

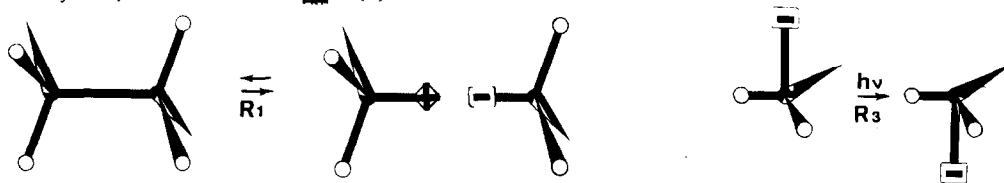
A GRAPH SYSTEM EQUIVALENT TO WOODWARD-HOFFMANN RULES

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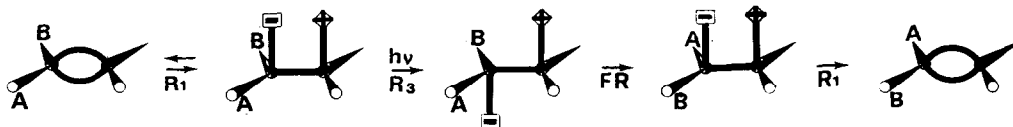
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Because of their Boolean structure, Woodward-Hoffmann rules (1) can be expressed as parity rules (1a,2,3). Since graphs are well suited to represent parity rules, we have tried to built an equivalent graph system, using the classical valence representations (tetrahedral carbon and Lewis formulas) of organic molecules and of electron displacements (Walden inversion (WI) at saturated carbon, with retention at both arriving and leaving groups) (4,5,6). In this classical approach, the double bond is represented by bent bonds (1b). We shall postulate that a concerted reaction may be decomposed into formal elementary steps of definite stereochemistry, free rotation (FR) around single bonds being allowed; the stereochemistry of a concerted reaction is determined by the stereochemistry of the elementary steps. Addition of a single new graphical rule (fig.) gives rise to most of Woodward-Hoffmann predictions for ground state chemistry : "(R1) Opening (or closure) of a single bond to  $C\oplus$  and  $C\ominus$  is only allowed with two retentions at both  $C\oplus$  and  $C\ominus$ " (7). The whole ground state chemistry can be described if a second rule is added : "(R2) Formal inversion of two tetrahedral carbons, at the same time, without motion of nuclei, is allowed". A last graphical rule (fig.) gives excited-state chemistry the opposite stereochemistry : "(R3) One photochemical excitation is represented by one (and only one) inversion at  $C\ominus$ ". (8)



We shall show that the steric course of pericyclic reactions deduced from these graphical rules is in full agreement with Woodward-Hoffmann rules :

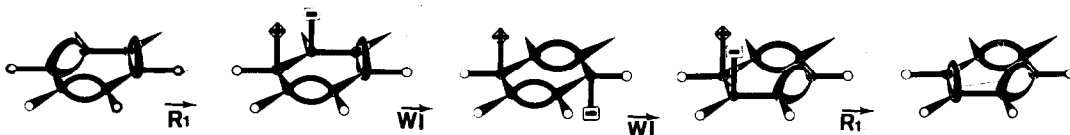
Aromaticity : Following a suggestion by Woodward (9), we shall define "aromaticity" as the possibility of formal exchange between two localized Kekulé structures : a) Ethylene is aromatic in the ground state; its isomerisation is possible by photochemical excitation (10).



b) Cyclobutadiene is not aromatic in the ground state, but in the excited state :

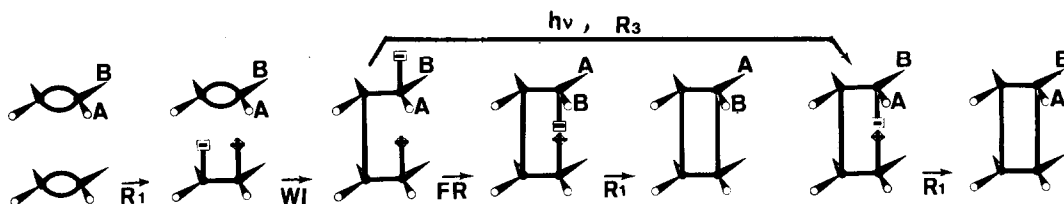


c) Cyclic conjugated systems with an odd number of double bonds – e.g. cyclohexatriene, fig. :

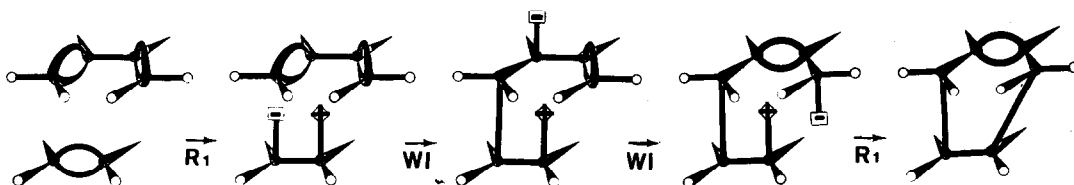


– are aromatic in the ground state ; with an even number of double bonds, in an excited state. This is equivalent to Hückel rule (11), but does not suppose a regular polygon of carbon nuclei

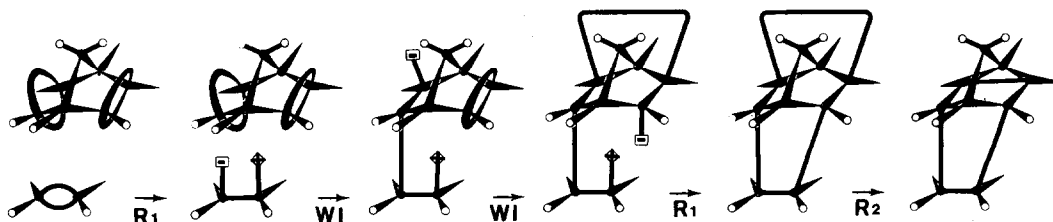
Cycloadditions and cycloreversions : The ethylene-to-ethylene ground-state addition gives the *supra-antara* product. The excited state addition gives the *supra-supra* product.



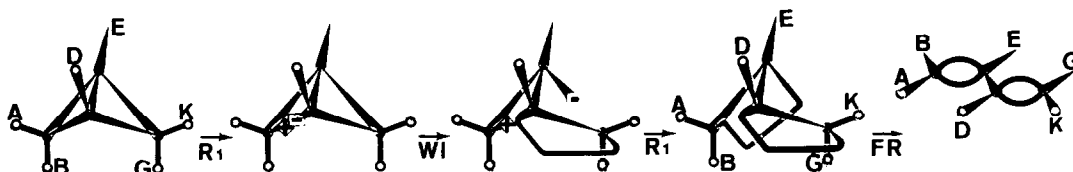
One extra double bond in one of the reagents evidently changes the stereochemistry of the addition : ethylene + butadiene is a *supra-supra* process in the ground state :



The *supra-supra* addition of olefins to bicycloheptadiene (1d) shows the use of rule 2 ( $R_2$ ) :

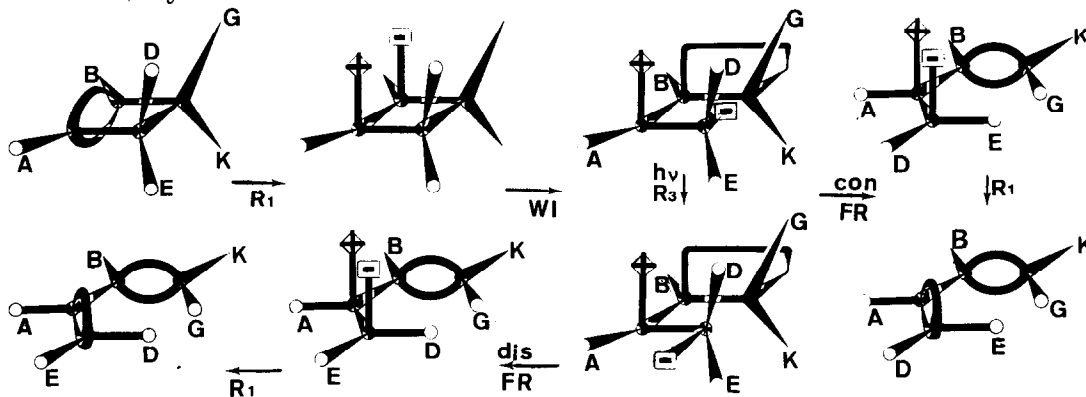


Some rearrangements are visualized using molecular models with tetrahedral carbon and flexible bent bonds : 2-4*cis*substituted bicyclobutane gives *cis,trans*disubstituted butadiene .(1e)

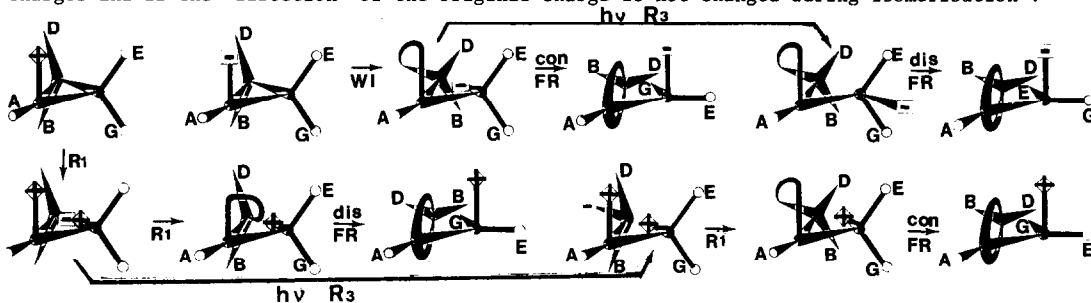


In the allowed conversion of prismane into benzene, secondary effects have to be introduced, as in the orbital symmetry treatment (1f), to rationalize the high activation energy.

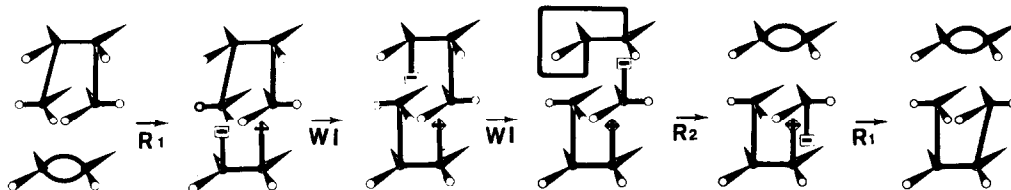
Electrocyclic reactions : Opening of cyclobutene is *conrotatory* in the ground state, and *disrotatory* in the excited state :



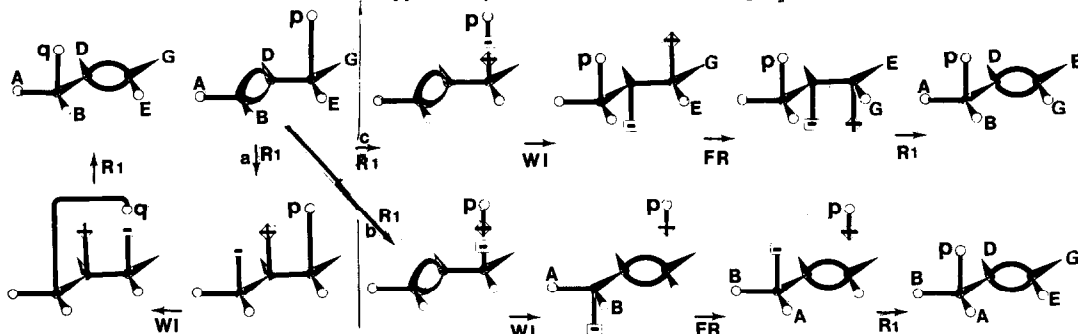
Changing the parity of the number of involved electron pairs, evidently change the stereochemistry of the process. Opening of cyclic ions is correctly predicted if  $\oplus$  and  $\ominus$  are taken as charges and if the "direction" of the original charge is not changed during isomerisation :



Group transfers and eliminations : A typical case is the allowed *supra-supra* transfer of two methyl groups from propane to ethylene, with inversion at both methyl carbon atoms.



Sigmatropic reactions : Thermal *suprafacial* 1,3 shifts are allowed — with one inversion (a) at the migrating carbon ( $q$  is inverted P), or (b,c) at one of the end groups — or with three inversions (d), (not represented here). (b) is equivalent to an *antarafacial* process with retention at P. [(c) and (d) have apparently not been discussed (1g).]



This treatment can be applied to the methylenecyclopropane rearrangement (12)

Conclusion : This graph system, a graphic translation of the parity rules, is thus equivalent to Woodward-Hoffmann rules for pericyclic reactions. Since it uses the classical formalism of organic chemistry, other (non-pericyclic) reactions may be described similarly. In fact, comparison, using this graph system, between addition or substitution reactions and analogous pericyclic reactions may give rise to new mechanistic questions.

- Notes -

- (1) R.B. WOODWARD, R. HOFFMANN, *The Conservation of Orbital Symmetry*, Verlag-Chemie, Weinheim, 1970. a) p. 169, b) p. 72, c) p. 86 (205, d) p. 106, e) p. 76, f) p. 110, g) p. 119.
- (2) J. MATHIEU, A. RASSAT, *Tetrahedron*, **30**, 1753 (1974) and references therein.
- (3) R.H. WOLLEMBERG, R. BELLOLI, *Chem. Brit.* **10**, 95 (1974); cf *Chem. Brit.* **10**, 361 (1974).
- (4) C.K. INGOLD, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca, N.Y., First Edition 1953.
- (5) R. ROBINSON, preface in M.J.J. DEWAR, *The Electronic Theory of Organic Chemistry*, Oxford University Press, Oxford, 1949.
- (6) R.J. GILLEPSIE, *Angew. Chemie*, **6**, 819 (1967) and references therein.
- (7)  $\diamond+$  and  $\square-$  can be taken as positive and negative changes (heterolytic formalism) or  $\alpha$  and  $\beta$  spins (homolytic formalism). This rule is equivalent to the inclusion of open bond structures ("ionic" or "biradical" structure) in the valence bond formulation of organic molecules (cf 1c). We use this rule as a formal representation. In the heterolytic formalism, the  $\diamond+$  center of "ionic" structure must be considered as a closely solvated cation, i.e. this  $\diamond+$  center is tetrahedral. In the homolytic formalism, Linnett type formula (I.W. LINNETT, *The Electronic Structure of Molecules*, Methuen, London, 1964) should be used, and attack of each  $\alpha$  and  $\beta$  spin should be made with inversion of the corresponding quartet at saturated carbon. Under this condition, both formalisms are equivalent. Although in hydrocarbons, the choice of  $\diamond+$  and  $\square-$  side of a bond is arbitrary, this may not be the case if heteroatoms are present, thus introducing "dipolar intermediates".
- (8) In the figures, only those atoms changing their position are labelled.
- (9) R.B. WOODWARD, *Symposium on Orbital Symmetry Correlation in Organic Chemistry*, Cambridge, January, 1969.
- (10) This simple photochemical rearrangement can also be described by a correlation diagram, in which a C2 axis is retained.
- (11) E. HÜCKEL, *Z. Physik*, **70**, 204 (1931)
- (12) W. von E. DOERING, L. BIRLADEANU, *Tetrahedron*, **29**, 499 (1973)