(b) M. E. Dempsey, J. D. Seaton, G. J. Schroepfer, and R. W. Trockman, *ibid.*, **239**, 1381 (1964); (c) M. E. Dempsey, ibid., **240**, 4176 (1965).

(10) (a) S. M. Dewhurst and M. Akhtar, *Biochem. J.*, **105**, 1187 (1967); (b) M. Akhtar and M. A. Parvez, *ibid.*, **108**, 527 (1968).

(11) (a) A. M. Paliokas and G. J. Schroepfer, *Biochem. Biophys. Res. Commun.*, **26**, 736 (1967); (b) A. M. Paliokas and G. J. Schroepfer, *J. Biol. Chem.*, **243**, 453 (1968); (c) M. Akhtar and S. Marsh, *Biochem. J.*, **102**, 462 (1967).

(12) D. J. Aberhart and E. Caspi, *J. Biol. Chem.*, **246**, 1387 (1971).

(13) (a) W. E. Harvey and K. Bloch, *Chem. Ind. (London)*, 595 (1961); (b) M. Slaytor and K. Bloch, *J. Biol. Chem.*, **240**, 4598 (1965).

(14) (a) A. M. Paliokas and G. J. Schroepfer, *Biochim. Biophys. Acta*, **144**, 167 (1967); (b) A. Fiecci, M. Galli Kienle, A. Scala, G. Galli, R. Paoletti, and E. Grossi Paoletti, *J. Biol. Chem.*, **247**, 5898 (1972).

(15) (a) J. E. van Lier and L. L. Smith, *Biochim. Biophys. Acta*, **210**, 153 (1970); **218**, 320 (1970); (b) J. E. van Lier and L. L. Smith, *Biochem. Biophys. Res. Commun.*, **40**, 516 (1970).

(16) (a) A. Nickon and W. L. Mendelson, *J. Org. Chem.*, **85**, 1894 (1963); **87**, 3921 (1965); (b) E. J. Corey and W. C. Taylor, *J. Amer. Chem. Soc.*, **86**, 3881 (1964); (c) W. Eisfeld, Dissertation, Göttingen, 1965, p 63; (d) D. R. Kearns, R. A. Hollins, A. U. Khan, R. W. Chambers, and P. Radlick, *J. Amer. Chem. Soc.*, **89**, 5455 (1967); (e) D. R. Kearns, R. A. Hollins, A. U. Khan, and P. Radlick, *ibid.*, **89**, 5456 (1967); (f) R. W. Murray and M. L. Kaplan, *ibid.*, **91**, 5358 (1969).

(17) Formation of **5a** from **2a** suggested as arising from participation of the $^1\Sigma_g{}^+$ excited state of molecular oxygen rather than the first $^1\Delta_g$ excited state[16d,e] has since been qualified.[18] Although hydrogen atom abstraction by excited dye molecules had previously not been thought likely,[16e] free-radical oxidation initiated by the $^3(n,\pi^*)$ sensitizer has recently been posited.[18a]

(18) (a) K. Gollnick, T. Franken, G. Schade, and G. Dörhöfer, *Ann. N. Y. Acad. Sci.*, **171**, 89 (1970); (b) C. S. Foote, *ibid.*, **171**, 105 (1970); (c) D. R. Kearns, *ibid.*, **171**, 106 (1970).

(19) A. Nickon and J. F. Bagli, *J. Amer. Chem. Soc.*, **81**, 6330 (1959); **83**, 1498 (1961).

(20) Melting points were taken on a calibrated Kofler block under microscopic magnification. Infrared absorption spectra were recorded over the range 400–4000 cm^{-1} on 1.5 mm diameter KBr disks incorporating the sample using a Perkin-Elmer Model 337 spectrophotometer equipped with a beam condenser lens. Ultraviolet light absorption spectra were recorded on 95% ethanol solutions using a Cary Model 14 spectrophotometer. Thin-layer chromatography was conducted with 20 × 20 cm chromatoplates of silica gel HF_{254} (E. Merck GmbH., Darmstadt), 0.25 and 1.0 mm thick, using specified solvent systems. Thin-layer mobility factors *R* for products derived from parent sterols **2a**, **3a**, or **4a** were measured using the appropriate parent sterol as unit mobility. Sterols were detected by viewing under 254-nm light, followed by spraying with *N,N*-dimethyl-*p*-phenylenediamine for peroxides,[8] and finally by spraying with 50% aqueous sulfuric acid and heating for full color display. Gas chromatography was conducted on 1.83 m long × 4 mm diameter silanized glass U-tubes packed with 3% SP-2401 on 100–120 mesh Supelcoport (Supelco Inc., Bellafonte, Pa.) using a Hewlett-Packard F&M Model 402 gas chromatograph equipped with a hydrogen flame ionization detector. Injection temperature was 250°; column temperature was 230°; detector temperature was 250°. Nitrogen was used as carrier gas at a flow rate of 20 ml/min. Retention time data (t_R) are expressed in terms of cholesterol as unit retention time in all cases. Preparative gas chromatography was achieved by collection of effluxing components in glass capillaries as previously described.[21]

(21) J. E. van Lier and L. L. Smith, *J. Chromatogr.*, **36**, 7 (1968).

(22) J. E. van Lier and L. L. Smith, *Steroids*, **15**, 485 (1970).

(23) Literature melting point and ultraviolet light absorption data for the common steroids were obtained, respectively, from (a) J. Jacques, H. Kagan, and G. Ourisson, "Tables of Constants and Numerical Data," Vol. 14, Pergamon Press, Oxford, 1965; (b) L. Dorfman, *Chem. Rev.*, **53**, 47 (1953).

(24) Chromatographic resolution and differentiation by color display of the parent sterols **1a** and **4a** as well as of their major hydroperoxides formed by radiation-induced oxidation are achieved using benzene–ethyl acetate (18:7), as follows: **1a**, red color, *R* 1.00; **4a**, orange-red color, *R* 0.91; **1b**, instant blue color, *R* 0.52; **1c**, instant blue color, *R* 0.57; **4b**, tan color, *R* ~0.37; **4c**, tan color, *R* 0.39. The chief product **3a** of singlet molecular oxygen attack on **1a** is not resolved from **1b** but the corresponding 3β,5α-diol **3c** is readily resolved from **1d** and from **1e** in a variety of solvent systems. The putative initial product of singlet molecular oxygen attack on **4a** as well as the secondary dihydroperoxides formed is resolved from **4b** and **4c** using multiple irrigation with benzene–ethyl acetate (18:7).

(25) (a) L. Caglioti, G. Cainelli, and G. Maina, *Tetrahedron*, **19**, 1057 (1963); (b) D. J. Aberhart, J. G. Lloyd-Jones, and E. Caspi, *Phytochemistry*, **12**, 1065 (1973).

(26) L. Tökés, G. Jones, and C. Djerassi, *J. Amer. Chem. Soc.*, **90**, 5465 (1968).

A Reexamination of the Origin of Regioselectivity in the Dimerization of Acrolein. A Frontier Orbital Approach

Peter V. Alston*

E. I. du Pont de Nemours & Company, Analytical Research Group, Spruance Plant, Richmond, Virginia 23261

Donald D. Shillady

Department of Chemistry, Virginia Commonwealth University, Richmond, Virginia 23284

Received March 18, 1974

The relative frontier orbital coefficient magnitudes of acrolein were determined from *ab initio* SCF molecular orbitals. These frontier orbital coefficients favor the experimentally observed regioisomer in the dimerization of acrolein. Various all valence electron semiempirical SCF MO methods agree with the *ab initio* calculations on the origin of regioselectivity in the reaction. First-order charge interactions were not useful in predicting the regioselectivity of the reaction. Generalized rules for the prediction of the regioselectivity in cycloadditions involving three terminal carbon atoms and one terminal oxygen atom are given.

The regioselectivity in the dimerization of acrolein has been of theoretical interest [1-5] over the last several years. Salem[3] found that Hückel orbital interactions favored regioisomer II whereas only regioisomer I occurs experimentally. A later calculation by Devaquet and Salem[4] using π SCF MO's and including first-order charge interactions as well as overlap was found to be in agreement with the experimental results. However, the major contribution (60–70%) to the stabilization of I relative to II arose from the electrostatic term. This is confusing because consideration of the π charge densities of acrolein would lead to the wrong prediction.[1] There is also some question about the reliability of the overlap energy term in this calculation because it predicts that the exo approach is more stable than the endo for regioisomer II. This prediction is contrary to orbital symmetry considerations[6,7] and experimental evidence,[8] which indicate that the endo configuration is more stsble than the exo. Later, Eisenstein, *et al.*,[1] was successful in predicting the observed regioisomer I using a frontier orbital approach based on Hückel orbitals. However, Houk[2] has recently found that various molecular orbital methods disagree on the relative coefficient magnitudes of the HOMO of acrolein. Consequently, the origin of the regioselectivity in the dimerization of acrolein is presently unclear. In this paper, we have reexamined this reaction

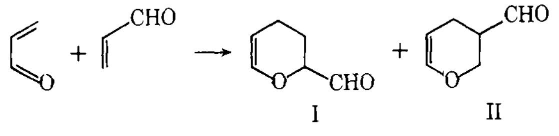
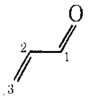


Table I
Eigenvectors of the Highest Occupied Molecular Orbital and the Lowest Unoccupied Molecular Orbital of Acrolein



Molecular orbital method	Conformational isomer	HOMO				LUMO			
		0	C-1	C-2	C-3	0	C-1	C-2	C-3
INDO	Cisoid	−0.578	−0.266	0.503	0.584	−0.499	0.483	0.386	−0.607
INDO	Transoid	0.578	0.273	−0.499	−0.586	−0.500	0.479	0.393	−0.605
CNDO/2	Cisoid	0.578	0.284	−0.494	−0.584	0.504	−0.468	−0.397	0.608
CNDO/2	Transoid	0.578	0.291	−0.489	−0.585	−0.504	0.464	0.404	−0.601
CNDO/S	Cisoid	0.391	0.052	−0.655	−0.644	0.367	−0.426	−0.479	0.675
CNDO/S	Transoid	0.391	0.063	−0.638	−0.661	−0.367	0.420	0.502	−0.662
Iterative extended Hückel	Cisoid	0.559	0.188	−0.461	−0.557	−0.675	0.576	0.225	−0.619
Iterative extended Hückel	Transoid	0.557	0.180	−0.465	−0.556	−0.680	0.577	0.213	−0.621
MINDO/2	Cisoid	−0.464	−0.175	0.598	0.630	0.428	−0.423	−0.471	0.645
MINDO/2	Transoid	−0.464	−0.187	0.584	0.639	0.425	−0.418	−0.490	0.635
Ab initio[a]	Transoid	0.415	0.223	−0.546	−0.595	0.574	−0.459	−0.464	0.653
Ab initio[b]	Transoid	0.391	0.227	−0.559	−0.583	0.565	−0.414	−0.490	0.683

[a] Reference 9. [b] Reference 10.

through *ab initio* and the various semiempirical molecular orbital methods to determine the origin of its regioselectivity.

Results and Discussion

Since the various semiempirical molecular orbital methods (CNDO/2, INDO, Hückel, extended Hückel, MINDO/2) disagree on the relative coefficient magnitudes of the frontier orbitals of acrolein,[2] we have determined the relative coefficient magnitudes from *ab initio* SCF calculations. We feel that the eigenvectors of the *ab initio* calculations should be more reliable than the semiempirical methods. One good STO minimal basis *ab initio* SCF calculation was available[9] in the literature and we have also carried out a minimal gaussian (4G) basis set calculation[10] using Clementi single ζ's.[11] Even though the two *ab initio* calculations use slightly different orbital screening constants, they agree well for the relative coefficient magnitudes of the frontier orbitals (Table I). Both methods predict that the highest occupied molecular orbital (HOMO) is a π molecular orbital and that the nonbonding molecular orbital is of lower energy. The lowest unoccupied molecular orbital (LUMO) is a π molecular orbital in both methods. The relative *ab initio* coefficient magnitudes of the frontier orbitals of *trans*-acrolein are given in Figure 1.

Since *ab initio* calculations require considerable amounts of computer time, it is advantageous to carry out such molecular orbital investigations with semiempirical methods. Therefore, the agreement of the various all-valence electron semiempirical methods with the *ab initio* calculations was determined.[12] The CNDO/S[14] and MINDO/2[15] methods predict similar frontier orbital coefficients for *trans*-acrolein (Table I). The relative coefficient magnitudes of these methods agree well with the *ab initio* calculations. The only disagreement is in the magnitude of the LUMO coefficient of the oxygen, which the semiempirical methods predict to be smaller in magnitude than the LUMO coefficient of the C-2 position. The INDO and CNDO/2[16] methods have several disagreements with the *ab initio* calculations on the frontier orbital coefficients. They predict a reversal in the relative LUMO coefficient magnitudes of the C-1 and C-2 positions and an oxygen HOMO coefficient of equal magnitude with the C-3 position. Finally, the iterative extended Hückel[17] method has the most disagreement with the *ab initio* calculations. Its disagreements are an oxygen HOMO coefficient of equal magnitude with the C-3 position, a reversal in the relative LUMO coefficients magnitudes of the C-1 and C-2 positions, and an oxygen LUMO coefficient that is larger than the C-3 coefficient.

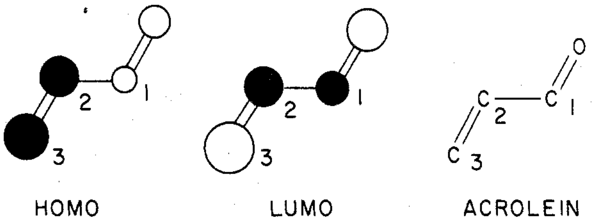


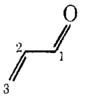
Figure 1. Relative coefficient magnitudes of the frontier orbitals of *trans*-acrolein from *ab initio* calculations.

When *trans*-acrolein is rigidly rotated to *cis*-acrolein, the only change in the relative coefficient magnitudes of the semiempirical frontier orbitals was that the HOMO C-2 coefficient became larger than the HOMO C-3 coefficient in the CNDO/S method (Table I). Even if this change in the relative CNDO/S coefficient magnitudes of HOMO is real, it will not affect the conclusions drawn from the frontier orbital coefficients concerning regioselectivity. Therefore, the relative *ab initio* coefficient magnitudes of the frontier orbital of *trans*-acrolein will be used for *cis*-acrolein.

It has been shown[1,2,7] that the regioselectivity of a concerted cycloaddition process can be predicted from perturbation molecular orbital theory. The expression for the energy change which accompanies the orbital overlap of two molecules involved in a cycloaddition process is as follows.[5]

$$\Delta E = 2\left(\sum_{R}^{\mathrm{occ}} \sum_{S}^{\mathrm{unocc}} - \sum_{R}^{\mathrm{unocc}} \sum_{S}^{\mathrm{occ}}\right) \frac{\left(\sum_{ab} c_a c_b \gamma_{ab}\right)^2}{E_R - E_S} \quad (1)$$

Table II
Net π Charges of Acrolein



Molecular orbital method	Conformational isomer	O	C-1	C-2	C-3
INDO	Cisoid	−0.228	+0.180	−0.023	+0.055
INDO	Transoid	−0.221	+0.175	−0.014	+0.060
CNDO/2	Cisoid	−0.200	+0.157	−0.019	+0.062
CNDO/2	Transoid	−0.193	+0.153	−0.011	+0.051
CNDO/S	Cisoid	−0.396	+0.341	−0.050	+0.105
CNDO/S	Transoid	−0.389	+0.340	−0.006	+0.055
Iterative extended Hückel	Cisoid	−0.127	−0.009	+0.030	+0.106
Iterative extended Hückel	Transoid	−0.123	−0.020	+0.029	+0.115
MINDO/2	Cisoid	−0.254	+0.217	−0.033	+0.070
MINDO/2	Transoid	−0.247	+0.215	−0.002	+0.035
Hückel[a]	Transoid	−0.529	+0.333	−0.034	+0.228

[a] Reference 1.

In this expression γ_{ab} is the atomic orbital transition state resonance integral for atomic orbitals a and b in MO's R and S, and c_a is the atomic orbital coefficient at atom a in the molecular orbital R. The theory predicts[2] that the principal stabilization of the transition state will arise from the HOMO–LUMO pair of addend frontier orbitals which are closest in energy, and that the larger terminal coefficients on each addend will become bonded preferentially in the transition state.[18] In the dimerization of acrolein, the four terminal atoms are not the same type. Thus, the resonance integral, γ_{ab}, will not be a constant in eq 1 and consideration must be taken of its magnitude. The γ_{CC} and γ_{CO} for a 2pσ, 2pσ overlap as a function of distance are available in the literature.[19] The γ_{CC} is significantly larger than γ_{CO} at interatomic distances of 3.0–1.75 Å; thus, the carbon–carbon orbital interactions will have the greater effect on the stability of the transition state. Consequently, only the carbon–carbon orbital interactions will be considered in predicting the regioselectivity in the dimerization of acrolein.

In this cycloaddition reaction both frontier orbital interactions, HOMO diene–LUMO dienophile and LUMO diene–HOMO dienophile, have the same energy separation and will equally affect the regioselectivity of the reaction.[20] Using the relative terminal coefficient magnitudes of acrolein in Figure 1, the theory predicts that both frontier orbital interactions favor the observed regioisomer I. The approach which yields regioisomer I allows bond formation between the C-3 positions of the reactants where the terminal coefficients of HOMO and LUMO are the largest (Figure 2). The other possible regioisomer II is not favored by either frontier orbital interactions because the largest coefficients of HOMO and LUMO do not become bonded (Figure 3). Thus, the frontier orbital approach accounts for the high degree of regioselectivity observed in the dimerization of acrolein.

When the terminal coefficients of the semiempirical methods are used in this approach, they also predict that both frontier orbital interactions favor regioisomer I. Even if we assume that γ_{CC} and γ_{CO} are equal in magnitude, thereby considering carbon–oxygen and carbon–carbon orbital interactions, all the SCF molecular orbital methods except the iterative extended Hückel favor regioisomer I.

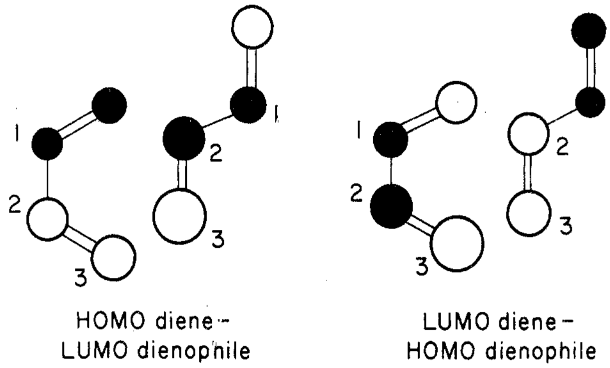


Figure 2. Frontier orbital interactions yielding regioisomer I.

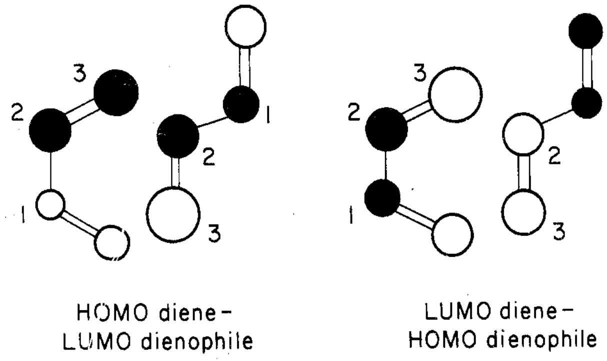


Figure 3. Frontier orbital interactions yielding regioisomer II.

Consideration was also given to the effect of secondary orbital interactions between the C-1 position of the dienophile (*trans*-acrolein) and the C-1 and C-2 positions of the diene (*cis*-acrolein) on the regioselectivity of the reaction (Figures 2 and 3). We found that the C-2 coefficient of the HOMO and the LUMO of the diene was larger than the corresponding C-1 diene coefficient. Thus, the stabilization of the endo transition state is greater when C-1 of the dienophile is near C-2 of the diene, thereby favoring the unobserved regioisomer II. Consequently, the secondary orbital interactions make a minor contribution to the stabilization of the regioisomers.

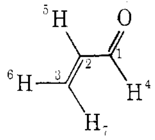
Earlier we stated that Devaquet and Salem[4] had indicat-

Table III
Change in Energy[a] Due to First-Order π Charge Interactions for the Dimerization of Acrolein

Molecular orbital method	Regioisomer			
	I (exo)	II (exo)	I (endo)	II (endo)
INDO	0.337	−0.368	0.411	−0.279
CNDO/2	0.310	−0.269	0.367	−0.202
CNDO/S	0.764	−0.725	1.187	−0.327
MINDO/2	0.316	−0.299	0.482	−0.141
Hückel	3.951	−3.412	3.826	−3.312

[a] In kilocalories per mole.

Table IV
Net Atomic Charges of Acrolein



Molecular orbital method	Conformational isomer	Net atomic charges							
		O	C-1	C-2	C-3	H-4	H-5	H-6	H-7
INDO	Cisoid	−0.286	+0.338	−0.042	+0.056	−0.078	+0.002	−0.002	+0.011
INDO	Transoid	−0.283	+0.334	−0.041	+0.045	−0.073	+0.015	0.0	+0.003
CNDO/2	Cisoid	−0.231	+0.244	−0.039	+0.009	−0.042	+0.014	+0.017	+0.029
CNDO/2	Transoid	−0.228	+0.239	−0.039	−0.001	−0.037	+0.027	+0.021	+0.018
CNDO/S	Cisoid	−0.468	+0.398	−0.073	−0.019	+0.017	+0.030	+0.048	+0.066
CNDO/S	Transoid	−0.462	+0.397	−0.044	−0.073	+0.020	+0.051	+0.057	+0.053
Iterative extended Hückel	Cisoid	−0.386	+0.136	+0.038	+0.028	+0.063	+0.041	+0.041	+0.040
Iterative extended Hückel	Transoid	−0.388	+0.137	+0.030	+0.019	+0.037	+0.039	+0.046	+0.073
MINDO/2	Cisoid	−0.353	+0.359	−0.019	−0.062	−0.004	+0.043	+0.056	+0.070
MINDO/2	Transoid	−0.346	+0.354	−0.090	−0.095	−0.003	+0.062	+0.066	+0.052
Ab initio[a]	Transoid	−0.215	+0.034	−0.272	−0.344	+0.176	+0.218	+0.205	+0.199

[a] Reference 10.

ed that first-order charge interactions were the major contributor (60–70%) to the stabilization of regioisomer I relative to regioisomer II. The expression for the change in energy due to first-order charge interactions is as follows.[4]

$$\Delta E = \sum_{a} \sum_{b} Q_a Q_b \frac{1}{R_{ab}}$$

In this expression Q_a is the total initial charge on atom a and R_{ab} is the distance between atoms a and b. If first-order charge interactions are the major contributor to the stability of the transition state, one should be able to predict the preferred regioisomer of the reaction from the net changes.[21] However, we find that the net π charges favor the unobserved regioisomer II for all the SCF molecular orbital methods investigated (Tables II and III). When all valence electrons are included, the net atomic charges of all the MO methods still favor the unobserved regioisomer II (Tables IV and V). Of the molecular orbital methods investigated, we feel that the CNDO/2 net charges are the more realistic because Hehre and Pople[22] have observed that CNDO/2 determined atomic populations of oxygen-containing compounds parallel quite closely those obtained from *ab initio* calculations. Thus, first-order charge interactions cannot be the origin of the regioselectivity observed in the dimerization of acrolein and are not the major contributor to the stabilization of regioisomer I relative to regioisomer II.

The iterative extended Hückel and minimal gaussian *ab initio* methods were not used in the above calculations because of the unrealistic atomic charge densities predicted by these methods. For example, the iterative extended Hückel predicts that all the atoms of acrolein except oxygen are positively charged (Table IV). This electron distribution appears to be another example of the method's overemphasis of ionic contributions. Also, the *ab initio* charge densities appear to be more characteristic of the basis set than a true effect.[23] For example, the method predicts that the C-2 and C-3 carbons have more electron density than the oxygen (Table IV).

Table V
Change in Energy[a] Due to First-Order Atomic Charge Interactions for the Dimerization of Acrolein

Molecular orbital method	Regioisomer			
	I (exo)	II (exo)	I (endo)	II (endo)
INDO	0.390	−0.168	0.591	−0.054
CNDO/2	0.301	−0.195	0.357	−0.166
CNDO/S	1.018	−0.944	1.388	−0.483
MINDO/2	0.447	−0.400	0.458	−0.244

[a] In kilocalories per mole.

The origin of the regioselectivity predicted from the first-order charge interactions in our calculations and those of Devaquet and Salem[4] does not have a simple interpretation because charge–charge interactions between many pairs of atoms play an important role. Consequently, the exact cause of Devaquet's and Salem's incorrect conclusion is impossible to determine without the atomic charge densities used in their calculations. However, the energy difference between the exo regioisomers calculated from the Hückel net π charges was 7.36 kcal/mol, while the less approximate CNDO/2 method predicts a difference of 0.579 kcal/mol from net π charges and 0.496 kcal/mol from the net atomic charges (Tables III and V). It appears that the use of π charge densities from π SCF molecular orbital methods can overemphasize the role of the first-order charge interactions, and this could lead to incorrect conclusions concerning regioselectivity. Thus, we feel that the origin of their incorrect conclusion probably lies with the π charge densities of the π molecular orbital method that they used.

Eisenstein, *et al.*,[1] was correct in analysis of the first-order charge interactions because of the Hückel π charge densities used, which allow a simple interpretation of these interactions. Their conclusion originated from the large negative charge on the oxygen and the large positive charge on the C-3 carbon whose interaction favors the unobserved regioisomer II. This electronic distribution causes the Hückel method to overemphasize the effect of first-order charge interaction in the dimerization of acrolein.

Conclusions

The dimerization of acrolein is under overlap control and there is no evidence that first-order charge interactions have a dominant role in determining its regioselectivity. Also, it appears that the atomic charge densities from the π SCF MO methods are too crude to be used in determining the energy change due to first-order charge interactions.

The frontier orbital approach used in analyzing the regioselectivity of the dimerization of acrolein can be applied to all cycloaddition reactions which involve terminal orbital interactions of three carbon atoms and one oxygen atom. The generalized rules are as follows.

(1) The principal stabilization of the transition state will arise from the HOMO-LUMO pair of addend frontier orbitals which are closest in energy.

(2) The larger carbon terminal coefficients on each addend will become bonded preferentially in the transition state.

(3) If the terminal carbon coefficients of either addend are equal in magnitude, the regioselectivity can be predicted from secondary orbital interactions.[7]

Finally, the relative coefficient magnitudes in Figure 1 and the above generalized rules can be used to predict the preferred regioisomer of any cycloaddition reaction involving acrolein. They correctly predict the preferred regioisomer in the cycloaddition of acrolein with styrene, acrylonitrile, and methyl acrylate.[24]

Acknowledgments. The authors thank the Virginia Commonwealth University Computer Center for a grant of computer time. They also thank Professor Hashmall of Georgetown University for providing the MINDO/2 program.

Registry No.—Acrolein, 107-02-8.

References and Notes

(1) O. Eisenstein, J.-M. Lefour, and N. T. Anh, *Chem. Commun.*, 969 (1971).

(2) K. N. Houk, *J. Amer. Chem. Soc.*, **95**, 4092 (1973).

(3) L. Salem, *J. Amer. Chem. Soc.*, **90**, 553 (1968).

(4) A. Devaquet and L. Salem, *J. Amer. Chem. Soc.*, **91**, 3793 (1969).

(5) W. C. Herndon, *Chem. Rev.*, **72**, 157 (1972), and references cited therein.

(6) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(7) P. V. Alston, R. M. Ottenbrite, and D. D. Shillady, *J. Org. Chem.*, **38**, 4075 (1973).

(8) K. N. Houk, *Tetrahedron Lett.*, 2621 (1970).

(9) A. Devaquet, *J. Amer. Chem. Soc.*, **94**, 5160 (1972).

(10) D. D. Shillady and C. Trindle, *Int. J. Quantum Chem., Symp.*, No. 7, 269 (1973).

(11) E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963).

(12) The geometry of *trans*-acrolein used in the molecular orbital calculations was obtained from the very accurate microwave spectrum by Wagner, *et al.*[13] The geometry of *cis*-acrolein was determined by rigid rotation from *trans*-acrolein. We found that the interpretations from the semiempirical HOMO-LUMO eigenvectors and atomic charge densities were independent of small changes in bond angles and bond lengths. Thus, there was no justification of the use of computer time for an extensive optimization of the conformational isomers of acrolein with each method. Furthermore, the iterative extended Hückel method does not take into account repulsion and can not be used to obtain equilibrium geometries. Also, the parameters of the CNDO/S method are optimized for excited-state properties and would not give a reliable equilibrium geometry. Small variations in the geometry of Wagner, *et al.*, for both conformational isomers of acrolein were carried out in the CNDO/2, INDO, and MINDO/2 methods. These variations indicated that the geometry of Wagner, *et al.*, is very close to the predicted equilibrium geometry for both *cis*-and *trans*-acrolein.

(13) R. Wagner, J. Fine, J. W. Simmons, and J. H. Goldstein, *J. Chem. Phys.*, **26**, 634 (1957).

(14) G. Keuhnlenz and H. H. Jaffé, *J. Chem. Phys.*, **58**, 2258 (1973). Available from Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind. 47401, Program No. 174. In our version we used 0.529167 Å/atomic unit, 27.21 eV/atomic unit, and double precision to be compatible with Pople's CNDO/2 program.

(15) J. A. Hashmall and S. Raynor, *J. Chem. Phys.*, **58**, 5464 (1973), and references cited therein.

(16) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970. Available from Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind. 47401, Program No. 141.

(17) R. Rein, N. Fukuda, H. Win, G. A. Clarke, and F. E. Harris, *J. Chem. Phys.*, **45**, 4743 (1966). The VOIP for carbon, oxygen, and hydrogen were obtained from B. J. Duke, *Theor. Chim. Acta*, **9**, 260 (1968). Calculations were carried to a self-consistency of 0.005 electron in charge.

(18) When the terminal coefficients are of equal magnitudes, the preferred regioisomer can be predicted from secondary orbital interactions.[7]

(19) K. N. Houk, J. Sims, C. R. Watts, and L. J. Luskus, *J. Amer. Chem. Soc.*, **95**, 7301 (1973).

(20) Molecular orbital calculations predict that the differences in the frontier orbital energies of *cis*-acrolein and *trans*-acrolein are less than 0.2 eV.

(21) In the calculations of the change in energy due to first-order charge interactions, the parallel planes of the interacting acrolein molecules were separated by a distance of 3 Å. The terminal atoms of the *cis*-acrolein molecule were symmetrically below the carbon–carbon double bond of the *trans*-acrolein molecule. Asymmetry in the approach of the molecules did not change the interpretations from atomic charge densities.

(22) W. J. Hehre and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 2191 (1970).

(23) J. A. Kroll and D. D. Shillady, *J. Amer. Chem. Soc.*, **95**, 1422 (1973).

(24) The coefficient magnitudes of the dienophiles were determined from CNDO/2 calculations.