both frontier orbital energies, and electron-withdrawing substituents (Z) lower both frontier orbital energies. Most of the last type of substituents (–COS, –COR, –CN) are both electron withdrawing and conjugating, so that the overall lowering of the HO is much less than that of the LU. For the diene orbital energies, the same effects operate, except that the magnitude of energy changes, which are roughly proportional to the square of the coefficient at the point of attachment, falls in the order ethylene > 1-diene > 2-diene.[8,22]

The relative magnitudes of the coefficients in Figures 1–3 are derived, for the most part, from calculations,[17,28] but are in agreement with qualitative considerations. Conjugating substituents increase the relative magnitude of the coefficient of the unsubstituted terminus of ethylene at the expense of the coefficient of the substituted terminus in both the HO and LU. Electron-releasing groups increase the remote coefficient in the HO and the nearby coefficient in the LU, as expected on inductive grounds.[8] For alkyl groups, the two coefficients are nearly identical in the LU.[17,28] Electron-withdrawing groups have exactly the opposite effect from that of donor groups if they interact only inductively (*e.g.*, $-CF_3$), but since most of the groups of this type are also conjugating, the LU's have the greater magnitude of the remote coefficient strengthened, while the difference in the HO coefficient magnitudes is diminished or reversed. CNDO/2,[28] INDO,[29] and *ab initio* SCF[30] calculations indicate that the HO coefficient at the unsubstituted terminus is largest, while Hückel,[8] extended Hückel,[28] and MINDO/2[31] calculations give the opposite result for the HO coefficients. Photoelectron spectra support the former calculations, because β-methylation of acrolein or methyl acrylate raises the highest π orbital energy by 1.39 and 1.64 times more, respectivity, than does α-methylation.[23]

The substituted butadiene orbitals in Figures 2 and 3 can be derived from similar considerations. The only equivocal cases involve 1-electron-withdrawing substituted dienes, where terminal coefficients are very similar for both the HO and LU orbitals.[28,32]

Once the relative coefficient magnitudes and orbital energies are known, the preferred Diels–Alder regioisomer can be predicted using the following generalizations. (1) The principal stabilization of the transition state will arise from interaction of the HO–LU pair of addend frontier orbitals which are closest in energy. (2) The larger terminal coefficient on each addend will become bonded preferentially in the transition state.[33]

The most frequently observed Diels–Alder reactions of unsymmetrical addends involve "conjugated" or "electron-rich" dienes and "conjugated" or "electron-deficient" dienophiles. For these reactions, the diene HO–dienophile LU interaction is largest (energy separation smallest), and the "ortho" regioisomer is favored with 1-substituted butadienes, the "para" regioisomer with 2-substituted butadienes. The other frontier orbital interaction also favors the same regioisomer. These regioisomers are preferred experimentally.[34] Similar considerations correctly rationalize the regioselectivity of Diels–Alder reactions of heterodienophiles.[35]

The coefficients at C-1 and -4 in the HO and LU of 1-substituted electron-deficient dienes are nearly the same, so that regioselectivity should be less pronounced in reactions of such compounds. This seems contrary to the few examples known,[34] and may indicate the influence of secondary orbital interactions between substituents.[15]

The only reversal of the "ortho-para" Alder regioselectivity rule should occur in reactions where the LU orbital of electron-rich dienes or dienophiles plays a controlling role. However, such a situation will not normally occur, since the LU of electron-rich alkenes is of high energy. Only when both diene and dienophile are electron rich will the "meta" orientation be favored.

Consideration of orbital energies and coefficients in this way reveals some of the difficulties that may arise from use of calculated frontier orbital energies and coefficients. First, calculated orbital energies often deviate from experimental energies, not only in an absolute sense, but in a relative sense as substituents are varied. Thus, orbital interactions which are in reality insignificant may be considered to be of great importance if calculated orbital energies are used. This may be the origin of the greater success of frontier orbital treatments than full calculations in some cases.[15] Second, with electron-deficient dienophiles, the use of some calculational methods gives incorrect relative magnitudes of HO coefficients and, therefore, incorrect regioselectivity predictions. Examples of this problem are the reversal of predictions for acrolein dimerization using Hückel or SCF calculations[6] as well as difficulties in predictions for regioselectivity with other electron-deficient addends.[6,13–15]

With the availability of generalized frontier orbital energies and coefficients summarized in Figures 1–3, qualitative applications to the rationalization and prediction of reactivity and regioselectivity in a multitude of concerted and nonconcerted reactions of alkenes are made possible.

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(30) A. Devaquet, *ibid.*, **94**, 5160 (1972).

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(32) T. Fueno and K. Yamaguchi, *J. Amer. Chem. Soc.*, **94**, 1119 (1972).

(33) This assumption[14] is not equivalent to the assumption of a nonconcerted reaction mechanism.

(34) Yu. A. Titov, *Russ. Chem. Rev.*, 31, 267 (1962); J. Sauer, *Angew. Chem., Int. Ed. Engl.*, **6**, 23 (1967); A. S. Onishchenko, "Diene Synthesis," Israel Program of Scientific Translations, Jerusalem, 1964.

(35) G. Kresze and U. Wagner, *Justus Liebigs Ann. Chem.* **762**, 106 (1972), and references therein.

(36) Camille and Henry Dreyfus Foundation Teacher Scholar Grant Recipient, 1972–1977.

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On Lewis Acid Catalysis of Diels–Alder Reactions

Sir:

The Diels–Alder reaction is the archetype of a concerted, intermolecular cycloaddition,[1] and yet Diels–

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(1) J. Sauer, *Angew. Chem., Int. Ed. Engl.*, **6**, 16 (1967).

Alder reaction rates, regioselectivity, and stereoselectivity, both in an exo–endo sense and in the extent and chirality of the asymmetry bias in reactions with chiral dienophiles, are markedly affected by Lewis acids. We wish to report how these phenomena are simply rationalized by the application of frontier orbital theory using generalized orbitals, as outlined in the preceding communication.[2]

Coordination of the nonbonding electrons of an α,β-unsaturated carbonyl or nitrile will result in a lowering of the energies of the π orbitals, as well as a redistribution of the orbital electron densities. Figure 1 shows the frontier MO's of protonated acrolein—a simple model for a Lewis acid coordinated dienophile—along with the frontier MO's of acrolein for comparison.[3–5] While the frontier orbitals of acrolein are basically slightly perturbed butadiene orbitals, those of protonated acrolein (1-hydroxyallyl cation) resemble those of an allyl cation mixed with a lone-pair orbital on oxygen.[6] Recent ^{1}H and ^{13}C nmr studies of this species in superacid solution support this model.[7] The predominant frontier orbital interaction in a Diels–Alder reaction with "normal electron demand" involves the diene HO and dienophile LU. This interaction is greatly facilitated by Lewis acid complexation, which lowers the dienophile LU energy to a large extent. Accelerations (10^{-6}-fold) by Lewis acids are not uncommon for reactions of dienes with dienophiles activated by one or more carbonyl or cyano groups.[8–11]

Accompanying these large rate accelerations, greatly increased regioselectivity is observed.[9,10] The regioselectivity of reactions of electron-rich or conjugated dienes and electron-deficient dienophiles is controlled by the diene HO–dienophile LU interaction.[2] As shown in Figure 1, the difference in magnitudes of the LU coefficients at atoms 1 and 2 of acrolein ($C_1^2 - C_2^2 = 0.20$) is smaller than the same difference for protonated acrolein ($C_1^2 - C_2^2 = 0.30$–0.43) so that reactions of the latter should be considerably more regioselective than those of the former.

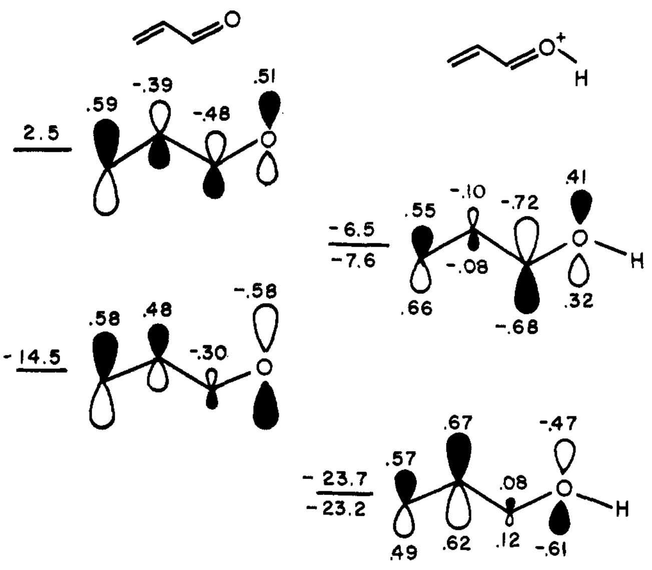

Figure 1. Frontier orbital energies (eV) and coefficients for acrolein and protonated acrolein.[3]

Experimentally, 2-phenyl-, chloro-, and methylbutadiene react with methyl acrylate to give para:meta ratios of 70–80:30–20 in the uncatalyzed reactions and $\geq$97:$\leq$3 in the AlCl$_3$-catalyzed reactions, while 1-methylbutadiene gives ortho:meta ratios of 90:10 and 98:2 for the uncatalyzed and AlCl$_3$-catalyzed reactions, respectively.[10] The considerations in the previous paper[2] indicate that electron-deficient diene–alkene pairs should react with lower regioselectivity than addend pairs of opposite electronic demand. Since the diene terminal coefficients in the HO are nearly identical, coordination of dienophile cannot increase regioselectivity substantially and may result in no change or a decrease in regioselectivity. 2-Cyanobutadiene reacts with para:meta ratios of 84:16 and 73:27 in the uncatalyzed and catalyzed reactions, while these ratios are 55:45 and 51:49 for 2-trifluoromethylbutadiene.[10]

Stereoselectivity (endo:exo ratios) also increases dramatically upon Lewis acid catalysis of Diels–Alder reactions.[11,12] For example, cyclopentadiene reacts with methyl acrylate to give endo:exo ratios of 82:18 and 99:1 in the uncatalyzed and the AlCl$_3\cdot$OEt$_2$-catalyzed reactions, respectively. As shown in Figure 2, the diene HO–dienophile LU secondary orbital interaction between the carbonyl carbon and the diene C-2 is greatly increased in coordinated carbonyls because the coefficient at the carbonyl carbon becomes very large in the latter species. The extent of asymmetric induction in Diels–Alder reactions of chiral dienophiles with dienes is dramatically increased in the Lewis acid catalyzed reactions.[13,14] A "tighter" transition state

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

(3) The orbital energies and coefficients in Figure 1 were obtained from CNDO/2 calculations[4] using 120° bond angles and standard bond lengths[4] for acrolein, and, for the protonated acrolein, 120° bond angles and either the same bond lengths as for acrolein (upper numbers) or bond lengths more suitable for a hydroxyallyl cation (C–C = 1.40 Å; C–O = 1.36 Å) (lower numbers). The latter model was calculated to be 12 kcal/mol more stable than the former. A recent CNDO/2 calculation showed that the bond lengths of the minimum energy geometry are intermediate between these extremes.[5]

(4) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.

(5) A. Dargelos, D. Loitard, and M. Chaillet, *Tetrahedron*, **28**, 5595 (1972).

(6) While the LU of protonated acrolein consists of ψ_2 of allyl mixed in an antibonding sense with the hydroxyl lone pair, the resemblance of the protonated acrolein HO to the component allyl and hydroxyl MO's is obscured, since this HO consists of the additive result of mixing allyl ψ_1 and ψ_2 with the hydroxyl lone pair in an antibonding and a bonding fashion, respectively.

(7) G. A. Olah, Y. Halpern, Y. K. Mo, and G. Liang, *J. Amer. Chem. Soc.*, **94**, 3554 (1972); see also M. Rabinovitz and A. Grinvald, *ibid.*, **94**, 2725 (1972), and references therein for discussions of BF$_3$-complexed aldehydes.

(8) P. Yates and P. Eaton, *J. Amer. Chem. Soc.*, **82**, 4436 (1960); G. I. Fray and R. Robinson, *ibid.*, **83**, 249 (1961); J. Sauer, D. Lang, and H. Wiest, *Chem. Ber.*, **97**, 3208 (1964); T. Inukai and M. Kasai, *J. Org. Chem.*, **30**, 3567 (1965); Y. Kishi, F. Nakatsubo, M. Aratani, T. Goto, S. Inoue, H. Kakoi, and S. Suguira, *Tetrahedron Lett.*, 5127 (1970).

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(10) T. Inukai and T. Kojima, *ibid.*, **35**, 1342 (1970); **36**, 924 (1971); *Chem. Commun.*, 1334 (1969).

(11) T. Inukai and T. Kojima, *J. Org. Chem.*, **32**, 869, 872 (1967).

(12) J. Sauer and J. Kredel, *Tetrahedron Lett.*, 731 (1966); T. Inukai and T. Kojima, *J. Org. Chem.*, 31, 2032 (1966); see also K. L. Williamson and Y.-F. L. Hsu, *J. Amer. Chem. Soc.*, **92**, 7385 (1970).

(13) J. D. Morrison and H. S. Mosher, "Asymmetric Organic Reactions," Prentice-Hall, Englewood Cliffs, N. J., 1971, pp 252–257, and references therein; J. Sauer and J. Kredel, *Tetrahedron Lett.*, 6359 (1966).

(14) H. M. Walborsky, L. Barasch, and T. C. Davis, *Tetrahedron*, **19**, 2333 (1963).

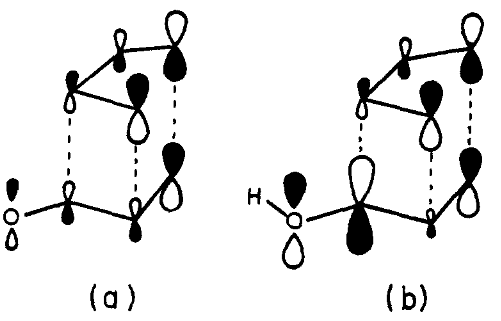

Figure 2. Diene HO–dienophile LU interactions in endo transitions states with (a) acrolein and (b) protonated acrolein.

in the catalyzed reactions resulting from the greatly increased secondary orbital interactions, as well as possible conformational changes in the complexed dienophile,[14] could reasonably be expected to cause such a large effect.

The model proposed here is similar to considerations of changes in dienophile electrophilicity made by others,[11] and suggests no change in mechanism from the normal concerted mechanism of the Diels–Alder reaction. However, this MO model does imply increased asynchroneity in bond-making processes, and if electrostatic effects (first-order interactions) are also considered, two-step mechanisms with cationic intermediates become probable in some cases. Several examples of the type are known,[15] and others have been suggested.[16] Nevertheless, the model proposed here shows that the phenomena generally observed on catalysis can be explained by the concerted mechanism, and allows predictions of the effect of Lewis acids on the rates, regioselectivity, and stereoselectivity of all concerted cycloadditions, including those of ketenes, 1,3 dipoles, and Diels–Alder reactions with "inverse electron demand."

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

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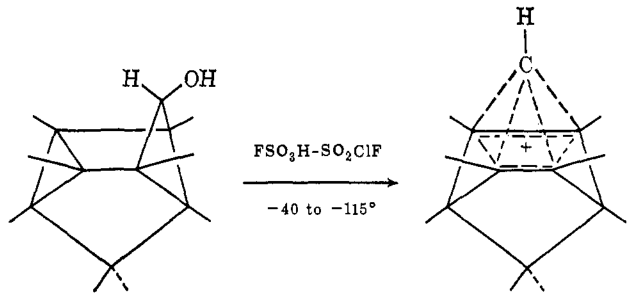
Degenerate Rearrangements of Bicyclo[3.2.1]octa-3,6-dien-2-yl Cations

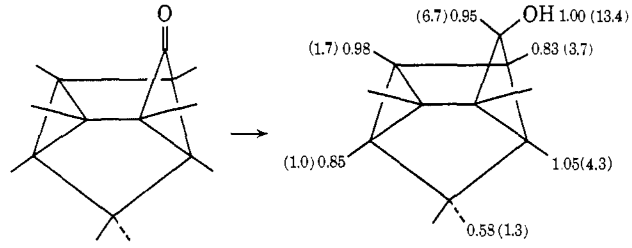
Sir:

We recently reported that the carbonium ion produced from **1** in FSO_3H–SO_2ClF over the temperature range −115 to −40° either has the symmetric structure **2** or is a mixture of ions which rapidly equilibrate with the same net effect on the ion's proton and ^{13}C nmr spectra.[1-3] We now find that replacement of the secondary hydrogen by a methyl group changes the structure of the carbonium ion produced; we also describe a novel and unexpected degenerate rearrangement of the ion which is formed.

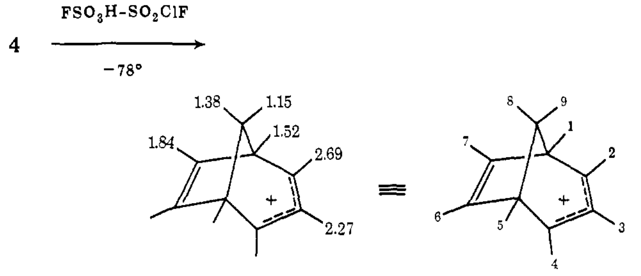


1 **2**

Treatment of **3**[4] (1.0 g in 10 ml of ether, 0°) with methyllithium gave a single crystalline tertiary alcohol **4**.[5-7] Unlike **1**, **4** did not give a sharp, well defined pmr spectrum over a wide temperature range in FSO_3H–SO_2ClF (1:4). But at −90° a well resolved spectrum was obtained, which we assign to the nonamethylbi-



3 **4**



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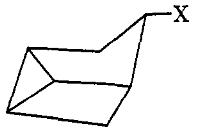
(1) H. Hart and M. Kuzuya, *J. Amer. Chem. Soc.*, 94, 8958 (1972).

(2) A similar ion is probably involved in the solvolysis of i: R. K.



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Lustgarten, *ibid.*, 94, 7602 (1972). Several systems which may be amenable to the formation of such ions have been described: R. M. Coates and K. Yano, *Tetrahedron Lett.*, 2289 (1972); S. Masamune, R. Vukov, M. J. Bennett, and J. T. Purdham, *J. Amer. Chem. Soc.*, 94, 8239 (1972).

(3) These ions are bis homo derivatives of the $(CH)_6^+$ ions discussed by W.-D. Stohrer and R. Hoffmann, *ibid.*, 94, 1661 (1972), and studied experimentally by S. Masamune and coworkers, *ibid.*, 94, 8955, 8956 (1972).

(4) H. Hart and G. M. Love, *ibid.*, 93, 6266 (1971).

(5) The structures show proton chemical shifts in ppm from TMS and in parentheses the relative slopes of the downfield shifts caused by adding $Eu(fod)_3$. The solvent for neutral substances was carbon tetrachloride. The internal reference for the carbonium ion spectra was $(CH_3)_4N^+BF_4^-$, δ 3.13.

(6) Analytical data and mass spectra were consistent with the structure.

(7) Nearly quantitatively yield, sublimes, ir 3450 cm^{-1}; the stereochemistry follows from the Eu-shift data.