# Kinetic Control of Stereochemistry in the Addition of Unsymmetrical Ketens to Cyclopentadiene

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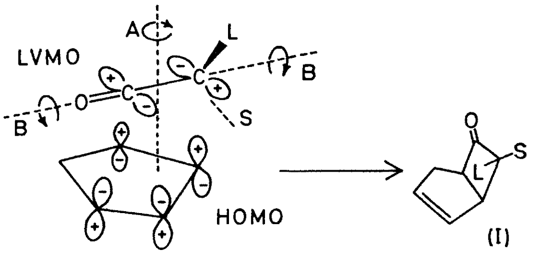
*Summary* Assumption of an initial crosswise approach of cyclopentadiene and a keten, combined with simple frontier orbital considerations, leads to a prediction of stereochemistry in the electrocyclic addition which has been confirmed by experiment.

WOODWARD AND HOFFMANN[1] have recently suggested that the cycloaddition of ketens to olefins, classified by them as $[\pi 2s + \pi 2a]$, is best understood in terms of MO symmetry if the initial approach of the two $\pi$-systems is crosswise. Use of this idea in considering the cycloaddition of an unsymmetrically substituted keten (with one large substituent, L, and a small one, S) to cyclopentadiene leads to a prediction of the stereochemical outcome.

In choosing the initial approach of the keten which minimises steric effects, two reasonable assumptions are made. Firstly, the oxygen of the keten, rather than the $\beta$ carbon with its bulky substituents, will be over the cyclopentadiene ring, and secondly, there will be a tendency for the smaller substituent to point downward toward the ring, minimising interaction with the H-atoms of the double-bond being attacked.

With assumption of this initial stereochemistry, the subsequent course of reaction can be followed by qualitative consideration of interaction of the frontier orbitals, *i.e.* the highest occupied MO (HOMO) of one component with the lowest vacant MO (LVMO) of the second component.[2] We choose the LVMO of the keten double bond and for simplicity, following Woodward and Hoffmann,[1] neglect the interaction of this double bond with the lone pair of the oxygen atom. The two possible situations are described in Figures 1 and 2. The motion of the keten relative to the cyclopentadiene required to complete the addition can now be resolved conveniently into two parts: the rotation of the keten about the centre of its double bond in the plane of the cyclopentadiene and simultaneous disrotatory opening of the double bond leading to *trans*-addition. The first part is known to be in the sense A (see Figures 1 and 2) as the final products are bicyclo[3,2,0]hept-2-en-6-ones (I) rather than the corresponding -7-ones which would result from the opposite rotation.† With this in mind, the second component must be as B for Figure 1 and C for Figure 2 and it remains to choose between these alternatives.



(I)

FIGURE 1

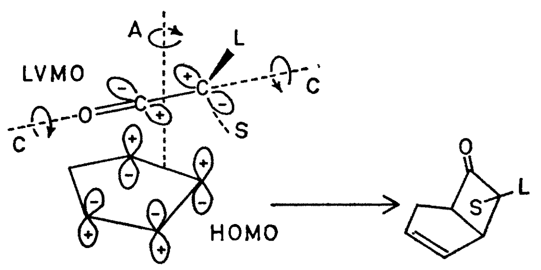
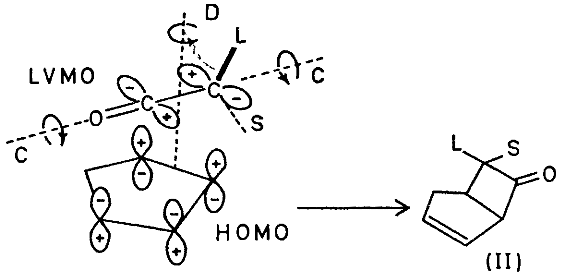


FIGURE 2

Motion (A + C) in Figure 2 in its initial stages leads to poor overlap in the newly forming $\sigma$-bonds and also produces a severe steric interaction between the substituent S and the cyclopentadiene. On the other hand, motion (A + B) in Figure 1 gives a smooth increase in overlap as the new $\sigma$-bonds form and, moreover, substituent S moves away from the cyclopentadiene ring. Clearly (A + B) is preferred and leads to the prediction that the smaller substituent of the keten will be *exo* in the bicycloheptenone.



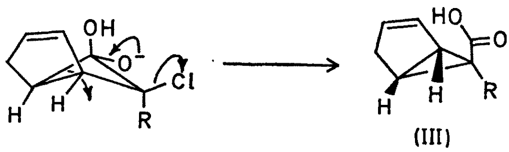
(II)

FIGURE 3

*Addition of* $\mathrm{RClC{=}C{=}O}$ *to cyclopentadiene*

| R | Yield % | 7-*endo*-Chloro epimer (%) | M.p. of *endo*-acid (III) |
|---|---|---|---|
| H[3,4] | 33 | 100 | Non-stereospecific ring contraction |
| Me[7a] | 88 | 27 | 95·5° |
| Et | 70 | 11·5 | 54° |
| $\mathrm{Pr^i}$ | 58 | 5·5 | 70° |

We have observed such a result experimentally. With cyclopentadiene and substituted chloroketens, $\mathrm{RClC{=}C{=}O}$, R=Me,[5,7a],‡ Et and $\mathrm{Pr^i}$ the proportion of *endo*-alkyl-ketone increases as the size of R increases[6] (Table). The relative stereochemistry of the adduct was derived by stereospecific base-catalysed ring-contraction of the separated epimeric ketones. The *endo*-chloroketones thus gave the corresponding *endo*-acids as in Equation 1, and these acids were shown to undergo iodo-lactonisation.



......(1)

(III)

Similarly chloroketen[3,4] and phenylchloroketen[7] give stereospecific addition in agreement with this kinetic approach control.§

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† The simple considerations above do not account for the preference of rotation A and, indeed, motions (C + D) in Figure 3 appear equally likely and should lead to bicyclo[3,2,0]hept-2-ene-7-ones (II) with the smaller substituent S again in the *exo*-position. A non-ideal "concerted" reaction has been suggested to account for the course of addition observed (G. Binsch, L. A. Feiler, and R. Huisgen, *Tetrahedron Letters*, 1968, 4497). An alternative explanation may involve secondary orbital interactions (in the initial stages of the addition) between the part of the orbital on oxygen (now considering interaction with the keten double bond) and that at the far end of the diene system from the point of attack. Qualitatively, this is not obvious however, and the interaction appears to vary considerably with the approach geometry.

‡ The observation that in more polar solvents more of the 7-*endo*-chloro-7-*exo*-methyl ketone is observed (ref. 5b) may be due to preferential solvation of the chloro-group increasing its effective size.

§ After preparation of this manuscript we noted a paper by W. T. Brady in which a similar but less detailed approach has been outlined· *Tetrahedron Letters*, 1970, 819.

[1] R. B. Woodward and R. Hoffmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 847.

[2] (a) L. Salem, *Chem. in Britain*, 1969, **5**, 449; (b) S. I. Miller, *Adv. Phys. Org. Chem.*, 1968, **6**, 202; (c) K. Fukui and H. Fujimoto, *Bull. Chem. Soc. Japan*, 1967, **40**, 2018.

[3] W. T. Brady, E. F. Hoff, R. Roe, jun., and F. H. Parry, *J. Amer. Chem. Soc.*, 1969, **91**, 5679.

[4] P. R. Brook, A. J. Duke, and J. R. C. Duke, *Chem. Comm.*, 1970, 574.

[5] (a) W. T. Brady and B. M. Holifield, *Tetrahedron Letters*, 1966, 5511; (b) W. T. Brady, R. Roe, jun., E. F. Hoff, and F. H. Parry *J. Amer. Chem. Soc.*, 1970, **92**, 146.

[6] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience, New York, 1965, p. 44.

[7] (a) Unpublished work with A. J. Duke; (b) W. T. Brady, E. D. Dorsey, and F. H. Parry, *J. Org. Chem.*, 1969, 2846.