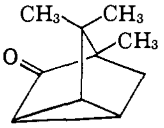
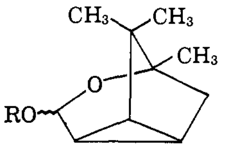
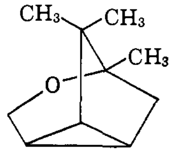
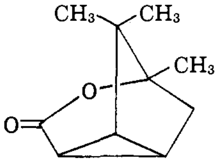

I

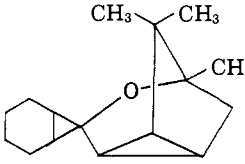

II

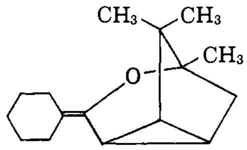

III

tillation yielded a crystalline solid, $C_{16}H_{24}O$, mp 37–39° (sealed capillary). *Anal.* Found: C, 82.43; H, 10.34; mol wt, 232 (mass spectrum).[3] This product, whose molecular formula showed it to be an adduct of I and cyclohexene, had bands in its infrared spectrum at 3.26 (sh), 3.38, 9.00, and 9.16 μ, but no bands in the hydroxyl stretching region or in the carbonyl or ethylenic double bond stretching regions. The oil, whose infrared spectrum was identical with that of the crystalline solid, showed in its nmr spectrum a complex group of signals with δ 0.25–2.0 ppm, superimposed upon which were three sharp singlets at δ 0.87, 0.97, and 1.06 ppm; there were no signals with $\delta > 2.00$ ppm. The ultraviolet spectrum of the crystalline solid had no maximum in the region 214.5–350 mμ; it showed end absorption with $\epsilon_{214.5}$ 290. Oxidation of the adduct with sodium dichromate and sulfuric acid gave the lactone IV[1,4,5] (22%) and adipic acid (14%).

These data require the assignment of structure V to the adduct. The closely related, alternative structure VI is excluded on the basis of the spectroscopic data, for, while the infrared spectrum of the adduct shows no band in the C=C stretching region, enol ethers are known to give rise to unusually strong C=C stretching bands.[6] Further, the end absorption in the ultraviolet spectrum of the adduct at 214.5 mμ is less than one-tenth of that reported for simple enol ethers.[7]


IV


V


VI

The formation of V is best interpreted as involving the formation of the carbene III followed by its addition to the double bond of cyclohexene[8] and lends strong support to the postulated intermediacy of this carbene in the formation of products of type II when I is irradiated in alcohols.[9]

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Research Council of Canada for support of this research.

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[3] We thank Professor D. B. MacLean and Dr. A. F. A. Wallis, McMaster University, for this spectrum.

[4] Due to miscalibration, the nmr signals previously reported for this compound are in error; we now find a complex group of signals at δ (CCl_4) 1.5–2.3 ppm with three sharp signals at 0.93, 0.98, and 1.20 ppm.

[5] This compound has recently been obtained also by H. E. Conrad, J. Hedegaard, I. C. Gunsalus, E. J. Corey, and H. Uda, *Tetrahedron Letters*, 561 (1965).

[6] G. D. Meakins, *J. Chem. Soc.*, 4170 (1953).

[7] G. Eglinton, E. R. H. Jones, and M. C. Whiting, *ibid.*, 2873 (1952).

[8] *Cf.* W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964, p 207.

(9) NOTE ADDED IN PROOF. Since the submission of this paper, two reports have appeared in which it is postulated that the photolysis of benzocyclobutene-1,2-dione involves formation of a carbenoid intermediate analogous to that proposed by ourselves: R. F. C. Brown and R. K. Solly, *Tetrahedron Letters*, 169 (1966); H. A. Staab and J. Ipaktschi, *ibid.*, 583 (1966). The latter workers have also succeeded in trapping this intermediate.

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On Molecular Orbital Correlation Diagrams, the Occurrence of Möbius Systems in Cyclization Reactions, and Factors Controlling Ground- and Excited-State Reactions. I

Sir:

Recently Woodward and Hoffmann[1] and Longuet-Higgins and Abrahamson[2] have presented some intriguing discussion of literature and theory. In three of these papers[1c,e,2] correlation diagrams[3] were used, while in two others[1a,b] the bonding or antibonding tendency of the highest occupied MO was considered as controlling reactions. These approaches are limited to symmetrical systems and require knowledge of the symmetry and energy of the reactant and product MO's.

The present papers (i) present another approach for symmetrical cyclic systems, (ii) suggest a method applicable to nonsymmetrical as well as symmetrical reacting systems, (iii) offer an interpretation relevant to photochemistry, and (iv) note the limitations of using only the highest occupied MO and comment on the bond-order criterion used earlier by the author.[4,5]

Some time ago Heilbronner[6] presented the fascinating idea that large-ring polyenes might be twisted once to give Möbius systems. He observed that a single sign inversion between a pair of adjacent p orbitals is characteristic of such Möbius systems and presented a formula for the MO energies.

In the case of Hückel cyclic systems, Frost and Musulin[7] have put forth the simple circle mnemonic (*cf.* Figure 1a) which gives the MO energies. Here the appropriate polygon is inscribed with one vertex down in a circle of radius 2β,[8] centered at zero (energy of an

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[1] (a) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, 87, 395 (1965); (b) *ibid.*, 87, 2511 (1965); (c) R. Hoffmann and R. B. Woodward, *ibid.*, 87, 2046 (1965); (d) *ibid.*, 87, 4388 (1965); (e) *ibid.*, 87, 4389 (1965).

[2] H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, 87, 2046 (1965).

[3] *Cf.*, e.g., C. A. Coulson, "Valence," Oxford University Press, London, 1952, pp 93, 100–101.

[4] H. E. Zimmerman, Abstracts, 17th National Organic Symposium, Bloomington, Indiana, June 1961, p 31.

[5] (a) H. E. Zimmerman and J. S. Swenton, *J. Am. Chem. Soc.*, **86**, 1436 (1964); (b) H. E. Zimmerman, *Pure Appl. Chem.*, 493 (1964).

[6] E. Heilbronner, *Tetrahedron Letters*, 1923 (1964).

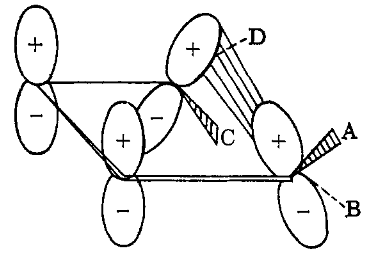
[7] A. Frost and B. Musulin, *J. Chem. Phys.*, **21**, 572 (1953).

[8] The circle radii will be 2β only if the overlap between adjacent orbitals is ethylenic. In Figures 1a and 1b it is approximated that all

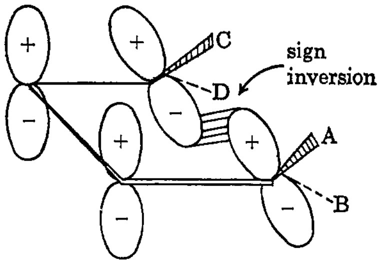
isolated p orbital electron); each vertex gives one MO energy by its vertical displacement.

It is now noted that a similar mnemonic device can be derived from the Heilbronner formula. However, here the Möbius polygon is inscribed with one *side* down, as in Figure 1b.[8]

The two type systems are germane to consideration of conrotatory *vs.* disrotatory ring closure.[1,2,9] Thus, the partially closed disrotatory (*e.g.*) butadiene has all of its basis set p orbitals with plus lobes overlapping and is a Hückel-like system. The conrotatory species has one sign inversion and is a Möbius system. Similarly, the larger rings are "Hückel" when disrotatory and "Möbius" when conrotatory. We use idealized Hückel and Möbius systems above as reaction models.



disrotatory
a Hückel system



conrotatory
a Möbius system

A comparison using the presently proposed circle mnemonic for Möbius systems shows that the Hückel systems are preferred where there are $4n + 2$ electrons while the Möbius systems are preferred where there are $4n$ electrons (*cf.* ref 6), and a reversal of the situation for singly excited species. Not only is the circle mnemonic useful in quickly assessing the likely stability of delocalized organic systems with a sign inversion enforced,[10] but also gives, without explicit calculation or prior knowledge of MO's, the correlation diagram in conrotatory (Hückel) and disrotatory (Möbius) ring closures. Furthermore, this device reveals each crossing of MO's during reaction. In using the circle mnemonic, we assume that it represents the orbital situation at a given stage of reaction, thermal or photochemical.

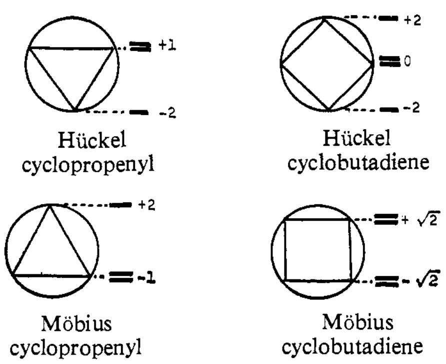


Figure 1. (A, top) Frost–Musulin-Hückel mnemonic; (B, bottom) present mnemonic device for Möbius systems.

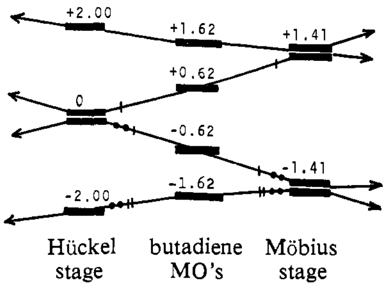


Figure 2. Hückel and Möbius closure of butadiene to cyclobutene. Dots represent electron population for ground-state reaction. Vertical lines show electrons for excited-state case.

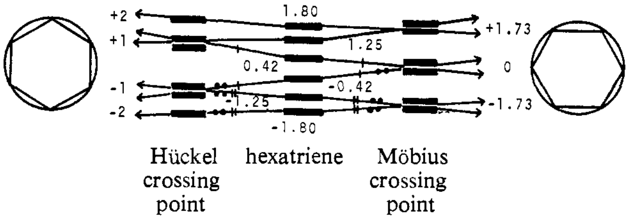


Figure 3. Hückel and Möbius closure of hexatriene to cyclohexadiene. Dots represent electron population for ground-state reaction. Vertical lines show electrons for excited-state case.

Using the MO energies for the four ring cases as given in Figure 1, and knowing the MO energies of reactant butadiene, we can sketch the Möbius and Hückel alternative closures as in Figure 2. In Figure 3 we apply the same reasoning to the hexatriene case. The MO electron populations in the ground- and excited-state examples given are considered to remain the same as in the reactant polyene up to the points along the reaction coordinate where degeneracies occur (*i.e.*, crossing points). The energies of the Hückel or Möbius species, appropriately populated, give an approximation to the energy of the reacting system *as the crossing point is approached.* The rules derived as given above are the same as obtained by the Woodward–Hoffmann[1] and Longuet-Higgins[2] groups.

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Received January 3, 1966

adjacent pairs of p orbitals overlap equally, whether in Hückel or Möbius systems. The circle diameter then diminishes equally.

(9) (a) E. Vogel, *Ann.*, **615**, 4 (1958); (b) W. von E. Doering, 10th Reactions Mechanisms Conference, Corvallis, Oregon, June 1964; (c) E. N. Marvell, G. Caple, and B. Schatz, *Tetrahedron Letters*, 385 (1965); (d) E. Vogel, W. Grimme, and E. Dinne, *ibid.*, 391 (1965); (e) E. Havinga and J. Schlatmann, *Tetrahedron*, **16**, 151 (1961); (g) D. S. Glass, J. Whathey, and S. Winstein, *Tetrahedron Letters*, 377 (1965). The preceding list is only representative.

(10) Möbius systems are found in a variety of organic reactions. One interesting example is the intermediate in 1,2-phenyl migrations which has a sign inversion in a triangular array of three p orbitals. Barrelene is another case.