Crystal and Molecular Structure of Tricarbonyl-(8,8-dibromobicyclo-[5.1.0]octa-2,4-diene)iron

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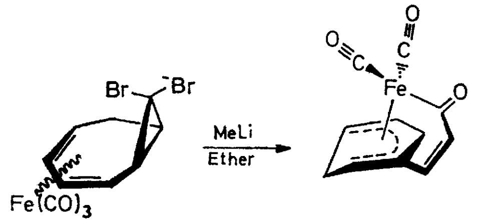
Single crystal *X*-ray analysis of the title compound (1) has established it as the precursor in an unusual rearrangement. Crystals are monoclinic, space group $P2_1/c$, with $Z = 4$ in a cell of dimensions a = 14·827(6), b = 6·816(3), c = 12·693(8) Å, β = 94·26(4)°. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares calculations to *R* 0·05 for 1533 observed data measured by diffractometer. The molecule shows evidence of strain due to intramolecular repulsive interactions of the *endo*-bromine atom with carbon atoms of the seven-membered ring. A possible reaction mechanism is suggested involving a spirocyclopropene intermediate.

WE have recently reported[1,2] the synthesis and the crystal and molecular structure of a novel carbonyliron complex, dicarbonyl-3-(η-cyclohexa-1,4-dienyl)propenoyliron (2). This compound was obtained as an unexpected rearrangement product from the methyllithium treatment of a precursor which, on the basis of its method of preparation and its spectral data, was believed to be tricarbonyl-(8,8-dibromobicyclo[5.1.0]-octa-2,4-diene)iron (1).



(1) (2)

Since the suggested transformation of (1) into (2) involved a dramatic rearrangement of the carbon skeleton, it was important to determine unequivocally the structure of the precursor (1). Herein we report the results of a three-dimensional *X*-ray structure analysis of this compound, which fully confirms the chemical structure and establishes a *trans*-relationship between the iron tricarbonyl moiety and the cyclopropane ring.

EXPERIMENTAL

Compound (1) was prepared from 8,8-dibromobicyclo-[5.1.0]octa-2,4-diene and dodecacarbonyltri-iron as previously reported.[2] Crystals from pentane were a mixture of bright yellow needles and plates. A suitable crystal (0·3 × 0·2 × 0·2 mm) was sealed in a thin-walled 0·5 mm capillary under argon in order to prevent the degradation which occurred when crystals were exposed to *X*-rays in air.

Preliminary unit-cell and space-group data were determined from Weissenberg and precession photographs (Mo-K_α radiation). Accurate cell dimensions were obtained by least-squares refinement of the setting angles for 34 accurately centred reflections in the ranges $2\theta = \pm (42·5° \pm 2·5°)$.

Crystal Data.—$C_{11}H_8Br_2FeO_3$, M = 403·85. Monoclinic, a = 14·872(6), b = 6·816(3), c = 12·693(8) Å, β = 94·26(4)°, U = 1283·1 Å^3, D_c = 2·091, Z = 4, $F(000)$ = 776. Space

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[1] P. Janse-van Vuuren, R. J. Fletterick, J. Meinwald, and R. E. Hughes, *Chem. Comm.*, 1970, 883.

[2] P. Janse-van Vuuren, R. J. Fletterick, J. Meinwald, and R. E. Hughes, *J. Amer. Chem. Soc.*, 1971, **93**, 4394.

group $P2_1/c$ from systematic absences. Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; $\mu(\text{Mo-}K_\alpha) = 77{\cdot}9$ cm^{-1}.

TABLE 1

Final atomic fractional co-ordinates ($\times 10^4$), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Br(*endo*)	1145(1)	1205(2)	4435(1)
Br(*exo*)	—430(1)	3972(2)	3569(1)
Fe	3488(1)	5907(2)	3842(1)
O(a)	2672(5)	8315(11)	2146(5)
O(b)	4126(6)	8733(13)	5460(7)
O(c)	5279(5)	5450(15)	3096(7)
C(a)	2998(5)	7424(13)	2829(7)
C(b)	3867(7)	7634(17)	4833(9)
C(c)	4591(6)	5637(17)	3384(8)
C(1)	1421(5)	5420(14)	3827(6)
C(2)	2250(6)	5519(14)	4547(7)
C(3)	2888(6)	4064(14)	4856(7)
C(4)	3298(6)	2993(14)	4088(8)
C(5)	3068(6)	3337(14)	3003(7)
C(6)	2147(7)	3151(21)	2417(9)
C(7)	1361(6)	4248(13)	2804(6)
C(8)	854(5)	3577(13)	3712(6)
H(1)	1000	6600	3900
H(2)	2000	6300	5000
H(3)	3100	4000	5400
H(4)	3700	2200	4300
H(5)	3500	2800	2500
H(*endo*)	1900	1700	2500
H(*exo*)	2200	3700	1800
H(7)	900	4600	2200

Hydrogen atoms are numbered according to the number of the carbon atom to which they are bonded. H(*exo*) and H(*endo*) refer to methylene hydrogen atoms.

Intensity data were measured by the θ—2θ scan mode over a base range in 2θ of 1·8° with allowance for dispersion; stationary background counts (40 s) were taken at each end of the scan. Intensities were measured in one quadrant of reciprocal space within the range $0 < \sin\theta/\lambda \leq 0{\cdot}549$. Of the 1761 examined, 1533 were considered observed, having intensity significantly above background having $F_o \geq 1{\cdot}58\,\sigma_F$. Corrections were made for Lorentz and polarization effects and for absorption.[3] Atomic scattering factors were calculated from the coefficients of ref. 4 for neutral iron, bromine, oxygen, carbon, and hydrogen, and those for iron and bromine were corrected for anomalous scattering.[3]

Crystal dimensions and bounding planes were characterized in a careful optical and goniometric study and absorption corrections[5] were calculated;* transmission values ranged from 0·136 to 0·269.

Structure Analysis and Refinement.—The structure was determined from a three-dimensional Patterson synthesis and iterative Fourier syntheses. Atomic co-ordinates and anisotropic thermal parameters were refined in a full-matrix least-squares analysis[6] using a weighting function $w = 1/\sigma^2$ with $\sum_{n=0}^{3} a_n|F_o|^n$. The coefficients, a_n, were derived from a least-squares analysis of the polynomial $||F_o| - |F_c|| = \sum_{n=0}^{3} a_n|F_o|^n$. After convergence of the refinement, hydrogen atoms were located in a difference-Fourier synthesis, assigned isotropic thermal parameters of the atoms to which they are bonded, and introduced into a final least-squares cycle. Two residuals were calculated, and final values were R 0·050 and R' 0·062 $\{R' = [\Sigma w(|F_o| - k|F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$; the data-to-parameter ratio was 9·9 : 1.

RESULTS AND DISCUSSION

Final atomic co-ordinates and anisotropic thermal parameters are presented in Tables 1 and 2.† All bond lengths and bond angles and a selected set of non-bonded interatomic distances are listed in Table 3. Estimated standard deviations, given in the Tables were calculated

TABLE 2

Thermal parameters * (Å^2 $\times$ 10), with estimated standard deviations in parentheses

Atom	β_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B
Br(*endo*)	638(4)	577(6)	648(6)	−179(4)	−53(4)	132(4)	593
Br(*exo*)	313(6)	894(8)	683(6)	−41(4)	−47(4)	−177(5)	564
Fe	283(5)	480(6)	438(6)	−21(4)	26(4)	122(5)	380
O(a)	60(4)	69(4)	57(3)	5(3)	3(3)	21(3)	59
O(b)	96(6)	74(5)	72(5)	−34(4)	−15(4)	3(4)	75
O(c)	37(3)	1·13(6)	1·06(5)	−1(4)	22(4)	34(5)	71
C(a)	36(4)	46(4)	44(4)	7(3)	4(3)	10(4)	40
C(b)	49(5)	63(6)	63(6)	−19(4)	−11(4)	19(5)	54
C(c)	37(5)	72(6)	66(6)	4(4)	12(4)	25(5)	52
C(1)	30(3)	45(4)	41(4)	−4(3)	2(3)	1(3)	38
C(2)	37(4)	50(4)	35(4)	−6(3)	6(3)	1(4)	40
C(3)	34(4)	68(5)	38(4)	−16(4)	−10(3)	26(4)	38
C(4)	32(4)	35(4)	77(6)	6(3)	8(4)	15(4)	42
C(5)	40(4)	49(4)	47(4)	10(3)	9(3)	−3(4)	43
C(6)	43(4)	63(7)	42(5)	4(4)	11(4)	−11(5)	46
C(7)	34(4)	55(4)	34(3)	4(3)	1(3)	−1(3)	40
C(8)	31(3)	47(4)	38(3)	−6(3)	−1(3)	1(3)	38

* Anisotropic B_{ij} (Å^2) are related to the dimensionless β_{ij} employed during the least-squares refinement, by $B_{ij} = 4\beta_{ij}/a_i^*a_j^*$ where β_{ij} is given by the expression $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. Isotropic thermal parameters were calculated from $B = 4[V^2 \det(\beta_{ij})]^{\frac{1}{3}}$.

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* A modified version of ABSCOR, a FORTRAN absorption correction program by N. W. Alcock, was used.

† Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20904 (9 pp., 1 microfiche). For details see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1973, Index issue.

[3] 'International Tables for *X*-ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1968, p. 215.

[4] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[5] J. De Menlenaer and H. Tompa, *Acta Cryst.*, 1965, **19**, 1014.

[6] W. R. Busing, K. O. Martin, and H. A. Levy, ORFLS, A FORTRAN Crystallographic Least-Squares Program, Report ORNL TM 305, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1962.

by use of the program listed in ref. 7; standard deviations of the lattice contents were included in the calculations. The Figure provides a perspective representation of the principal structural features of the molecule of (1).

TABLE 3

Interatomic distances (Å) and bond angles (deg), with estimated standard deviations in parentheses

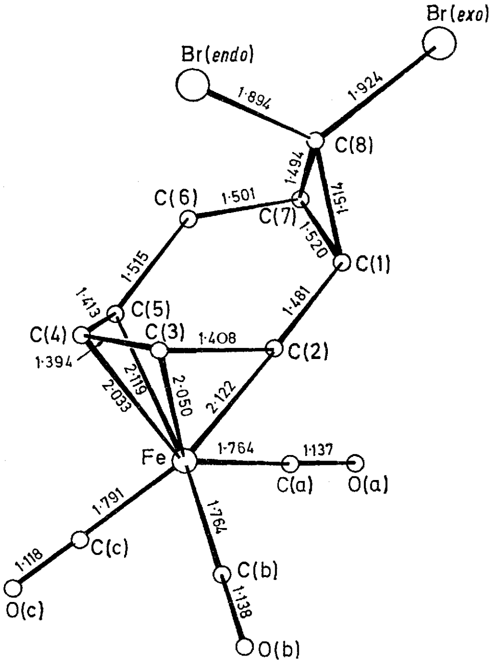
(*a*) Distances

C(1)–C(2)	1·481(11)	C(2)–H(2)	0·8
C(1)–C(7)	1·520(11)	C(3)–H(3)	0·8
C(1)–C(8)	1·514(11)	C(4)–H(4)	0·8
C(2)–C(3)	1·408(13)	C(5)–H(5)	1·0
C(3)–C(4)	1·394(14)	C(b)–H(*endo*)	1·1
C(4)–C(5)	1·413(13)	C(b)–H(*exo*)	0·8
C(5)–C(6)	1·515(13)	C(7)–H(7)	0·9
C(6)–C(7)	1·501(12)	C(2) · · · C(b)	2·804(13)
C(7)–C(8)	1·494(11)	C(5) · · · C(c)	2·767(14)
Br(*endo*)–C(8)	1·894(9)	C(5) · · · C(2)	2·808(14)
Br(*exo*)–C(8)	1·924(8)	C(b) · · · C(c)	2·587(17)
Fe–C(2)	2·122(9)	C(a) · · · C(b)	2·770(14)
Fe–C(3)	2·050(8)	C(a) · · · C(c)	2·710(13)
Fe–C(4)	2·033(10)	C(a) · · · C(2)	2·835(12)
Fe–C(5)	2·119(10)	C(a) · · · C(5)	2·795(13)
Fe–C(a)	1·764(9)	Br(*endo*) · · · Br(*exo*)	3·142(2)
Fe–C(b)	1·784(13)	Br(*endo*) · · · C(2)	3·367(9)
Fe–C(c)	1·791(10)	Br(*endo*) · · · C(3)	3·256(8)
C(a)–O(a)	1·137(10)	Br(*endo*) · · · C(4)	3·484(9)
C(b)–O(b)	1·138(12)	Br(*endo*) · · · C(5)	3·791(9)
C(c)–O(c)	1·118(11)	Br(*endo*) · · · C(6)	3·334(14)
C(1)–H(1)	1·0		

(*b*) Angles

C(1)–C(2)–C(3)	131·7(9)
C(2)–C(3)–C(4)	119·6(8)
C(3)–C(4)–C(5)	120·5(8)
C(4)–C(5)–C(6)	127·5(9)
C(5)–C(6)–C(7)	119·6(8)
C(6)–C(7)–C(1)	122·9(9)
C(7)–C(1)–C(2)	123·0(8)
C(1)–C(7)–C(8)	60·3(5)
C(7)–C(8)–C(1)	60·7(5)
C(8)–C(1)–C(7)	59·0(5)
Br(*endo*)–C(8)–Br(*exo*)	110·8(4)
C(2)–Fe–C(3)	39·4(4)
C(3)–Fe–C(4)	39·9(4)
C(4)–Fe–C(5)	39·7(4)
C(a)–Fe–C(b)	102·7(4)
C(b)–Fe–C(c)	92·7(5)
C(c)–Fe–C(a)	99·4(4)
Fe–C(a)–O(a)	176·4(8)
Fe–C(b)–O(b)	179(1)
Fe–C(c)–O(c)	179(1)
C(2) · · · C(b) · · · C(c)	92·0(5)
C(b) · · · C(c) · · · C(5)	92·5(5)
C(c) · · · C(5) · · · C(2)	88·3(4)
C(5) · · · C(2) · · · C(b)	87·2(4)

Cycloheptadiene Ring System.—The cycloheptadiene ring consists of two very nearly planar segments intersecting at C(2) and C(5) with a dihedral angle of 139·9°. The four-atom diene segment is planar to within ±0·004 Å (Table 4). The three C–C bonds of the π-system are nearly equal, and their mean (1·405 Å), is typical of values observed in other conjugated diene–tricarbonyliron complexes.[8] The drastic shortening of the central bond of the diene and the concomitant lengthening of the lateral bonds from values expected for the free ligand, *e.g.* 1·48 and 1·34 Å respectively for buta-1,3-diene,[9] have received extensive discussion.[10] Angles C(2)–C(3)–C(4) and C(3)–C(4)–C(5) are each within 1σ of 120°.



A diagram of the molecule showing the principal structural features

TABLE 4

Equations of least-squares planes, referred to an orthonormal basis related to the crystallographic basis as ($\hat{a}$, $\hat{b}$, $\hat{c}^*$). Distances (Å) of atoms from planes are given in square brackets

Plane (*A*): C(1), C(2), C(5)—(7)

$$0\cdot26699x + 0\cdot83052y - 0\cdot48883z = 1\cdot13003$$

[C(1) −0·038, C(2) 0·040, C(5) −0·043, C(6) 0·050, C(7) +0·009, C(8) 1·156]

Plane (*B*): C(2)—(5)

$$0\cdot73160x + 0\cdot68170y - 0\cdot00684z = 4\cdot65778$$

[C(2) −0·002, C(3) 0·004, C(4) −0·004, C(5) 0·002, Fe −1·583]

Although the complementary five-atom segment of the cycloheptadiene ring exhibits deviations from planarity an order of magnitude larger than those of the diene, it is, nevertheless, very nearly planar (Table 4). This requires an unusually large bond angle of 120° at the methylene carbon. The slight shortening from normal aliphatic carbon–carbon distances observed for the bonds adjacent to the cyclopropane ring is consistent with previous observations.[11]

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[7] W. R. Busing, K. O. Martin, and H. A. Levy, OR FFE, A FORTRAN Crystallographic Function and Error Program, Report ORNL TM 306, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

[8] M. R. Churchill and R. Mason, *Proc. Roy. Soc.*, 1967, *A*, **301**, 433.

[9] A. Almenningen, O. Bastiansen, and M. Traetteberg, *Acta Chem. Scand.*, 1958, **12**, 1223.

[10] M. R. Churchill and R. Mason, *Adv. Organometallic Chem.*, 1967, **5**, 93; S. F. A. Kettle and R. Mason, *J. Organometallic Chem.*, 1966, **5**, 97; B. Dickens and W. N. Lipscomb, *J. Chem. Phys.*, 1962, **37**, 2084.

[11] C. J. Fritchie, *Acta Cryst.*, 1966, **20**, 27.

Despite the asymmetry imparted to the molecule by the dibromocyclopropane, the cycloheptadiene–tricarbonyliron complex retains a remarkably good *pseudo*-mirror. The root-mean-square displacement of involved atoms from mirror symmetry is 0·03 Å.

Iron–Ligand System.—Bond lengths and angles in the tricarbonyliron–diene complex are typical of those observed in similar complexes.[7] Bonding interactions occur between the four carbon atoms of the diene system with mean iron–carbon distances of 2·04 and 2·12 Å for internal and terminal carbons respectively. In the tricarbonyliron, a characteristic [8] deviation from local C_{3v} symmetry results from the reduction of the C(b)–Fe–C(c) angle to nearly 90°. This allows the atoms C(b) and C(c) to form, with C(2) and C(5), the basal plane of what can reasonably be described as a square pyramid about the iron; [12] the apex of this pyramid, tilted only 4·8° from the normal to the basal plane, is occupied by the third carbonyl carbon, C(a). Consistent with previous observations,[12] the iron is displaced slightly (0·23 Å) from the basal plane, toward the apical carbonyl group.

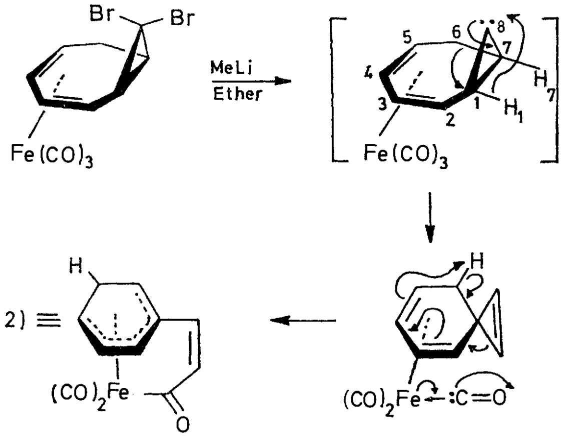
gem-*Dibromocyclopropane Ring.*—The cyclopropane ring is virtually undistorted, as is apparent from the similar carbon–carbon bond lengths: C(1)–C(7) 1·520(11), C(11)–C(8) 1·514(11), and C(7)–C(8) 1·494(11) Å. These distances are in excellent agreement with corresponding bond lengths for other cyclopropane derivatives,[13] and for an analogously substituted cyclopropane, 8,8-dibromo-1,4,4,-trimethyltricyclo[5.1.0.0^{3,8}]octane.[14]

The observed carbon–bromine bond lengths [1·894(9) and 1·924(8) Å] for the *endo*- and *exo*-Br–C(8) bonds respectively, are somewhat shorter than those typically observed for aliphatic carbon–bromine bonds. 1·94(1) Å has been taken as a typical value for such bonds [15] and recent structure determinations of bromine derivatives suggest that 1·96 Å or longer might not be unusual.[16] We presume our shorter Br–C bonds reflect the unusual hybridization of the carbons of the cyclopropane ring. The aforementioned report of a *gem*-dibromocyclopropane [14] provides no clear indication of the carbon–bromine bond length to be expected.

The two bromines are not disposed symmetrically about the plane of the cyclopropane ring, the *endo* being 0·18 Å nearer the ring plane than the *exo*; angles between the ring plane and the C(8)–Br bonds are 51·2 and 59·6° for Br(*endo*) and Br(*exo*) respectively. While the latter angle is consistent with corresponding angles observed in cyclopropane and several derivatives,[11,17] the former is significantly diminished. This appears to result from non-bonded interactions between the *endo*-bromine and carbon atoms of the seven-membered ring. [Table 3 gives Br · · · C distances; since the sum of non-bonded radii ordinarily observed for carbon and bromine is *ca.* 3·75 Å,[18] repulsive interactions of Br(*endo*) with these carbons should be substantial.]

The diminution of the angle between the C(8)–Br(*endo*) vector and the plane of the cyclopropane ring leads to a Br(*endo*)–C(8)–Br(*exo*) angle of 110·8(4)° compared with an H–C–H angle in cyclopropane itself of 115·1°.[17a] The resulting distance between bromine centres is only 3·142(2) Å. A value for the Br(*endo*)–C(8)–Br(*exo*) angle approximately twice that of the Br(*exo*)–C(8)–cyclopropane ring angle, *viz. ca.* 120°, might well be expected in the absence of steric interactions affecting the Br(*endo*) position; this would correspond to Br · · · Br of *ca.* 3·30 Å.

The strain introduced into the molecule by interactions of Br(*endo*) with the seven-membered ring is further evidenced in the dihedral angle between the cyclopropane ring and the mean plane of carbon atoms C(1), C(2), C(6), and C(7). Whereas we observe a value of 114·6°, a typical value for the corresponding angle in substituted cyclopropanes lacking the intramolecular interactions with a bulky *endo*-group appears to be *ca.* 109°.[11]*



SCHEME

The strained geometry of this molecule has an analogue in a *gem*-diphenylcyclopropane derivative [13b] wherein a similar asymmetry of the phenyl groups with respect to the cyclopropane ring was observed; in this case, the dihedral angle between the cyclopropane ring and the adjacent plane is 115·0°. Once again, both distortions

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* Corresponding dihedral angles calculated from the atomic coordinates for the tricyclo[5.1.0.0^{2,4}]octan-5-one derivative [14] were 109·6 and 108·2°.

[12] O. S. Mills and G. Robinson, *Acta Cryst.*, 1963, **16**, 758.

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[14] G. Reck, *Tetrahedron*, 1970, **26**, 599.

[15] *Chem. Soc. Special Publ.*, No. 18, 1965.

[16] J. Delhi and P. Groth, *Acta Chem. Scand.*, 1969, **23**, 587; B. Hesper, H. J. Geise, and C. Romers, *Rec. Trav. chim.*, 1969, **88**, 871; E. M. Gopalakrishna, A. Cooper, and D. A. Norton, *Acta Cryst.*, 1969, **B25**, 1601; A. Perales, S. Martinez-Carrera, and S. Garcia-Blanco, *ibid.*, p. 1817.

[17] (*a*) O. Bastiansen, F. N. Fritsch, and K. Hedberg, *Acta Cryst.*, 1964, **17**, 538; (*b*) M. A. M. Meester, H. Schenk, and C. H. MacGillavry, *ibid.*, 1971, **B27**, 630; R. E. Long, H. Maddox, and K. N. Trueblood, *ibid.*, 1969, **B25**, 2083; A. Hartman and F. L. Hirschfeld, *ibid.*, 1966, **20**, 80.

[18] A. I. Kitaigorodskii, 'Organic Chemical Crystallography,' Consultants Bureau, New York, 1961, p. 7.

can be ascribed to interactions of a bulky *endo*-group with the adjacent ring system.

Possible Reaction Mechanism.—The structure of (1) and the configurational relationship between the *gem*-dibromocyclopropane and the tricarbonyliron having been established, the question arises as to the mechanism for the unusual transformation (1) ⟶ (2).

One possibility would involve formation of a spirocyclopropene intermediate *via* a novel ring contraction, as shown in the Scheme.

A study of models suggests that, in this spiro-compound, one of the reactive sp^2-cyclopropene carbons would be proximate to one of the carbonyl groups on the iron atom. If this carbonyl group were to form a stable interaction with the enonyl group, a 1,2-hydrogen shift in the cyclohexadienyl ring would permit the π-system to maintain a favourable geometry for interaction with the Fe^{I}-group.

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