a Pyrex well with a Hanovia 450-W lamp. The solution was filtered, concentrated, and chromatographed on basic alumina III. Elution with benzene afforded two bands, a wide yellow band which proved to be the title compound, followed by a narrow orange band which proved to be cyclooctatrienonediiron hexacarbonyl. Concentration of the yellow band gave an oil which was crystallized from ether–pentane to give cyclooctatrienoneiron tricarbonyl as an orange solid, 2.14 g (36%) mp 98–100 °C. This compounds proved to be identical with the compound reported earlier by King.[11]

Benzylideneacetoneiron Tricarbonyl. Benzylideneacetone (4.0 g, 27 mmol) and $Fe(CO)_5$ (10 ml, 75 mmol) were photolyzed in a Pyrex well in benzene (150 ml) for 8 h using a 450-W Hanovia lamp. The dark-red solution was filtered, concentrated under reduced pressure, and then heated in benzene for several hours at 60 °C until the 2095 cm^{-1} band in the infrared (benzylideneacetoneiron tetracarbonyl) disappeared. The solution was refiltered, concentrated, and then chromatographed on silica gel eluting with 5% ethyl acetate in benzene. The material was collected, concentrated, and rechromatographed to give dark-red crystals, 4.6 g (mp 88–89 °C), identical with the material reported by Lewis.[21] The overall yield was 60%: ^{1}H NMR (C_6D_6) δ 2.6 (s, 3 H, $-CH_3$), 13.03 (d, 1 H), 5.35 (d, 1 H), 6.88 (m, C_6H_5).

3-Penten-2-oneiron Tricarbonyl. A solution of 3-penten-2-one (3.0 g, 36 mmol) and iron pentacarbonyl (10.5 g, 53 mmol) in benzene was photolyzed for 15 h in a Pyrex well with a 450-W Hanovia lamp. The solution was filtered and concentrated, and the residue was diluted in hexane and refiltered. Evaporation of the hexanes yielded the 3-penten-2-oneiron tricarbonyl as a reddish brown oil (3.66 g, 45%): ^{1}H NMR ($CDCl_3$) δ 1.62 (d, 3 H), 2.30 (m, 1 H), 2.57 (s, 3 H), 5.51 (d, 1 H); ^{13}C NMR ($CDCl_3$, in ppm downfield from Me_4Si) 17.6 (C_1 or C_5), 20.6 (C_1 or C_5), 57.0 (C_3), 84.5 (C_4), 142.0 (C=O), 208.5 (C≡O).

Bicyclo[4.2.0]octa-2,4-dien-7-oneiron Tricarbonyl (IX). A. Using Benzylideneacetoneiron Tricarbonyl. Cyclooctatrienone (0.624 g, 5.2 mmol) and benzylideneacetoneiron tricarbonyl (1.5 g, 5.2 mmol) were heated at 60 °C in degassed benzene for 50 h. The solution was filtered, concentrated in vacuo, and the yellow-orange oil dissolved in pentane. The free benzylideneacetone was crystallized from the pentane solution at 0 °C, and the residue was chromatographed on silica gel. Elution with benzene afforded a trailing yellow band which proved to be the desired bicyclo[4.2.0]octa-2,4-dien-7-oneiron tricarbonyl complex (IX). Recrystallization from ether–pentane afforded 0.743 g (55% of the complex as pale-yellow crystals: mp 67–68 °C; ir (C_6H_6) 1980, 2055, and 1782 cm^{-1}. For ^{1}H NMR and ^{13}C NMR, see Tables I and II.

Anal. ($C_{11}H_8FeO_4$) C, H.

B. Using 3-Penten-2-oneiron Tricarbonyl. The above procedure was repeated using 3-penten-2-oneiron tricarbonyl (1.0 g, 4 mmol) as the transfer reagent with cyclooctatrienone (0.42 g, 3.5 mmol). After the reaction was complete, the free penten-2-one was removed in vacuo (0.2 mmHg), and the remaining bicyclic ketone complex was crystallized from pentane–ether to give 0.545 g (60%) of the pale-yellow solid.

6,8,8′-Trideuterio Bicyclo[4.2.0]octa-2,4-diene-7-one (IX-d_3). The above procedure was repeated using 2,7,7′-trideuteriocycloocta-2,4,6-trienone (50 mg) and an excess of the 3-penten-2-oneiron tricarbonyl. Workup as above yielded 30 mg of the trideuterated ketone complex.

Bicyclo[4.2.0]octa-2,4-dien-7-oliron Tricarbonyl (XV). Sodium borohydride (0.60 g, 16 mmol) was added in small portions to a solution of bicyclo[4.2.0]octa-2,4-dien-7-oneiron tricarbonyl (1.0 g, 3.8 mmol) in methanol, followed by stirring for 1 h. Water (100 ml) was added, and the solution was extracted with ether. The ether layer was dried (K_2CO_3) and concentrated. Recrystallization of the residue (ether–pentane) afforded 0.71 g (71%) of the light-yellow crystalline alcohol: mp 112–116 °C; ir (C_6H_6) 1970, 1980, 2050 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.03 (m, 1 H), 1.56 (bs, 1 H), 2.30 (m, 2 H), 3.01 (m, 1 H), 3.17 (t, 1 H), 3.49 (t, 1 H), 3.95 (bs, 1 H), 5.44 (t, 1 H), 5.62 (t, 1 H).

Anal. ($C_{11}H_{10}FeO_4$) C, H, Fe.

7-Methylbicyclo[4.2.0]octa-2,4-dien-7-oliron Tricarbonyl (XVI). To an ether solution (30 ml) of bicyclo[4.2.0]octa-2,4-diene-7-oneiron tricarbonyl (0.53 g, 2 mmol) at −77 °C was added 17 ml (3 mmol) of a 2.1 M solution of methyllithium, followed by stirring for 1 h. The reaction mixture was allowed to warm to room temperature and the excess methyllithium quenched with water. The ether layer was dried (K_2CO_3), concentrated, and recrystallized (ether–pentane) to give 0.5 g (93%) of the light-yellow crystalline alcohol; mp 68 °C with decomposition; ir (C_6H_6) 2050, 1970 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.05 (m, 1 H), 1.15 (s, 3 H), 1.57 (bs, 1 H), 1.98 (qd, 1 H), 2.09 (m, 1 H), 2.47 (m, 1 H), 3.10 (t, 1 H), 3.37 (t, 1 H), 5.34 (t, 1 H), 5.59 (t, 1 H).

Anal. ($C_{12}H_{12}FeO_4$) C, H, Fe.

Reaction of 7-Methyl-7-hydroxybicyclo[4.2.0]octa-2,4-dieneiron Tricarbonyl (XVI) with Sodium Methoxide–Methanol. The alcohol (0.15 g, 0.4 mmol) was stirred with sodium methoxide (0.054 g, 1 mmol) in refluxing methanol for 12 h. The solution was cooled and ether added, followed by extraction with saturated ammonium chloride and water. The ether layer was dried and concentrated to give 0.104 g (94%) of (5-(2-oxopropyl)cyclohexa-2,4-diene)iron tricarbonyl as a pale-yellow oil: ir (C_6H_6) 2050, 1970, and 1720 cm^{-1}. The ^{1}H NMR (see Table III) of the compound was identical with that of the same compound prepared by the method of Birch.[21]

Reaction of IX with Sodium Methoxide–Methanol. Bicyclic ketone complex IX (0.20 g, 0.8 mmol) was stirred in 0.02 M sodium methoxide in methanol (10 ml), for 6 h at 25 °C. After addition of ether (50 ml), the solution was treated with saturated ammonium chloride, followed by extraction with water. After drying (K_2CO_3), the ether solution was concentrated and recrystallized (pentane) to give 0.15 g (70%) of the (5-(carbomethoxymethyl)cyclohexa-2,4-diene)iron tricarbonyl ester (XIV) as pale-yellow crystals: mp 42 °C; ir (C_6C_6) 1970–80, 2050, 1740.

Anal. ($C_{12}H_{12}FeO_5$) C, H, Fe.

XIV-d_3. By repeating the above procedure using methanol-d_1 (10 ml), 0.14 g (65%) of the ester-d_3 complex (XIV-d_3) was isolated.

XIV-d_2. The ester complex XIV (30 mg) was stirred in 5 ml of 0.02 M sodium methoxide in methanol-d_1. Workup as above gave 20 mg of the dideuterated complex (XIV-d_2).

Bicyclo[4.2.0]octa-2,4-diene-7-one. Complex IX (0.150 g, 0.58 mmol) was stirred over cerric ammonium nitrate (3.5 g, 6.4 mmol) adsorbed on alumina (10 g) in a solution of ether-pentane at −30 °C for 3 h. The mixture was filtered, and solvent was removed in vacuo at −30 °C. The remaining organic residue was flash distilled at −25 °C (10^{-4} mm) to give 20 mg (29%) of the title compound as a clear oil: ^{1}H NMR (CDCl$_3$, −30 °C) δ 3.00–3.81 (m, H_1, H_{8a}, H_{8b}), 4.23 (m, H_6), 5.56 (m, 1 H, vinyl), 5.91 (m, 2 H, vinyl), 6.05 (1 H, vinyl).

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