

THERMAL DEGENERATE REARRANGEMENT OF

1,2-DIMETHYLENECYCLOBUTANE IRON TRICARBONYL

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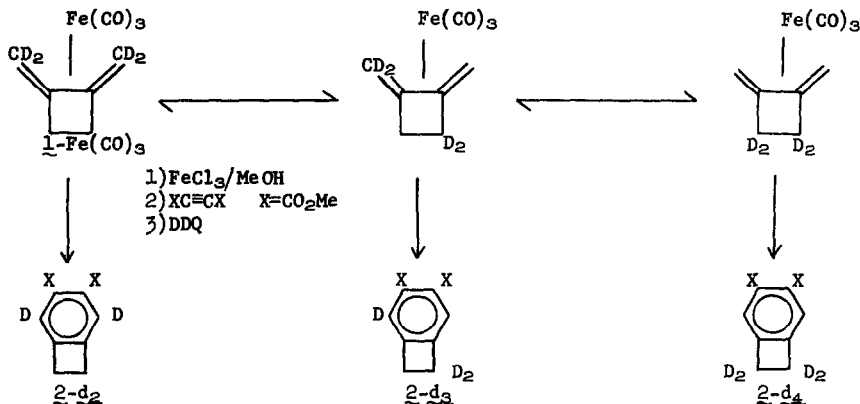
SUMMARY

Vapor phase pyrolysis of bis-1,2-(dideuteriomethylene) cyclobutane iron tricarbonyl at 170° resulted in hydrogen scrambling. Degradation of the rearrangement product indicated that either one exomethylene group was exchanging with one ring methylene or hydrogens were being reversibly transferred from the ring carbons to the exocyclic ones. Mechanisms that would explain either possibility involve the intermediacy of a sigma bonded iron with a π -allyl ligand.

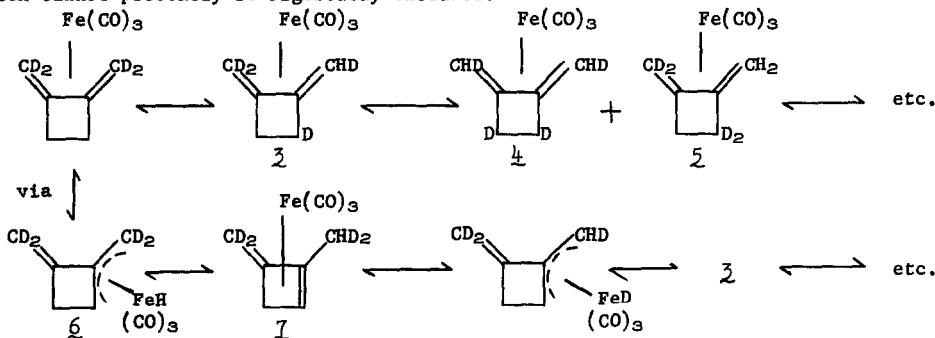
Having examined the thermally induced degenerate rearrangements of bis-1,2-(dideuteriomethylene)cyclobutane, 1, at temperatures greater than 250°,¹ and recognizing the importance of thermal rearrangements of diene iron tricarbonyls in either their preparation² or upon heating^{3,4} we subjected the iron tricarbonyl complex of 1 to vapor phase thermolysis. After heating at 170° for 3 hours, 40% of 1-Fe(CO)₃ was recovered and its pmr had, in addition to the AA'BB' pattern at δ 3.15 ppm, two new peaks of equal intensity at δ 0.67 and δ 2.03 ppm. The new peaks were in the same position as those of the exocyclic methylenes of perprotio-1-Fe(CO)₃ and constituted 14% of the total protium in the pyrolysate. Information on the position of the deuteriums in the rearranged product was obtained by degradation of the rearranged material by oxidation with ferric chloride in methanol², then treatment of rearranged 1 with excess dimethyl acetylene dicarboxylate and dehydrogenation with excess dichlorodicyanobenzoquinone (DDQ) to give the 3,4-dicarbomethoxy bicyclo[4.2.0]octa-1,3,5-trienes, 2,¹ which had the following distribution of deuterium: 2-d₂ (67.5%); 2-d₃ (29.7%); 2-d₄ (2.70%).

Unlike the rearrangement of 1 which requires temperatures in excess of 250° and proceeds via an intermediate freely rotating 2,2'-bisallyl biradical which equilibrates all four methylene groups giving a 2-d₃:2-d₄ ratio of 2¹, the rearrangement of 1-Fe(CO)₃ appears to equili-

brate only one exomethylene group with a ring methylene by the scheme:

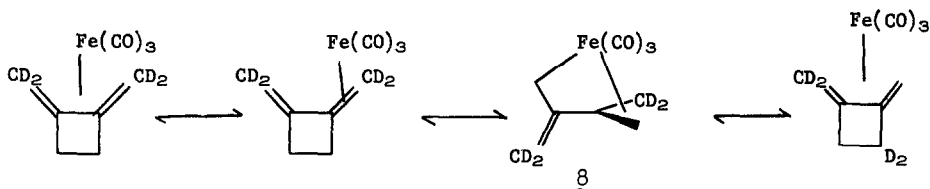


The possibility that the isomerization results from reversible hydrogen deuterium shifts to give a species like $\underline{3}$ which could go on to $\underline{4}$ and $\underline{5}$ possibly via a β -methylene cyclobutene complex cannot presently be rigorously excluded.⁵



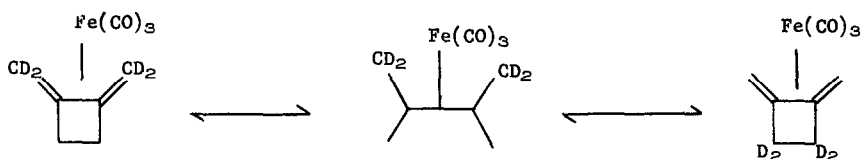
The methylenecyclobutene complex presumably would be formed via an iron hydride pi allyl intermediate like $\underline{6}$.

If carbon exchange occurs involving exchange of two methylenes each time then a mechanism that will account for the fact is one which starts with formation of a coordinately unsaturated isomeric compound which reacts with the weak cyclobutane bond to form a sigma bonded π allyl intermediate $\underline{8}$ which would revert to starting material or the proper initial rearrangement product. This mechanism borrows heavily from the previous mechanistic hypotheses observations



with diene iron tricarbonyl complexes, namely the formation of a coordinately unsaturated olefin iron tricarbonyl system presumed to be involved in the thermal racemization of chiral diene iron tricarbonyl complexes⁶ and the occurrence of a thermal unstable sigma bonded π allyl iron tricarbonyl moiety in a di-iron tricarbonyl allene trimer⁷ as well as that in bullvalene,⁸ semi-bullvalene⁹ and perhaps vinylcyclopropanes.¹⁰ It may be generally true that bonds cross conjugated with the diene iron tricarbonyl system may break and form sigma bonds to iron resulting in a π allyl complex. The same conclusion is derived from the alternative hydrogen shift pathway.

Whether or not a 16 electron olefin iron tricarbonyl complex is absolutely necessary as an intermediate in these processes is as yet unknown. However, it is clear that numerous fascinating questions in this area of thermal reactions are as yet unanswered. Interesting is the fact that the iron tricarbonyl moiety does not simply migrate across the face of the molecular system interchanging pairs of methylenes pairwise. The 18 electron rule may be the interdiction despite the relatively large distance between all of the peripheral atoms and the iron.¹



Acknowledgement:

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