Frontier Molecular Orbital Control of Stereochemistry in Organometallic Electrocyclic Reactions

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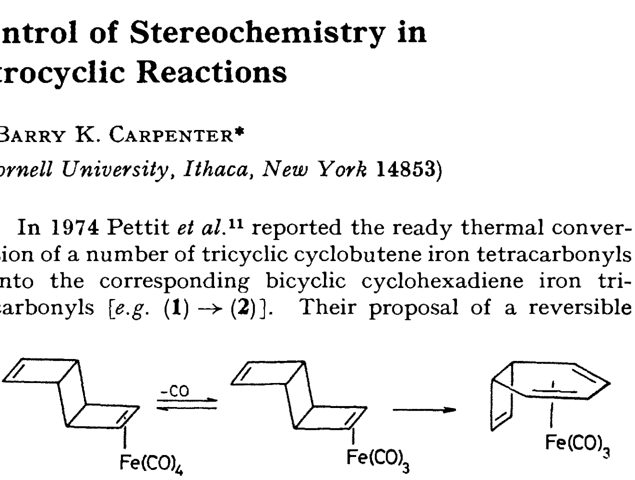
Summary A qualitative molecular orbital picture is presented that allows the classification of certain transition metal promoted ring-openings as allowed or forbidden, and further shows that for allowed disrotatory ring-openings the rotational mode that bends the breaking σ bond towards the metal should be preferred whereas for forbidden disrotatory reactions bending of the σ bond away from the metal is the lower energy process.

Following the obvious success of the concept of orbital symmetry conservation[1] in the field of organic chemistry, there have been a number of attempts to develop similar rules for organometallic reactions.[2–6] Initial interest waned when it was discovered that some apparent examples of organometallic pericyclic reactions[7,8] were, in fact, not concerted processes.[9,10]

We begin here by considering two organometallic reactions that do still appear to be pericyclic processes. Both are iron carbonyl promoted ring-openings, the first a cyclobutene–butadiene conversion[11] and the second a methylenecyclopropane–trimethylenemethane transformation.[12,13]

In 1974 Pettit *et al.*[11] reported the ready thermal conversion of a number of tricyclic cyclobutene iron tetracarbonyls into the corresponding bicyclic cyclohexadiene iron tricarbonyls [*e.g.* (**1**) → (**2**)]. Their proposal of a reversible loss of carbon monoxide from (**1**) followed by an irreversible ring-opening was strongly supported by the observation that added carbon monoxide or olefins decreased the rate of reaction. It is the second step of the reaction that appears to be a true pericyclic process.



(1) (2)

The iron carbonyl promoted ring-opening of phenyl or vinyl substituted methylenecyclopropanes reported by Noyori[12] and Billups[13] could be imagined to be analogous processes (Scheme).†

We have studied the prototypes for these reactions by extended Hückel molecular orbital theory.[14] Our results

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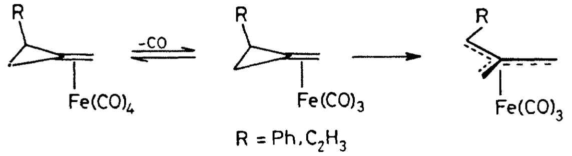
† In fact Billups *et al.* (W. E. Billups, L.-P. Lin, and B. A. Baker, *J. Organometallic Chem.*, 1973, **61**, C55) have suggested an alternative non-pericyclic mechanism. However, in the following communication we present experimental results that rule out this alternative mechanism, at least for the ring-opening of phenylmethylenecyclopropane.



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have led to a rather simple qualitative description of the ring-opening step, allowing classification of the disrotatory modes as being allowed or forbidden by orbital symmetry conservation and, furthermore, allowing discrimination between the two stereochemically distinct disrotatory processes for each complex.

One can assemble a qualitative set of molecular orbitals for tricarbonyl(cyclobutene)iron and for tricarbonyl(methylenecyclopropane)iron from the molecular orbitals for the hydrocarbon and those for an iron tricarbonyl fragment.[15] This procedure is illustrated in Figure 1 for tricarbonyl(cyclobutene)iron.

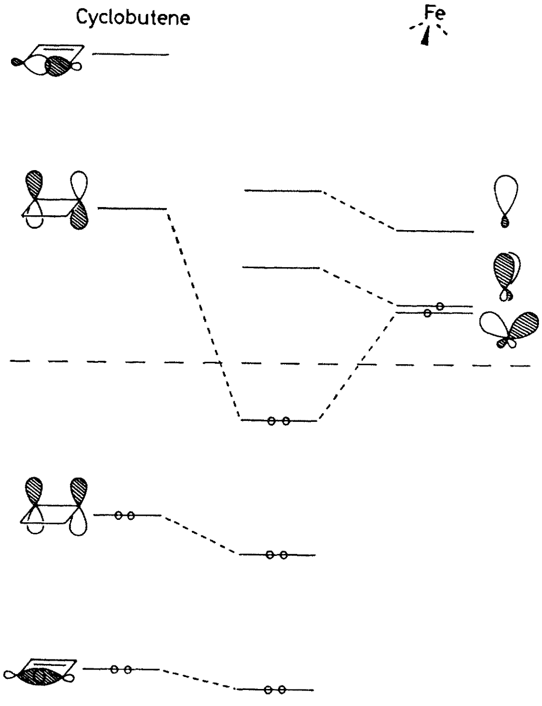

FIGURE 1

Figure 1 shows that the highest occupied molecular orbital (HOMO) can be described as a bonding interaction between an antisymmetric metal orbital and the cyclobutene π* orbital. A precisely analogous HOMO is expected for tricarbonyl(methylenecyclopropane)iron (except that the symmetric member of the originally degenerate iron tricarbonyl orbitals is now used). Both expectations are confirmed by extended Huckel calculations on the complexes.

As disrotatory ring-opening begins to occur the orbitals of the σ bond will start to mix with the ligand π orbitals and the metal orbitals. In the case of tricarbonyl(cyclobutene)iron, symmetry requires that it be the antisymmetric σ* orbital that mixes into the HOMO. Since σ* is a higher lying orbital, perturbation theory dictates that it will mix in a bonding way,[16] thereby transforming the HOMO of the reactant into a bonding, occupied orbital of the product, making the reaction allowed by orbital symmetry conservation.

The tricarbonyl(methylenecyclopropane)iron ring-opening provides a striking contrast. Now the HOMO is symmetric with respect to the xz plane (Figure 2) and so it is the bonding σ orbital that will mix into the HOMO. Since σ is a lower lying orbital, perturbation theory requires that it mix in an antibonding sense,[16] thereby transforming the HOMO into an antibonding orbital of the product, rendering the reaction forbidden by virtue of its failure to conserve orbital symmetry.

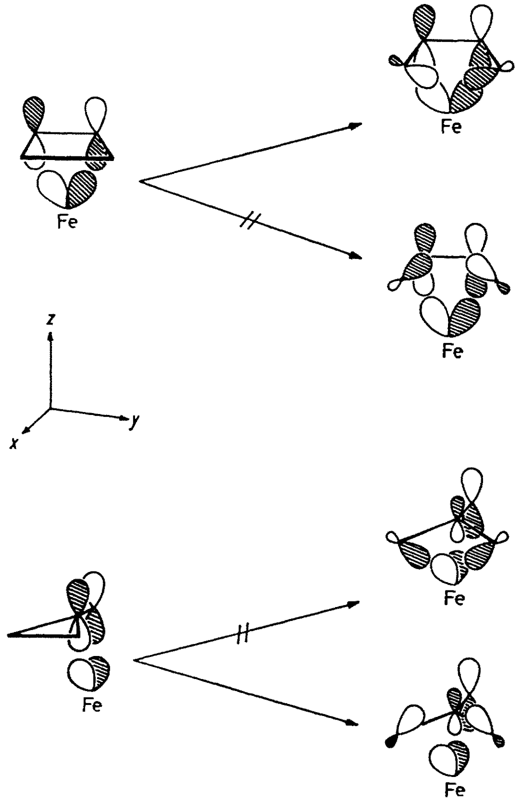

FIGURE 2

These frontier molecular orbital descriptions are confirmed by analysis of the full correlation diagrams for the ring-opening reactions. In the cyclobutene case both reactant and product have 18 occupied valence orbitals of a' symmetry‡ and 12 of a'' symmetry, whereas for tricarbonyl(methylenecyclopropane)iron the reactant has 19 a' and 11 a'' occupied valence orbitals while the product has 18 a' and 12 a''.

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‡ These orbitals come from an extended Huckel calculation and were classified according to the C_s point group.

Since the mixing of σ^* into the HOMO of cyclobutene occurs in a bonding way, the lower energy mode should be the one that bends the breaking σ bond down towards the metal, thereby maximizing overlap between the erstwhile σ^* orbital and the metal orbital Conversely the out of phase interaction between the σ orbital and the metal orbital in the ring-opening of tricarbonyl(methylenecyclopropane) iron can be minimized by bending the bond up away from the metal (Figure 2)

We believe that these results for tricarbonyl(cyclobutene)-iron and tricarbonyl(methylenecyclopropane)iron can be extrapolated to allow a general prediction for transition metal promoted electrocyclic reactions If the HOMO of the reactant is symmetric with respect to the plane bisecting the breaking σ bond, disrotatory ring-opening will be nominally forbidden by orbital symmetry and so should occur preferentially with bending of the breaking bond away from the metal If the HOMO is antisymmetric then disrotatory ring-opening is allowed and should occur preferentially with bending of the σ bond towards the metal §

Since the conrotatory mode of ring-opening does not maintain a symmetry element it is difficult to determine from qualitative arguments whether it should be more or less favourable than either of the disrotatory processes In an attempt to investigate this problem further we have performed extended Huckel calculations on an approximate reaction co-ordinate for each of the three ring-opening modes of tricarbonyl(cyclobutene)iron and tricarbonyl(methylenecyclopropane)iron The relative activation energies are found to be disrotatory-towards $<$ conrotatory $<$ disrotatory-away and conrotatory $<$ disrotatory-away $<$ disrotatory-towards, respectively It should be emphasized that the approximations inherent in the extended Huckel method[14] and the assumed reaction co-ordinates for the ring-openings do not allow a quantitative estimate of the energy differences between the various reaction stereochemistries In the case of the tricarbonyl(methylenecyclopropane)iron ring-opening the calculated difference in activation energy between the conrotatory mode and the disrotatory-away mode is so small that their relative preference is uncertain

In comparing our calculations with known experimental results we are encouraged by the observation[11] that the ring-opening of (**1**), which must occur in the disrotatory-towards mode, occurs *ca* 500 times as fast¶ as the corresponding ring-opening of the free hydrocarbon In the following communication we present experimental evidence that suggests that ring-opening of tricarbonyl(2-phenylmethylenecyclopropane)iron may occur in the disrotatory-away sense in accordance with our frontier molecular orbital picture

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§ It will of course, be the highest occupied orbital containing a significant contribution from the hydrocarbon ligand that is important Non-bonding metal orbitals or orbitals primarily concerned with bonding to the ancillary ligands are irrelevant

¶ The quoted[11] half-lives for the complex and for the free hydrocarbon differ by a factor of *ca* 250, but there is a statistical factor of 2 favouring the free hydrocarbon

[1] R B Woodward and R Hoffmann, 'The Conservation of Orbital Symmetry,' Academic Press, New York, 1970
[2] R Pettit, H Sugahara, J Wristers, and W Merk, *Discuss Faraday Soc* , 1969, **47**, 71
[3] F D Mango and J H Schachtschneider, *J Amer Chem Soc* , 1967, **89**, 2484
[4] M J S Dewar *Angew Chem Internat Edn* , 1971, **10** 761
[5] K Fukui and S Inagaki, *J Amer Chem Soc* , 1975, **97**, 4445
[6] R G Pearson *Chem Brit* , 1976 **12**, 160, 'Symmetry Rules for Chemical Reactions,' Wiley, New York, 1976
[7] H Hogeveen and H C Volger, *J Amer Chem Soc* , 1967 **89**, 2486
[8] K C Bishop, *Chem Rev* , 1976, **76**, 461 and references therein
[9] L Cassar and J Halpern, *Chem Comm* , 1971, 1082
[10] L Cassar, P E Eaton, and J Halpern, *J Amer Chem Soc* , 1970, **92**, 3515
[11] W Slegeir, R Case J S McKennis, and R Pettit *J Amer Chem Soc* , 1974, **96**, 287
[12] R Noyori, T Nishimura, and H Takaya, *Chem Comm* , 1969, 89
[13] W E Billups L P Lin and O A Gansow, *Angew Chem Internat Edn* , 1972, **11**, 637
[14] R Hoffmann, *J Chem Phys* , 1963, **39**, 1397 R Hoffmann and W N Lipscomb, *ibid* , 1962, **36**, 2179, 3489, 1962, **37**, 2872
[15] M Elian and R Hoffmann, *Inorg Chem* , 1975, **14**, 1058
[16] R Hoffmann, *Accounts Chem Res* , 1971, **4**, 1