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ISOMERIZATION OF BICYCLO[5.1.0]-2,4-OCTADIENEIRON TRICARBONYL TO BICYCLO[4.2.0]-2,4-OCTADIENEIRON TRICARBONYL*

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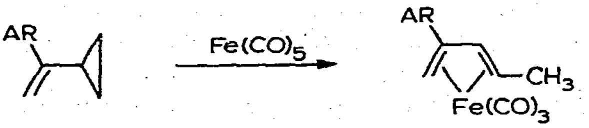
Summary

It has been shown that bicyclo[5.1.0]-2,4-octadieneiron tricarbonyl undergoes thermal isomerization to bicyclo[4.2.0]-2,4-octadieneiron tricarbonyl. The first-order rate constant for this process at 120.6° was determined to be 1.8×10^{-5} s^{-1} which corresponds to $\Delta F^{\ddagger} = 31.8$ kcal/mol. Gas chromatographic results coupled with a kinetic analysis very strongly suggest that 1,3,5-cyclooctatrieneiron tricarbonyl is an intermediate in this isomerization. Two plausible mechanisms are offered to explain this rearrangement.

Introduction

There has been much recent interest in the reactions of vinyl cyclopropanes with iron carbonyls to form organoiron carbonyl complexes in which the vinyl cyclopropane ligands have undergone skeletal rearrangement [1—6]. Sarel and Ben-Shoshan [1] have shown that vinyl cyclopropane derivatives of general structure I react with iron pentacarbonyl at 140° to form dieneiron tricarbonyl complexes of general structure II. It was suggested that these reactions might proceed through σ,π-allyl intermediates such as III.



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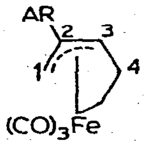

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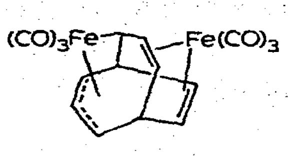
When polycyclic vinyl cyclopropanes are employed such that C_4 becomes a bridgehead carbon, rearrangement to the diene complex is prevented and the σ,π-allyl species III may be isolated. This was first demonstrated by Aumann [2] who isolated both IV and V from the reaction of bullvalene with diiron nonacarbonyl. Further examples have been provided by Aumann [3], Eisenstadt [4], Moriarty [5] and Rosenblum [6].



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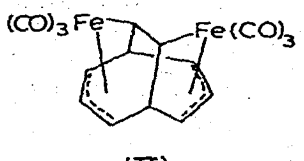

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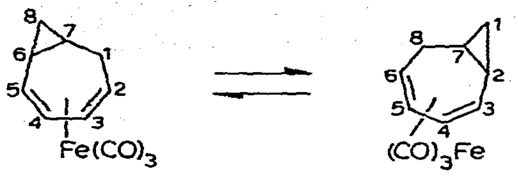
Recently our interests have been focused on investigations of thermal isomerizations of organic ligands which are already bound to transition metals. In this regard, vinyl cyclopropane type complexes have received relatively little attention. Grimme [7] has reported that bicyclo[6.1.0]nonatrienemolybdenum tricarbonyl, VI, isomerizes to bicyclo[4.2.1]nonatrienemolybdenum tricarbonyl while Aumann [8] has recently shown by deuterium labeling studies that bicyclo[5.1.0]-2,4-octadieneiron tricarbonyl, VII, undergoes a degenerate isomerization as illustrated below.



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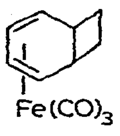

(VIII)

In this paper we wish to report our investigation of the thermal isomerization of VII to bicyclo[4.2.0]-2,4-octadieneiron tricarbonyl, VIII*.

Results and discussion

Pure samples of bicyclo[5.1.0]octadieneiron tricarbonyl, VII, were prepared in good yield by photolysis through Pyrex of equimolar amounts of iron pentacarbonyl and bicyclo[5.1.0]-2,4-octadiene in benzene followed by chromatography on alumina. Initial NMR studies revealed that the diene complex VII could be thermally isomerized to the bicyclo[4.2.0]-2,4-octadieneiron tricarbonyl complex VIII by heating at 100° in degassed heptane for long periods of time. Quantitative rates of isomerization of VII to VIII could be conveniently measured by direct gas chromatographic analysis of the complexes. A typical kinetic run consisted of heating a thoroughly degassed octane solution of VII at 120.6°, taking aliquots at ca. one hour intervals and analyzing for the ratio of VII to VIII by gas chromatography. Results of three kinetic runs are illustrated in Table 1.

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* The isomerization of VII to VIII has also been observed by R. Aumann (personal communication).

TABLE 1

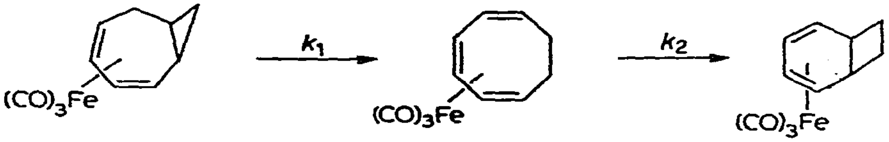
RATES OF ISOMERIZATION OF VII TO VIII[a]

Temperature (°C)	k (s^{-1})	$\Delta F^{\ddagger}$ (kcal/mol)
110 ± 1	$6.7 \pm 1 \times 10^{-6}$	31.8
120.6 ± 0.1	$1.7 \pm 0.1 \times 10^{-5}$	31.8
120.6 ± 0.1	$1.8 \pm 0.1 \times 10^{-5}$	31.8

[a] Determined by gas chromatographic analysis on a 6′ × 1/4″ column packed with 3% UC-W98 on Chromosorb W 60-80 102°, He flow 85 ml/min. Retention times of VII, VIII and IX were 10.4, 7.9 and 11.5 min respectively.

In each case the isomerization followed good first-order kinetics and at both 120.6 and 110° the free energy of activation, $\Delta F^{\ddagger}$, determined from the rate constant was 31.8 kcal/mol.

Early in the isomerization a small peak in the gas chromatogram appeared with a retention time (11.5 min) which corresponded exactly to the retention time of the 1,3,5-cyclooctatrieneiron tricarbonyl, IX, under the conditions. This peak was broad and in the tail of VII (10.4 min); its area could not be measured precisely but at 2—4 h it could be estimated to be ca. 2—3% of the area of the peak for VIII. We feel this is a strong indication that the triene complex IX is an intermediate in the isomerization of VII to VIII and that the reaction proceeds as illustrated (eqn.1).



(VII) (IX) (VIII)

(1)

Further support for this contention comes from a kinetic analysis. We have previously determined the first-order rate constant, k_2, for conversion of IX to VIII as $k_2 = 7 \times 10^{-5}$ s^{-1} at 102° [9]. Extrapolation to 120.6° yields a predicted k_2 of 4.7×10^{-4} s^{-1}. Applying consecutive first-order kinetics, the concentration of IX during the reaction were it an intermediate is given by eqn.2.

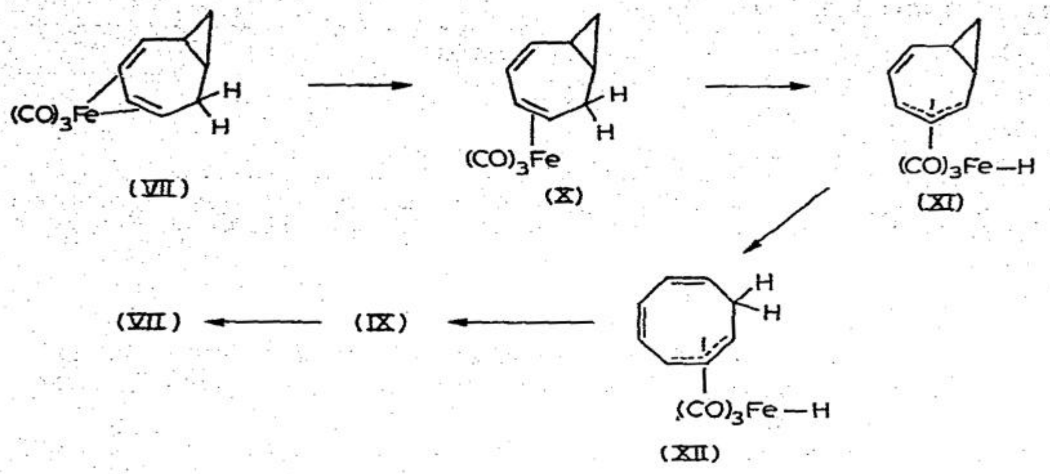
$$[\mathrm{IX}] = \frac{k_1 a}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right) \tag{2}$$

(where a = initial concn. of [IX])

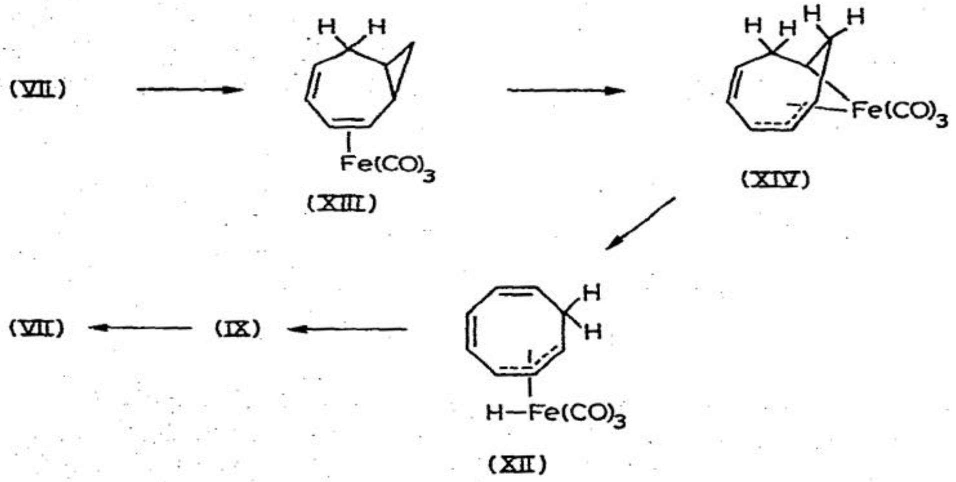
Using $k_1 = 1.7 \times 10^{-5}$ s^{-1} and $k_2 = 4.7 \times 10^{-4}$ s^{-1}, the predicted concentrations of IX at various time intervals are 3.0% at 1 h, 3.4% at 2 h (time of IX max), 3.1% at 4 h, 2.4% at 8 h, and 1.8% at 12 h. These percentages are in qualitative agreement with the gas chromatographic results and thus support the idea that IX is indeed an intermediate.

Assuming triene complex IX is an intermediate, two plausible mechanisms can be suggested. These are illustrated as mechanisms A and B.

MECHANISM A



MECHANISM B



Mechanism A involves formation of the hydridoiron π-allyl complex XI via the *dihapto* unsaturated complex X*. Complex XI then undergoes ring opening to the hydridoiron π-allyl complex XII which collapses to the triene complex IX, the immediate precursor to VIII. Mechanism B entails again initial formation of a *dihapto* unsaturated complex XIII* which is followed by oxidative addition to the cyclopropane ring to yield the σ,π-allyl complex XIV. XIV then undergoes β-metal hydride elimination to yield the hydridoiron π-allyl complex XII which may collapse to triene IX.

Although both mechanisms appear plausible**, it should be noted that for

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* This species may represent either an intermediate or the transition state.

** A referee has suggested the possibility of a third mechanism similar to B in which the intermediate rather than XIII is the *dihapto*-iron tricarbonyl complex of bicyclo[5.1.0]-2,5-octadiene. This complex could be obtained from collapse of XI. This mechanism appears less probable than mechanism B but cannot be ruled out on the basis of presently available data.

B each step has to some extent precedent. The formation from iron carbonyls of σ,π-allyl complexes such as XIV has been amply demonstrated [2—6] and was discussed in the introduction. The β-metal hydride elimination of XIV to form XII is a well known and facile general decomposition route for alkyl transition metal derivatives [10], while hydridoiron π-allyl species such as XII have been frequently invoked to explain olefin isomerizations by iron carbonyls [11]. In mechanism A, the ring opening of a species such as XI has no precedent in the literature. The hydridoiron π-allyl species itself is a fairly high energy intermediate and for mechanism A to be plausible the ring opening of XI must necessarily be rather facile.

The comparison of the thermal isomerization of complex VII with that of the free ligand, bicyclo[5.1.0]-2,4-octadiene, is of considerable interest. Whereas VII rearranges to only VIII at 120°, the isomerization of the free diene reported by Doering and Roth [12] requires substantially higher temperatures (225°) and yields an equilibrating mixture of 1,3,5-cyclooctatriene, 1,3,6-cyclooctatriene and bicyclo[4.2.0]-2,4-octadiene. These initial products are thermally labile at 225° and yield secondary products of tricyclo[3.2.1.0^{2,7}]-3-octene-benzene, and ethylene*. In that the diene ligand can readily be oxidatively cleaved from the iron, isomerization of substituted derivatives of VII may represent synthetically useful routes to certain substituted cyclooctatrienes and bicyclo[4.2.0]octadienes.

Experimental

General

Gas chromatography was performed on an Hewlett—Packard 5750 Research Chromatograph using a flame ionization detector and helium as the carrier gas. IR spectra were recorded on a Perkin—Elmer 421 spectrometer while PMR spectra were obtained using a Jeol-C60HL spectrometer. Nitrogen gas was purified by passing it first through concentrated sulfuric acid and then through a heated column of BASF catalyst R3-11.

Bicyclo[5.1.0]-2,4-octadiene

This diene was prepared using the modification of the Simmons—Smith reaction reported by Rawson and Harrison [13]. A mixture of zinc dust (17 g) and copper chloride (2.5 g) in 40 ml of ether was heated at reflux under nitrogen for 0.5 h. Distilled cycloheptatriene (12 g) and methylene iodide (40 g) were added in ether dropwise and the mixture heated at reflux for 24 h. The ether layer was then decanted onto ice and washed with 100 ml 1 *N* HCl, 100 ml 5% sodium bicarbonate, twice with distilled water and dried over anhydrous magnesium sulfate. The ether was removed at water aspirator pressure and the remaining mixture of hydrocarbons was distilled away from polymeric material by bulb to bulb distillation under high vacuum. GLC analysis (6′× 1/4″ 20% UCW-98 on Chromosorb W 60-80 mesh, 70°) indicated a ca. 12—14% yield of the

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* In that the rearrangement of bicyclo[5.1.0]-2,4-octadiene is clearly much slower than complex VII, the free diene ligand cannot be invoked as an intermediate in the isomerization of VII.

diene. Careful spinning band distillation of the hydrocarbon mixture yielded ca. 1.0 g of pure bicyclo[5.1.0]-2,4-octadiene (b.p. 56°, 50 mmHg). The PMR spectrum (CCl_4, int. TMS) exhibited bands at δ 0.53 (1H, m), 1.08 (2H, m), 1.68 (1H, m), 2.42 (2H, m), 5.68 (3H, m) and 6.23 ppm (1H, quartet).

Bicyclo[5.1.0]-2,4-octadieneiron tricarbonyl (VII)

Bicyclo[5.1.0]-2,4-octadiene (1.0 g) and iron pentacarbonyl (2.5 g) in 200 ml of degassed benzene were irradiated through Pyrex in a standard photochemical well at room temperature for 3 h using an Hanovia 450 W lamp. The benzene was removed using a rotary evaporator and the remaining oil was chromatographed under nitrogen on Woelm alumina (grade 1.5, basic) using degassed hexane as eluant. The first yellow band to elute was VII. Removal of all volatiles by high vacuum yielded 2.0 g (86%) of VII as a yellow solid. The spectral data (IR, PMR) obtained for VII were identical to those for VII when obtained by hydride reduction of the bicyclo[5.1.0]octadienyliron tricarbonyl cation [8,14].

Rate measurements

To a small Schlenck tube which had been soaked in an ammonium hydroxide solution overnight, rinsed with distilled water and dried and flamed under high vacuum was added 29 mg of VII in 0.6 ml of degassed octane. This solution was degassed on a high vacuum line using two freeze-pump-thaw cycles and kept under nitrogen. The tube was then immersed in a glycerine bath maintained at a constant temperature of 120.6 ± 0.1° by a Haake FS Constant Temperature Circulator. At 1 h intervals the tube was quenched and a 1.0 μl sample withdrawn by syringe. The tube was thoroughly flushed with nitrogen, recapped, and replaced in the glycerine bath. The withdrawn sample was analyzed by GLPC on a 6′ × ¼″ column packed with 3% UC-W98 on Chromosorb W 60-80 mesh (Column 102°, injection port 113°, He flow 85 ml/min). Under these conditions retention times of VIII, VI and IX were 7.9 min, 10.4 min and 11.5 min respectively. Kinetics were followed for ca. 2.5 half-lives. That VIII was indeed the product of thermal isomerization was verified by heating ca. 0.5 g of VII in degassed heptane for several half-lives, isolating the product and verifying by PMR that it was identical to authentic VIII [9,15].

Acknowledgements

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References

1 (a) S. Sarel, R. Ben-Shoshan and B. Kirson, J. Amer. Chem. Soc., 87 (1965) 2517;
  (b) R. Ben-Shoshan and S. Sarel, J. Chem. Soc., Chem. Commun., (1969) 883.
2 R. Aumann, Angew. Chem., Int. Ed. Engl., 10 (1971) 188,189.
3 (a) R. Aumann, Angew. Chem., Int. Ed. Engl., 10 (1971) 190;
  (b) R. Aumann, Angew. Chem., Int. Ed. Engl., 11 (1972) 522;
  (c) R. Aumann, J. Organometal. Chem., 47 (1973) C29.
4 (a) A. Eisenstadt, Tetrahedron Lett., (1972) 2005.
  (b) Y. Becker, A. Eisenstadt and Y. Shvo, J. Chem. Soc., Chem. Commun., (1972) 1156.

5 R.M. Moriarity, C.-L. Yeh and K.C. Ramey, J. Amer. Chem. Soc., 93 (1971) 6709.
6 D. Ehntholt, A. Rosan and M. Rosenblum, J. Organometal. Chem., 56 (1973) 315.
7 W. Grimme, Chem. Ber., 100 (1967) 113.
8 R. Aumann, Angew. Chem., Int. Ed. Engl., 12 (1973) 574.
9 M. Brookhart, N.M. Lippman and E.J. Reardon, J. Organometal. Chem., 54 (1973) 247.
10 G. Wilkinson, Pure Appl. Chem., 30 (1972) 627 and refs. therein.
11 (a) C.P. Casey and C.R. Cyr, J. Amer. Chem. Soc., 95 (1973) 2248 and refs. therein;
(b) T.H. Whitesides and J.P. Neilan, J. Amer. Chem. Soc., 95 (1973) 5811.
12 W. von E. Doering and W.R. Roth, Tetrahedron, 19 (1963) 715.
13 R.J. Rawson and J.T. Harrison, J. Org. Chem., 35 (1970) 2057.
14 A. Davison, W. McFarlane, L. Pratt and G. Wilkinson, J. Chem. Soc., (1962) 4821.
15 (a) T.A. Manuel and F.G.A. Stone, J. Amer. Chem. Soc., 82 (1960) 366,6241;
(b) W. McFarlane, L. Pratt and G. Wilkinson, J. Chem. Soc., (1963) 2162.