The Cope Rearrangement Revisited

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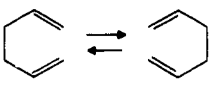
Abstract: This paper attacks the problem of reducing the activation energy of a Cope rearrangement to a negative number. The molecular orbitals of semibullvalene and the transition state for its Cope rearrangement are constructed. Then the effect of different substituent patterns on the energy of reactant or transition state is evaluated with emphasis on the effect of substituents on the strength of the cyclopropane 2–8 σ bond and on the destabilizing AS transition state orbital. The interesting general conclusion is that in this molecular framework the substituents are as likely to promote or retard a reaction by influencing the stability of reactant or product as they are by influencing the transition state. Specifically strong equilibrium preferences are predicted for π-electron donor or acceptor substituents unsymmetrically substituted, and a lowering or raising of the Cope rearrangement activation energy on appropriate symmetric substitution.

The remarkable elaboration of the Cope rearrangement forms one of the intellectually most pleasing chapters of modern chemistry.[1] The archetypal degenerate rearrangement of hexa-1,5-diene (**1**) is greatly facilitated in the nondegenerate rearrangement of *cis*-1,2-divinylcyclopropane (**2**) to cyclohepta-1,4-diene (**3**).[2,3]



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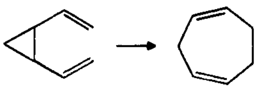
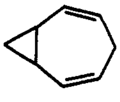


2 **3**

Degeneracy is restored in the rearrangement of homotropilidene (**4**)[1,3] and culminates in the striking structure of bullvalene (**5**).[1,3,4] While sequential Cope rearrangements readily make all carbon atoms equivalent in bullvalene, the activation barrier to this rearrangement can be decreased still further. This occurs in dihydrobullvalene (**6**),[5] barbaralone (**7**),[6a] barbaralane (**8**),[6] and semibullvalene (**9**).[7] Table I shows some of the measured free energies of activation.



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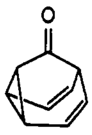

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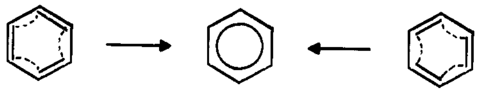
Table I. $\Delta F^{\ddagger}$ in Some Cope Rearrangements

Compd	$\Delta F^{\ddagger}$, kcal/mol	Ref
1,5-Hexadiene-*1,1'-d*$_2$	35.5	*a*
Protonated barbaralone	>13.8	*b*
1,3,5,7-Tetramethylhomotropilidene	13.6	*c*
Bullvalene	12.8	*d*
Barbaralone	9.6	*e*
Barbaralane	7.8	*f*
Octamethylsemibullvalene	6.4	*g*

[a] V. Toscano and W. von E. Doering, unpublished work, cited in footnote 12 of ref 6a. [b] P. Ahlberg, J. B. Grutzner, D. L. Harris, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 3478 (1970). [c] L. Birladeanu, quoted in footnote 3b of F. A. L. Anet and G. E. Schenck, *Tetrahedron Lett.*, 4237 (1970). [d] A. Allerhand and H. S. Gutowsky, *J. Amer. Chem. Soc.*, **87**, 4092 (1965). [e] J. S. Lambert, *Tetrahedron Lett.*, 1901 (1963). [f] See ref 6. [g] See Anet and Schenck, footnote *c*.

The recognition of the Cope rearrangement as a symmetry-allowed [3,3]sigmatropic shift or a ${}_{\pi}2 + {}_{\sigma}2 + {}_{\pi}2$ cycloaddition[8] complements our understanding of this interesting reaction. Symmetry-allowed reactions, though electronically favored, still proceed with sizable activation energies. So far it is only in one class of molecules, the cyclopolyenes, that the geometrical factors have become so favorably arranged that the ultimate of transition-state stabilization—a negative activation energy—is achieved. Thus we may consider benzene the transition state for the symmetry-allowed ${}_{\pi}2_s + {}_{\pi}2_s + {}_{\pi}2_s$ cycloaddition in a cyclohexatriene. Extending this line of reasoning it becomes natural to ask whether other classes of allowed reactions can be brought to such a stage of perfection. The Cope rearrangement systems, where we already know activation energies of only 6 kcal/mol, are obvious subjects for theoretical scrutiny.



The purpose of this paper is to analyze in what ways the activation energy for the Cope rearrangement may be modified, and to suggest realistic candidates for the achievement of our goal—the Cope rearrangement which cannot be frozen out.

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(1) A classic account of this research is given by W. von E. Doering and W. R. Roth, *Angew. Chem.*, **75**, 27 (1963).

(2) E. Vogel, K.-H. Ott, and K. Gajek, *Justus Liebigs Ann. Chem.*, **644**, 172 (1961).

(3) W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).

(4) G. Schröder, *Angew. Chem.*, **75**, 722 (1963).

(5) R. Merényi, J. F. M. Oth, and G. Schröder, *Chem. Ber.*, **97**, 3150 (1964); G. Schröder, J. F. M. Oth, and R. Merényi, *Angew. Chem.*, **77**, 774 (1965).

(6) (a) W. von E. Doering, B. M. Ferrier, E. T. Fossel, J. M. Hartenstein, M. Jones, Jr., G. Klumpp, R. M. Rubin, and M. Saunders, *Tetrahedron*, **23**, 3943 (1967); (b) U. Biethan, H. Klusacek, and H. Musso, *Angew. Chem.*, **79**, 152 (1967); (c) H. Tsuruta, K. Kurabayashi, and T. Mukai, *Tetrahedron Lett.*, 3775 (1967).

(7) H. E. Zimmerman and G. L. Grunewald, *J. Amer. Chem. Soc.*, **88**, 183 (1966); see also R. Criegee and R. Askani, *Angew Chem.*, **80**, 531 (1968), for octamethylsemibullvalene.

(8) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 2511 (1965); *Angew. Chem.*, **81**, 797 (1969).

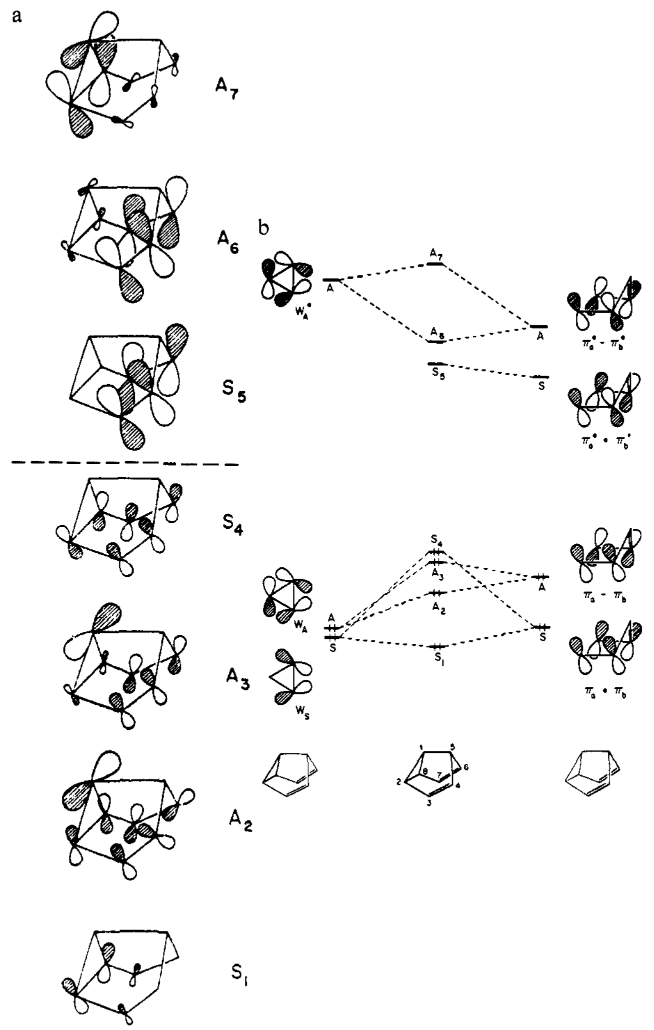
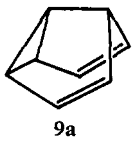


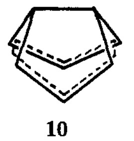
Figure 1. (a) Higher occupied and lower unoccupied molecular orbitals of semibullvalene. The atomic orbital sizes represent only approximately the magnitude of the relevant coefficients; their directions are similarly idealized. Orbitals below dashed line are occupied. Symmetry designations and energy ordering are after b. (b) Semibullvalene molecular orbitals (middle) constructed from the interaction of cyclopropane (left) and pentadiene (right) fragment orbitals. S and A denote symmetry or antisymmetry with respect to molecular plane.

Semibullvalene

Our analysis focuses first on the structural unit of semibullvalene, since the activation energy for the degenerate rearrangement of **9a** to **9b** is the lowest on record. The potential energy diagram relating **9a** to **9b**



9a



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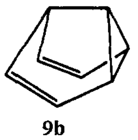
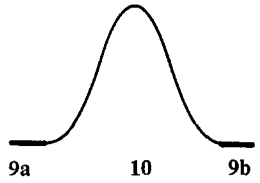


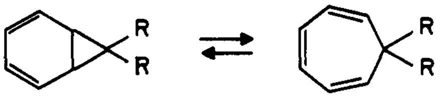
9b

via the transition state **10** is shown schematically below.



No great philosophical insight is required for the recognition that a lower activation energy can be achieved by destabilizing the reactant or product, or by stabilizing the transition state, or by some combination of both. We begin by considering the effects of substituents on the reactant and product semibullvalene.

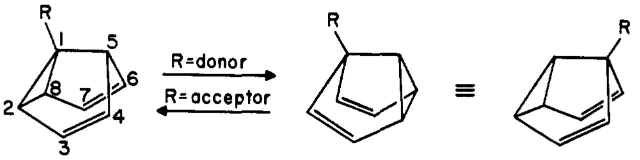
Substituents on a cyclopropane ring influence the stability of ring bonds. An analysis of this phenomenon has already been given elsewhere,[9] rationalizing the remarkable sensitivity of the norcaradiene–cycloheptatriene equilibrium to substituents at the 7 position. It was shown that the Walsh orbitals of the cyclopropane



11 **12**

interact in a π manner with π acceptors so as to strengthen the 1–6 bond in **11** and with π donors so as to weaken the same bond. π acceptors thus shift the equilibrium to the norcaradiene side, π donors to the cycloheptatriene side.[9]

The same argument can be applied directly to semibullvalene. Consider the rearrangement of **13** to **14**.



13 **14**

In **13** the substituent is on the cyclopropane ring, while in **14** it is on a "normal" tertiary carbon. If R is a π acceptor it will strengthen the 2–8 bond in **13** but will have little effect on **14**. Thus **13** should be more stable than **14**. Similarly if R is a π donor it will weaken the 2–8 bond of **13** and shift the equilibrium to **14**.

In order for our argument to be valid it is necessary that the valence orbitals of semibullvalene contain the Walsh orbitals of cyclopropane or a set of comparable symmetry.

Figure 1a shows the relevant orbitals of semibullvalene, as obtained from an extended Hückel calculation.[10,11] These orbitals are constructed in Figure 1b from the interaction of, at right, a penta-1,4-diene fragment with the same geometry as the corresponding unit (carbons 3–7) in semibullvalene and, at left, an undistorted cyclopropane. This reconstruction explains some unusual features of the orbitals of semibullvalene and thus merits detailed discussion.

The pentadiene double bonds are held in close proximity in semibullvalene. Through-space interaction dominates.[12] Thus, the symmetric combinations $\pi_a + \pi_b$ and $\pi_a{}^* + \pi_b{}^*$ emerge at lower energy than the antisymmetric $\pi_a - \pi_b$ and $\pi_a{}^* - \pi_b{}^*$. The computed splittings are comparable to those in other homoconjugated dienes.[13] $\pi_a + \pi_b$ and the symmetric Walsh orbital W_S interact to yield S_1 and S_4 of semibullvalene;

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(9) R. Hoffmann, *Tetrahedron Lett.*, 2907 (1970); H. Günther, *ibid.*, 5173 (1970).

(10) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); R. Hoffmann and W. N. Lipscomb, *ibid.*, **36**, 2179, 3489 (1962); **37**, 2872 (1962). The parameters were the same as those used previously, except for a hydrogen exponent of 1.3.

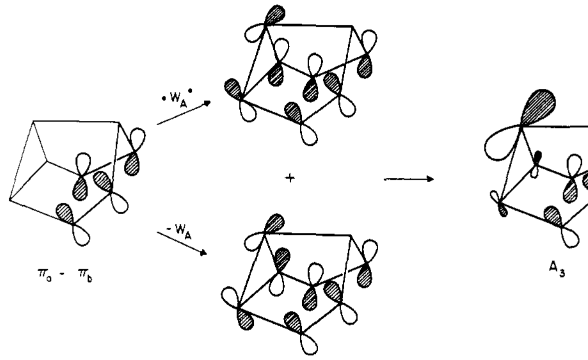
(11) The semibullvalene geometry was a model one, with C_1–C_5, C_1–C_2, and C_2–C_8, 1.54 Å; C_3–C_4, 1.34 Å; C_2–C_3 and C_4–C_5, 1.52 Å; C_3–H and C_4–H, 1.08 Å; all the other CH's, 1.09 Å. Some representative angles are 123 = 108°, 234 = 109°, 345 = 110°, 215 = 100°, 156 = 107°.

(12) R. Hoffmann, *Accounts Chem. Res.*, **4**, 1 (1971).

(13) P. Bischof, R. Gleiter, E. Heilbronner, V. Hornung, and G. Schröder, *Helv. Chem. Acta*, **53**, 1645 (1970), and references therein.

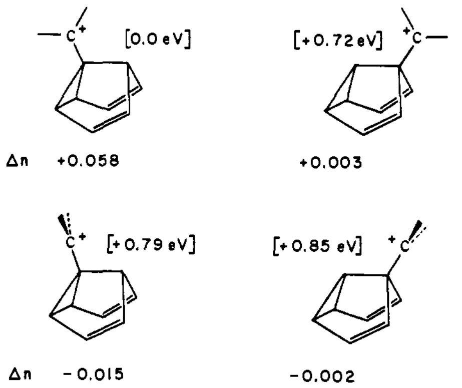
similarly W_A mixes with $\pi_a - \pi_b$ to give A_2 and A_3. These four orbitals contain double-bond and Walsh character about equally, whereas the corresponding antibonding orbitals, $\pi_a^* \pm \pi_b^*$ and W_A^*, being more disparate in their unperturbed energies, mix less.

Of interest is the shape of the highest occupied antisymmetric orbital A_3. This orbital resembles in its nodal properties the Walsh orbital W_A, but with enhanced coefficient at C-1 and diminished coefficients at C-2 and -8. The size of the coefficient at position 1 is of course important with respect to the interaction of substituents at that position. The reason for the distorted shape of A_3 is the following. The orbital is based on $\pi_a - \pi_b$ mixing into itself W_A in an antibonding way and W_A^* in a bonding manner.[14]



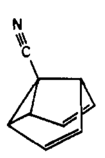
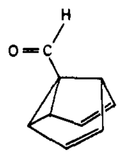
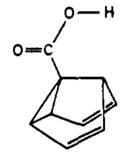
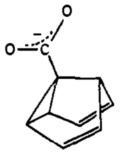
It is now clear that semibullvalene possesses among its valence orbitals a set of the proper symmetry to interact with π donors or acceptors at position 1. An acceptor will interact strongly with A_2 and A_3, especially with A_3, whose energy is closer to the acceptor level, and whose coefficient at position 1, as explained above, is very large indeed. Electron transfer out of A_2 and A_3 to the acceptor will be accompanied by strengthening of the 2–8 σ bond.

We next tested our qualitative arguments with some extended Hückel calculations. Consider a semibullvalenyl carbonium ion in which the carbinyl group is substituted at position 1 or 5 and is held in a bisected or perpendicular conformation. The semibullvalene geometry is fixed throughout. The diagram below notes energies in electron volts relative to the most stable form and overlap population changes for the 2–8 bond relative to the unsubstituted semibullvalene. These bond-order changes, Δn, are positive if the 2–8 bond is stronger than in semibullvalene, negative if it is weaker.



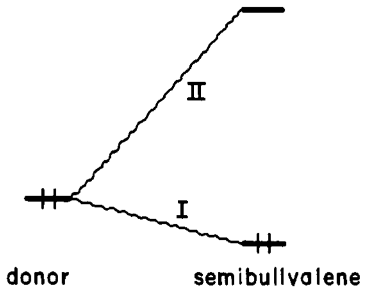
A carbonium ion center is of course an acceptor *par excellence*. The great stabilization of the bisected cyclopropylcarbinyl geometry is no surprise.[9,15,16] Note that in agreement with our expectations this acceptor prefers position 1 to position 5, and in the π interacting bisecting conformation at position 1 it strengthens the crucial 2–8 σ bond. In the perpendicular conformation at 1, and in all conformations at 5, such a substituent has little effect.

Our considerations carry over directly to other acceptor substituents. Thus we find significant stabilization of the molecules **15**, **16**, **17**, and **18**. Below each structure we give the energy difference favoring substitution at position 1 over that at position 5, and the extent of strengthening of the 2–8 bond.

	15	16	17	18
ΔE	0.37 eV	0.43 eV	0.40 eV	0.37 eV
Δn	+0.020	+0.030	+0.024	+0.021

The interaction of the semibullvalene orbitals with a π donor such as NR_2, OR, or halogen has some interesting features. Consider the level diagram shown below, in which the semibullvalene has been schematized by a two-level system. Bond-order changes following interaction are easily predictable. No large bond order change is to be expected from interaction I between donor and occupied semibullvalene levels, since charge transfer from donor to semibullvalene is balanced by charge transfer in the opposite direction. The only significant bond order effects are to be expected from interaction II, by which electron density is transferred from the donor to the unoccupied semibullvalene orbitals. The only low-lying unoccupied orbital with sizable electron density at position 1 or 5 is A_7, an antisymmetric orbital which is 2–8 antibonding. We thus expect that a donor will decrease 2–8 bonding but only if it is located at position 1 and is oriented in a π way to interact with the antisymmetric A_7.



The accompanying energetics are less obvious. In the case of an acceptor it was clear that maximum stabilization was associated with maximum bond-order effect. This is not necessarily so for the donor. Two cases must be distinguished, depending on the relative position of the donor level. If the donor level is low, interaction I will dominate over II, the donor level will move up, and the system will be destabilized in just that conformation which gives maximum bond-order changes. If the donor level is high, interaction II will dominate, the donor level will move down, and the

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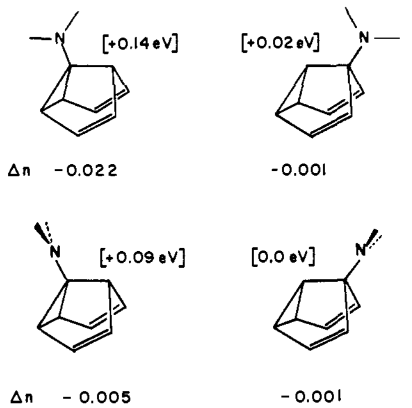
(14) See ref 12 for the simple rules governing orbital mixing.

(15) (a) R. Hoffmann, *Tetrahedron Lett.*, 3819 (1965); (b) R. Hoffmann *J. Chem. Phys.*, 40, 2480 (1964).

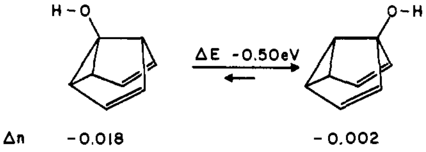
(16) R. Hoffmann and R. B. Davidson, *J. Amer. Chem. Soc.*, 93, 5699 (1971).

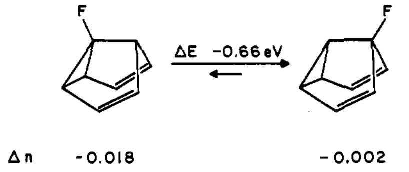
equilibrium geometry will coincide with that of maximum bond-order effect. With the normal donor substituents we have studied we expect the first possibility to be followed.

These considerations are clarified by examination of the effects of a typical donor, the amino group, calculated here in a planar geometry. The most stable geometry is that with least orbital interaction—NH_2 at the 5 position in a symmetric perpendicular geometry. But the geometry with maximum bond order effect, *i.e.* the expected weakening of the 2–8 bond, is at higher energy. This is the bisected antisymmetric conformation of NH_2 at position 1.

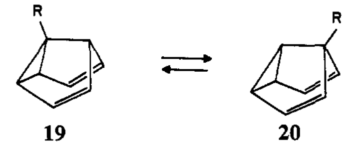


Two further donor substituents we tested were hydroxy and fluoro. Both of these groups have low-lying lone-pair orbitals. We would accordingly expect strong destabilization on 1 substitution. This is confirmed in our calculations. Of course the hydroxy group can escape this destabilization by rotating out of conjugation, while the fluorine lacks this option.





We summarize our conclusions at this stage. In considering π-electron donating or accepting substituents at positions 1 and 5 of semibullvalene, we predict that π-electron donors will shift the Cope equilibrium markedly toward **20**, while π-electron acceptors will shift the equilibrium in the opposite direction, toward **19**. Substitution at position 5, the tertiary carbon, is expected to have no significant effect on the strength of the 2–8 bond, while substitution at position 1, on the cyclopropane ring, is expected to strengthen the 2–8 bond if R is a π-electron acceptor, and weaken the same bond if R is a π donor.



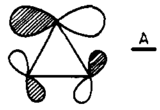
19 **20**

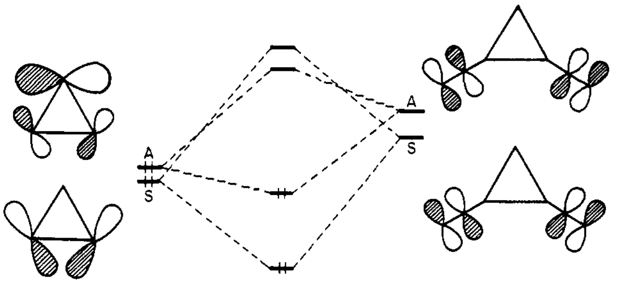
Another pattern of substitution by which stability of the reactant or product in the Cope rearrangement may be affected is shown below. Consider the case of R = CN, a π acceptor. As discussed previously,[9] a single π acceptor substituted at position 1 in a model cyclopropane, **23**, weakens the 1–2 and 1–3 bonds while strengthening 2–3. Since these effects should, to a first approximation, be additive, we would expect that in a disubstituted cyclopropane, such as **24**, the 1–2 bond should be severely weakened. This is because the bond-weakening effects of charge transfer to the acceptor should reinforce each other in this bond, while in the other bonds the bonding and antibonding effects should approximately cancel each other.

21 **22**

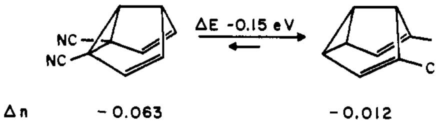
23 **24**

Alternatively we consider the interaction of a symmetric and antisymmetric acceptor orbital combination with the Walsh orbitals of cyclopropane, as shown below. The interaction of symmetric levels will decrease, and the interaction of antisymmetric levels increase, the 1–2 bond order. But the symmetric Walsh orbital has more electron density than its antisymmetric counterpart at the two carbons to which the acceptors are attached. Therefore the symmetric interaction should be stronger, resulting in a net decrease of the 1–2 bond order. These arguments are confirmed by extended Hückel calculations on a model disubstituted cyclopropane.



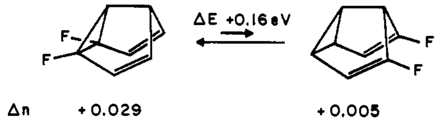


While the above considerations applied to the cyclopropane part of semibullvalene would correctly predict that 2,8-dicyano substitution leads to 2–8 bond weakening, it would be premature to assume that the **25** to **26** equilibrium is shifted to the right. Examination of the semibullvalene orbitals (Figure 1) reveals that through A_2, A_8, and S_4 the molecule should be responsive to acceptor substitution at sites 4 and 6 as well. As shown by the results of the calculation below the balance



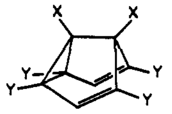
25 **26**

struck appears to be the one where 4,6 substitution is favored. The results for a typical donor are complementary. The second partial conclusion we reach is



then the following. In considering substituents at positions 2, 4, 6, and 8 of semibullvalene, π-electron donors at any of these sites will strengthen the 2–8 bond and π-electron acceptors will weaken it. The effects will be accentuated upon 2,8 disubstitution.

The next logical step is to put these arguments all together and devise a pattern of substitution which maximally weakens the 2–8 bond in reactant and product. Such a pattern is given in **27**, where X is a



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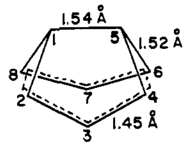
π-electron donor and Y a π-electron acceptor. For a model compound with X = F and Y = CN we calculate a Δn of -0.086 for the 2–8 bond.

The Cope Rearrangement Transition State

We now turn to the problem of stabilizing the transition state for the Cope rearrangement in semibullvalene. As a transition state model we used the following C_{2v} geometry.[17] The dihedral angle between the five-



membered ring planes was varied and gave an energy minimum at approximately 95°. The extended Hückel valence orbitals at this minimum are shown in Figure 2, classified in symmetry with respect to the two mirror planes.

The level ordering is the expected one for two strongly interacting allyl systems.[18–20] The splitting between the nonbonding allyl combinations SA and AA is 2.7 eV. This large energy gap is certainly sufficient to assure that the ground state of this system is a singlet. The magnitude of this splitting is a consequence not only of direct through-space interaction. The AA orbital interacts strongly with a combination of 1–2, 1–8, 5–4, and 5–6 σ bonds—the 95° dihedral angle is near optimal for such allylic type mixing.[21] The resultant mixing in of p orbitals at positions 1 and 5 is significant not only for determining the energy gap but also for assessing the role of substituents at these positions.

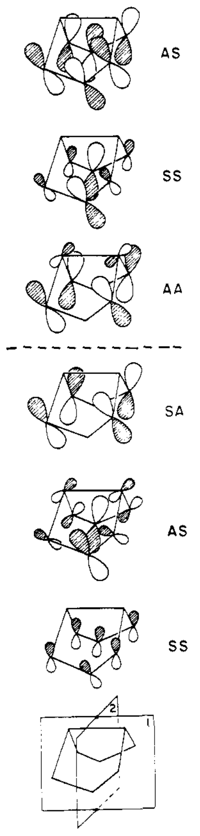
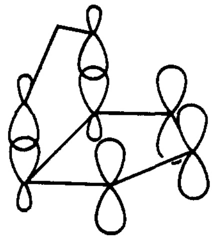
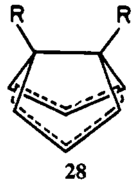


Figure 2. Molecular orbitals of Cope rearrangement transition state for semibullvalene. The magnitudes and directions of orbitals are idealized, as in Figure 1a. Orbitals below dashed line are occupied.



The crucial orbital destabilizing the transition state of the Cope rearrangement is the occupied AS orbital. This was clearly recognized by Doering, Roth, and Berry.[22] Our attempts to lower the energy of this transition state clearly must focus on the stabilization of this orbital by various acceptors.

Consider first the substituent pattern **28**. The two



28

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[17] The angle strain within the five-membered ring was averaged over all five available angles. The allylic hyrogens are constrained to lie in the plane of the five carbons in their ring. We note here that Brown, Dewar, and Schoeller[18] have in a MINDO/2 calculation on the "boat" transition state of the Cope rearrangement of hexa-1,5-diene found that the hydrogens corresponding to those at carbons 3 and 7 in semibullvalene are tilted toward each other, in accord with an antibonding interaction between these centers.

[18] A. Brown, M. J. S. Dewar, and W. Schoeller, *J. Amer. Chem. Soc.*, **92**, 5516 (1970).

[19] W. von E. Doering and W. R. Roth, *Tetrahedron*, **18**, 67 (1962).

[20] (a) R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 4389 (1965); (b) R. Hoffmann, A. Imamura, and G. D. Zeiss, *ibid.*, **89**, 5215 (1967).

[21] For a discussion of through-space and through-bond interaction of orbitals see ref 12; R. Hoffmann, E. Heilbronner, and R. Gleiter, *ibid.*, **92**, 706 (1970).

[22] See ref 1, footnote 10, and ref 19 footnote 13.

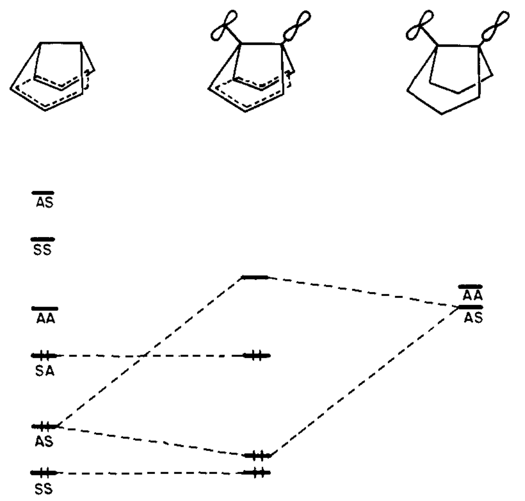
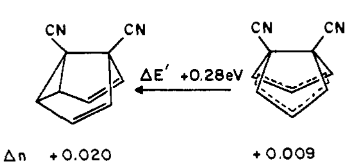


Figure 3. Interaction diagram for the mixing of two acceptor orbitals (right) with semibullvalene transition state orbitals (left). Symmetry classification uses the two planes defined in Figure 2. Only the chemically significant mixing of occupied donor with unoccupied acceptor orbitals is shown.

acceptor groups R generate low-lying unfilled orbitals of AS and AA symmetry. The former combination interacts with the AS allylic combination by virtue of the antisymmetric contribution present at positions 1 and 5 of that orbital (see Figure 3). It would appear that transition-state stabilization would thus be achieved.

This does not necessarily imply that the activation energy for the Cope rearrangement will be lowered. We must simultaneously examine the effects of any given substituent pattern on both the transition state and the "collapsed" reactant or product. Going back to the discussion of the previous section it will be recalled that whereas the effect of an acceptor at position 5 was negligible, the same substituent at position 1 enhanced the strength of the 2–8 bond. We therefore have the undesirable conclusion that in substituent pattern **28** product, reactant, and transition state are all stabilized.

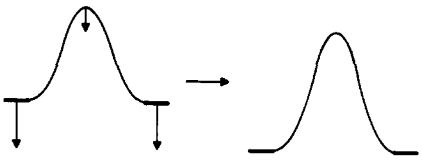
Gradations in stabilization obviously exist and we turn to our molecular orbital calculations to help us decide if the transition state is more or less stabilized than the reactant and product. Extended Hückel total energies by themselves are poor guides to total stability, but good indicators of relative energetic trends. In the case at hand they make the transition state for the unsubstituted Cope rearrangement of semibullvalene more stable than the collapsed molecule, geometries not optimized in either case. Therefore, instead of the absolute energies we compare for each case how the difference in energy between ground and transition states is changed for a given set of substituents, relative to that difference for unsubstituted semibullvalene. In the case of the cyano group we obtain the following result.



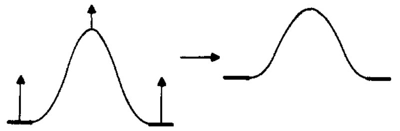
29 **30**

$\Delta E'$ is the difference in activation energy of the Cope rearrangement relative to semibullvalene, a positive value implying that the activation energy is raised by substitution, a negative value implying that it is lowered. The Δn values are as before the increments to the 2–8 bond orders upon substitution, a positive value implying a stronger bond.

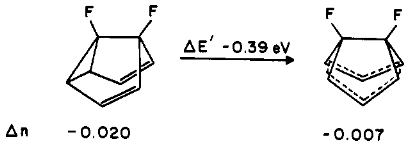
In the cyano case we thus find that the activation energy to the Cope rearrangement is increased, *i.e.*, while both transition state and reactant are stabilized, the latter is more so. This is reflected in the bond orders as well—the direct conjugation with the Walsh orbital in the reactant **29** is more effective than the hyperconjugative interaction through the bridgeheads in **30**.



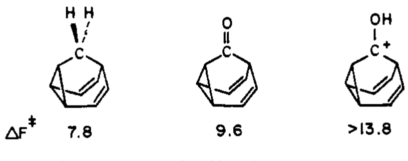
An immediate consequence of the above argument is that it is worthwhile to try an identical pattern of donor substituents. Here both transition state and reactant are destabilized, but the latter more so.



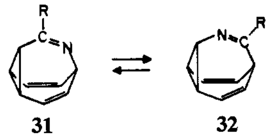
This is confirmed by an EH calculation with a fluorine substituent. It might be worthwhile to pause here briefly and to survey some experimental results, heretofore difficult to explain on classical grounds, but now easily comprehensible with our orbital analysis.



The barbaralane series now forms a clear pattern. The more pronounced the carbonium ion acceptor character at position 9, the higher the activation energy of the Cope rearrangement.



Several substituted azabullvalenes were synthesized by Paquette and coworkers.[23] These molecules undergo a ready Cope rearrangement between **31** and **32**, as



31 **32**

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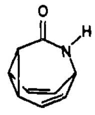
(23) (a) L. A. Paquette and T. J. Barton, *J. Amer. Chem. Soc.*, **89**, 5480 (1967); (b) L. A. Paquette, T. J. Barton, and E. B. Whipple, *ibid.*, **89**, 5481 (1967); (c) L. A. Paquette, J. R. Malpass, G. R. Krow, and T. J. Barton, *ibid.*, **91**, 5296 (1969).

well as a more complex Cope sequence at elevated temperatures. In the case of R = ethoxy the low-temperature rearrangement clearly favors structure **31**, to the extent of approximately 2 kcal/mol.[24] In the polarized C=N double bond it is clear that the carbon end is the electron acceptor, the nitrogen end the electron donor. An EH calculation favors structure **31** by 0.37 eV. Thus the observed equilibrium preference is in accord with our expectations. Similarly we would anticipate the Cope equilibria to favor the indicated structures for **33**,[23,25] **34**,[26] and **35**.[6]



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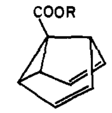

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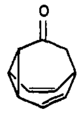

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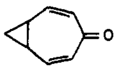
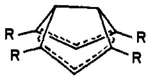


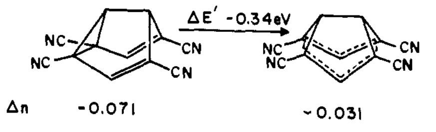
36

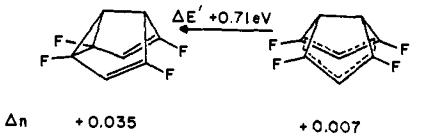
If we momentarily leave the bullvalene and semibullvalene frameworks we can similarly understand why the Cope rearrangement of homotropone, **36**,[27] lies on the indicated side. Here the ketone oxygen lone pair is the lone-pair donor.[28]

We return to the theoretical discussion and next consider the substitution pattern shown below. The four



acceptor orbitals generate an AS combination to stabilize the crucial transition-state orbital of the same symmetry. Not only is this interaction a favorable one, but the acceptor orbitals also are of the proper symmetry to stabilize the other occupied transition-state orbitals. On the side of the "collapsed" reactant or product semibullvalene we have already shown that acceptor substitution at positions 2, 4, 6, and 8 weakens the 2–8 bond. The substitution pattern, however, stabilizes the semibullvalene molecule as a whole. Thus it is only the relative weighting of transition state *vs.* product stabilization which leads us to the conclusion that the activation energy for the Cope rearrangement will be reduced. This is confirmed by extended Hückel calculations on the CN case shown below. As expected, donor substitution, here illustrated by the F case, drives the reaction the other way. The optimal combination of the two substitution patterns discussed leads us to suggest that a molecule of the type **37** is likely to have a negative activation energy for the Cope rearrangement. In the special case of X = F and Y = CN we obtain a $\Delta E'$ of -0.59 eV favoring the transition state, relative to semibullvalene. It should be clear that if the reverse pattern of substitution to that in **37** is used, *i.e.*, X interchanged with Y, that the activation energy of the rearrangement should be increased.





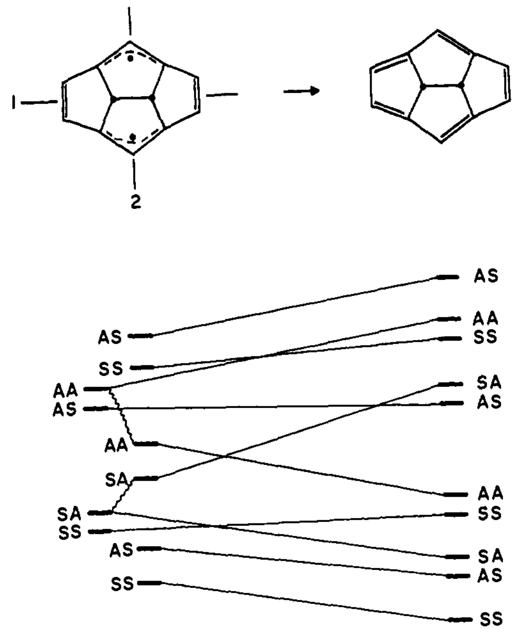
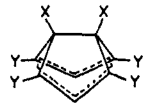


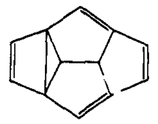
Figure 4. Interaction diagram building up the orbitals of **40** from two ethylenes and two interacting allyl groups.



X = π-donor
Y = π-acceptor

37

We might mention here the amusing effects of a variant of the above-described acceptor substitution pattern. Consider two ethylenes attached across the 2,8 and 4,6 positions to form **38**. The Cope rearrangement of **38** should be strongly inhibited. This is because the level pattern in the transition state **39** is so strongly perturbed by the ethylene groups that the ordering of interacting nonbonding orbitals is switched (see Figure 4). The perturbed transition state becomes the electronically stabilized but strained cyclodecapentaene **40**.



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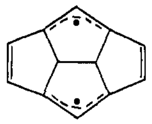

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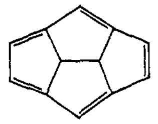

40

We note at this point that the highly interesting problem of determining the preferred position for a substituent on the fluxional bullvalene system cannot be directly solved by our simple considerations.[29] Simi-

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(24) H. Klose and H. Günther, *Chem. Ber.*, **102**, 2230 (1969). Note, however, that the assigned structure of alkoxybullvalenes is counter to our theoretical argument: J. F. M. Oth, R. Merényi, J. Nielsen, and G. Schröder, *Chem. Ber.* **98**, 3385 (1965).

(25) This preference was analyzed by a line of reasoning similar to ours in ref 23c, footnote 9.

(26) J. E. Baldwin, private communication.

(27) O. L. Chapman and R. A. Fugiel, *J. Amer. Chem. Soc.*, **91**, 215 (1969).

(28) For a discussion of a related system see R. Gleiter and R. Hoffmann, *Angew. Chem.*, **81**, 225 (1969).

(29) (a) G. Schröder and J. F. M. Oth, *Angew. Chem.*, **79**, 458 (1967); (b) E. Vogel, W. Grimme, W. Meckel, H. J. Riebel, and J. F. M. Oth, *Angew. Chem.*, **78**, 599 (1966); (c) H. Günther, H. Klose, and D. Wendisch, *Tetrahedron*, **25**, 1531 (1969).

larly the directive influence of substituents which are not simply classified as π donors or acceptors (*e.g.*, CF_3[30]) remains to be worked out.

Finally an interesting historical sidelight on our arguments is that in some cases we were led to the conclusion that the activation energy for a reaction is more influenced by the effect of substituents on reactant or product than their effect on the transition state. Now this is the way substituent effects were explained many years ago. Then the focus changed, perhaps too sharply, to the effect of substituents on the transition state or intermediate in a reaction. We look forward to a balanced theory of substituent effects.

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(30) R. S. H. Liu and C. G. Krespan, *J. Org. Chem.*, **34**, 1271 (1969).

An INDO Theoretical Study of Conjugation into and through the Cyclopropane Ring

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Contribution from the Department of Chemistry, University of Alabama, University, Alabama 35486. Received February 18, 1971

Abstract: Semiempirical calculations, in the INDO approximation, were performed on a series of *trans*-2-vinylcyclopropylcarbinyl derivatives, **a–f**, where the carbinyl group was CH_3 (**a**), $CH_2\cdot$ (**b**), CH_2^+ (**c**), $CF_2\cdot$ (**d**), CF_2^+ (**e**), or BH_2 (**f**), as well as on the acyclic 4-penten-1-yl cation and radical. From a consideration of optimized bond lengths, barriers to rotation, preferred conformations, charge densities, unpaired spin densities, and π-bond orders it was concluded that strong conjugation of the cyclopropyl ring with the carbinyl carbon existed, and the strength of this interaction increased as the electron demand of the carbinyl carbon increased. However, these calculations did not support a measurable transmission of conjugation through the ring into the vinyl group except in **c**. Even in **c** the magnitude of this transmitted conjugation was small. The preferred geometry of the carbinyl carbon in difluoro radical **d** was nonplanar despite conjugative interactions with the ring and fluorines. Conversely, the planar geometry was more stable in difluorocarbonium ion where these conjugative interactions were stronger.

To evaluate the magnitude of conjugation, both into and through the cyclopropyl ring, we undertook a theoretical study of a series of cyclopropylcarbinyl cations, radicals, and boron derivatives using the INDO method first developed by Pople and coworkers.[3] The basic model molecule chosen was *trans*-2-vinylcyclopropylcarbinyl system **1**, where X = CH_3, $CH_2\cdot$, CH_2^+, $CF_2\cdot$, CF_2^+, and BH_2. The degree of conjugation into and through the ring was evaluated by obtaining charge densities (or unpaired spin densities) at each atom, optimized bond lengths, barriers to rotation about the ring–carbinyl carbon and ring–vinyl group bonds, π-bond order in the ring–vinyl group bond, and the preferred conformations of **1a–f**.

Delocalization into Ring. It has been known for some time that cyclopropyl groups stabilize adjacent carbonium ion[4] and radical[5,6] centers. For example, cyclopropylcarbinyl derivatives solvolyze at markedly enhanced rates compared to their acyclic counterparts. Cyclopropylcarbonium ions have been directly observed by nmr spectroscopy and extensive charge delocalization into the ring was demonstrated by large downfield shifts of the β-cyclopropyl hydrogens.[4e–g,i] The barrier to cyclopropyl rotation in tertiary cyclopropylcarbinyl cations is 12–14 kcal/mol with the

1a, X = CH_3
b, X = $CH_2\cdot$
c, X = CH_2^+
d, X = $CF_2\cdot$
e, X = CF_2^+
f, X = BH_2

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(2) Undergraduate Honors Research Fellows 1969–1970, Department of Chemistry.

(3) (a) J. A. Pople, D. L. Beveridge, and P. A. Bobosh, *J. Chem. Phys.*, 47, 2026 (1967); also see (b) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.

(4) (a) N. C. Deno, *Progr. Phys. Org. Chem.*, 2, 129 (1964); (b) M. Hanack and H. J. Schneider, *Angew. Chem., Int. Ed. Engl.*, **6**, 666 (1967); (c) H. Hart and J. M. Sandri, *J. Amer. Chem. Soc.*, **81**, 320 (1959); (d) H. Hart and P. A. Law, *ibid.*, **86**, 1957 (1964); (e) N. C. Deno, J. S. Liu, J. O. Turner, D. N. Lincoln, and R. E. Fruit, Jr., *ibid.*, **87**, 3000, 4533 (1965); (f) C. U. Pittman, Jr. and G. A. Olah, *ibid.*, **87**, 2988, 5123 (1965); (g) D. S. Kabakoff and E. Namanworth, *ibid.*, **92**, 3234 (1970); (h) M. Simonetta and S. Winstein, *ibid.*, **76**, 18 (1954); (i) P. von R. Schleyer and G. W. VanDine, *ibid.*, **88**, 2321 (1966); (j) G. A. Olah, D. P. Kelly, and C. L. Jeuell, and R. D. Porter, *ibid.*, **92**, 2544 (1970); (k) J. C. Martin and B. R. Ree, *ibid.*, **91**, 5882 (1969), and references cited in these papers.

(5) (a) E. S. Huyser and D. T. Wang, *J. Org. Chem.*, **29**, 2720 (1964); (b) H. Hart and R. A. Cipriani, *J. Amer. Chem. Soc.*, **84**, 3697 (1962); (c) C. G. Overberger and A. Lebovits, *ibid.*, **76**, 2723 (1954); (d) J. C. Martin, J. E. Schultz, and J. W. Timberlake, *Tetrahedron Lett.*, **46**, 4629 (1967), and references therein.

(6) (a) G. A. Russell and H. Malkus, *J. Amer. Chem. Soc.*, **89**, 160 (1967); (b) N. L. Bauld, R. Gordon, and J. Zoeller, Jr., *ibid.*, **89**, 3948 (1967); (c) J. K. Kochi, P. J. Krusic, and D. R. Eaton, *ibid.*, **91**, 1877, 1879 (1969).