Secondary Orbital Interactions Determining Regioselectivity in the Lewis Acid Catalyzed Diels–Alder Reaction. II

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Frontier orbital theory and the theoretical model of the Lewis acid complexed dienophile have been used to predict the effect of Lewis acid catalysis on the regioselectivity of the Diels–Alder reaction between unsymmetrically substituted dienes and dienophiles. This theoretical approach is applied to the three general types of uncatalyzed Diels–Alder reactions and general cases for predicting the effect of catalysis on the regioselectivity of the normal electron demand reaction are given. The effect of polysubstitution on the frontier orbital coefficients of butadiene is also determined. Dipole–dipole interactions were not useful in predicting the changes in regioselectivity.

The use of frontier orbital theory to predict the reactivity and the regioselectivity of concerted cycloaddition reactions has been extremely successful.[1–6] General rules for predicting the regioselectivity of the uncatalyzed concerted [2π + 2π] and [4π + 2π] cycloaddition reactions from the frontier orbital interactions have been proposed.[1c,2d,4,5b] Also, the role of Lewis acid catalysis in the Diels–Alder reaction has been determined.[2c,5a] The important changes in the frontier orbital properties of the dienophile acrolein upon complexation with a Lewis acid was a substantial lowering of the frontier orbital energies, an increase in the magnitude of the LUMO coefficient of the carbonyl carbon, and an increase in the difference in the magnitudes of the LUMO coefficients of the alkene moiety. From these changes, a catalyzed transition state completely dominated by the HOMO diene–LUMO dienophile interaction and having greatly increased secondary orbital interactions was predicted. Houk and Strozier[2c] also proposed that Lewis acid catalysis will increase the regioselectivity from the uncatalyzed reaction for dienes with terminal coefficients of different magnitudes, while dienes with terminal coefficients of nearly equal magnitude will have no change or a decrease in regioselectivity.

In our investigation of the origin of the regioselectivity in the Lewis acid catalyzed Diels–Alder reaction between unsymmetrically substituted dienes and dienophiles, we have observed some discrepancies with experimental results in Houk and Strozier's explanation. However, these discrepancies are eliminated if secondary orbital interactions are considered. This is in agreement with our earlier investigations[1a] concerning the importance of secondary orbital interactions in determining the regioselectivity in the uncatalyzed Diels–Alder reaction. Consequently, in this paper, the theoretical model of the Lewis acid complexed dienophile and the frontier orbital approach (including secondary orbital interactions) is used to explain the origin of the change in the regioselectivity of the uncatalyzed Diels–Alder reaction with catalysis.

Results and Discussion

The frontier orbital approach to regioselectivity used in this paper is based on the second-order perturbation expression for the energy change which accompanies the orbital interaction of two molecules involved in a cycloaddition process. In this expression γ_{rs} is the atomic orbital transition state resonance integral for atomic orbitals r and s in the molecular orbitals, R and S. The c_r's and c_s's are the atomic orbital coefficients of the atomic orbitals in the molecular orbitals R and S, respectively, which have a bonding interaction in the transition state. The closed-shell repulsion is neglected in our approach because the overlap as represented by eq 1 has been shown to be the dominant interaction by many investigators.[1–6] The first-order charge interactions are also neglected because even when two polar molecules react as in the dimerization of acrolein, the regioselectivity is determined by the overlap and the first-order charge interactions favor the unobserved regioisomer.[1c] However, the effect of electrostatic forces will be considered later through the dipole–dipole interactions. A more detailed discussion of the theory is presented in a review by Herndon.[6]

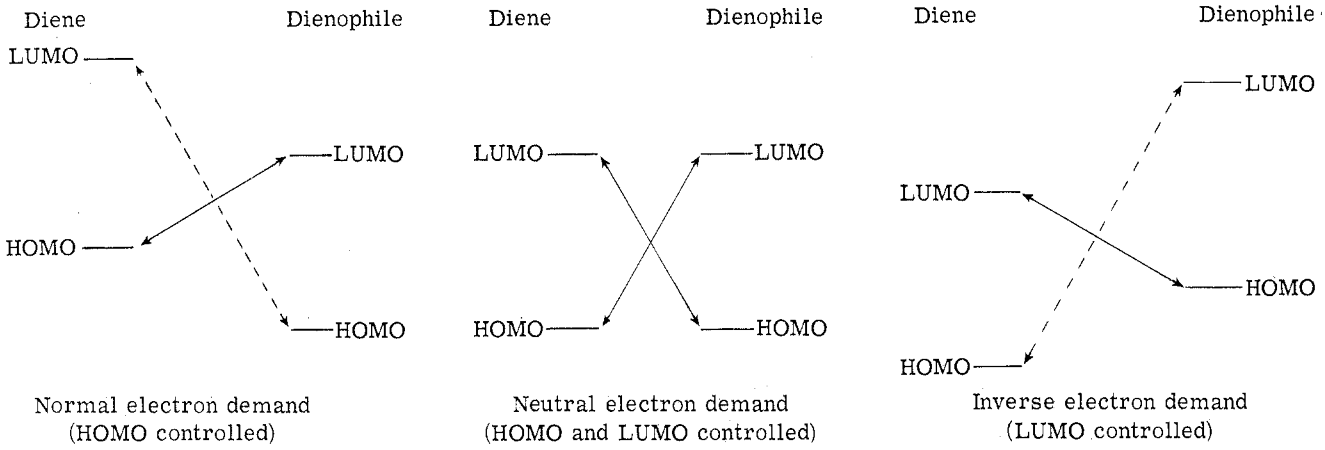
$$\Delta E = 2\left(\sum_{R}^{\text{occ}}\sum_{S}^{\text{unocc}} - \sum_{R}^{\text{unocc}}\sum_{S}^{\text{occ}}\right)\frac{\left(\sum_{rs} c_r c_s \gamma_{rs}\right)^2}{E_R - E_S} \qquad (1)$$

From eq 1, Sustmann[3] has classified the Diels–Alder reaction into three general types depending on the HOMO–LUMO arrangement of the diene and dienophile. The three types are the normal electron demand, the inverse electron demand, and the neutral electron demand (Chart I). The normal electron demand reaction is dominated by the HOMO diene–LUMO dienophile interaction, while the inverse electron demand reaction is dominated by the HOMO dienophile–LUMO diene interaction. In the neutral electron demand reaction, neither frontier orbital interaction is dominant and both significantly affect the regioselectivity and reactivity of the reaction. We will now apply the theoretical approach to the prediction of the effect of Lewis acid catalysis on the regioselectivity of the three types of Diels–Alder reactions.

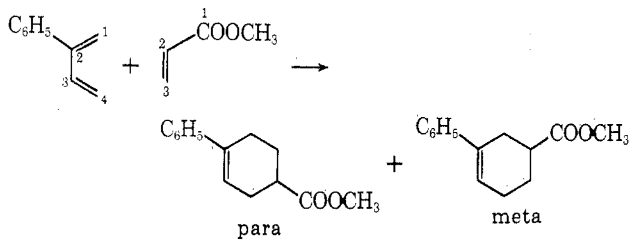
Normal Electron Demand. The effect of Lewis acid catalysis on the regioselectivity of the normal electron demand Diels–Alder reaction can be simplified into the following two frontier orbital interactions: (1) interaction of the terminal HOMO coefficients of the diene with the LUMO coefficients of the alkene moiety of the dienophile; (2) interaction of the HOMO secondary orbital coefficients of the diene with the LUMO secondary orbital coefficient of the dienophile. By considering which regioisomer the two interactions favor and the relative importance of the two interactions, predictions concerning the change in the regioselectivity of the uncatalyzed Diels–Alder reaction with Lewis acid catalysis can be made. This approach is illustrated in the following experimental cases.

The reaction of 2-phenyl-1,3-butadiene with methyl acrylate is an example in which there is a large difference in the magnitudes of the terminal HOMO coefficients of the

Chart I
HOMO–LUMO Orbital Arrangements of the Three Types of Diels–Alder Reactions



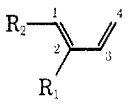
diene. These coefficients favor the para regioisomer (Table I).[7] Since catalysis increases the difference in the magnitudes of the LUMO coefficients of the alkene moiety of the dienophile, these terminal interactions in the catalyzed reaction will favor the para regioisomer even more than in the uncatalyzed reaction. However, the secondary orbital interactions between the HOMO of the diene and the LUMO of the dienophile favor the ortho regioisomer; that is, the endo transition state is more stable when the LUMO coefficient at C-1 of the dienophile is near the larger HOMO coefficient at C-2 of the diene (larger than the diene HOMO coefficient at C-3). Since secondary orbital interactions are increased with catalysis, they favor an increase in the amount of the ortho regioisomer formed. Thus, the two frontier orbital interactions predict opposite effects on the regioselectivity by catalysis. Experimentally, increased preference for the para regioisomer is observed (Table II); thus, the terminal interactions will dominate over the secondary orbital interactions in such cases. Also, the dienes, 2-methyl- and 2-chloro-1,3-butadiene, have similar HOMO coefficients to the 2-phenyl case and yield the predicted increase in regioselectivity with catalysis.[11]



The diene, 2-cyano-1,3-butadiene, has INDO and CNDO/2 HOMO coefficients similar to the 2-chloro and 2-methyl cases, but the regioselectivity in its catalyzed reaction with methyl acrylate is decreased from the uncatalyzed reaction. However, the semiempirical molecular orbital methods disagree on the relative HOMO coefficients of 2-cyano-1,3-butadiene (Table I); consequently, the regioselectivity cannot be reliably predicted from such coefficients. Also, for reactions between electron-deficient dienes and dienophiles, the HOMO dienophile–LUMO diene interaction could have a significant role in determining the regioselectivity.[4]

The 2-cyano-1,3-butadiene case points out a difficulty in the approach itself, which is that the relative magnitudes of

Table I
Eigenvectors of the HOMO of Monosubstituted 1,3-Butadienes



Registry no.	R_1	R_2	Molecular orbital method	Eigenvectors[a] C-1	C-2	C-3	C-4
78-79-5	CH_3	H	INDO	0.614	0.420	0.348	0.506
	CH_3	H	CNDO/2	0.621	0.417	0.340	0.498
2288-18-8	C_6H_5	H	INDO	0.572	0.341	0.214	0.335
	C_6H_5	H	CNDO/2	0.568	0.341	0.195	0.328
5167-62-4	CN	H	INDO	0.595	0.405	0.342	0.490
	CN	H	CNDO/2	0.600	0.405	0.335	0.485
	CN	H	Iterative extended Hückel	0.542	0.318	0.370	0.509
3036-66-6	H	OCH_3	CNDO/2	0.445	0.492	0.289	0.498
126-99-8	Cl	H	CNDO/2	0.546	0.346	0.266	0.397
	Cl	H	Iterative extended Hückel	0.601	0.334	0.224	0.394
381-81-7	CF_3	H	INDO	0.549	0.404	0.434	0.574
504-60-9	H	CH_3	INDO	0.531	0.456	0.350	0.534
	H	CH_3	CNDO/2	0.524	0.462	0.342	0.531
627-22-5	H	Cl	CNDO/2	0.423	0.400	0.266	0.423

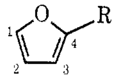
[a] These are the absolute values of the P_z coefficients. The other atomic orbital coefficients are zero for HOMO.

Table II
Regioisomer Ratios of the Diels–Alder Reaction between Unsymmetrically Substituted Dienes and Dienophiles

Diene	Dienophile	Uncatalyzed para:meta	Catalyzed para:meta	Ref
2-Phenyl-1,3-butadiene	Methyl acrylate	80:20	97:3	a
2-Chloro-1,3-butadiene	Methyl acrylate	87:13	98:2	a
2-Trifluoromethyl-1,3-butadiene	Methyl acrylate	55:45	51:49	a
2-Cyano-1,3-butadiene	Methyl acrylate	84:16	72:27	a
2-Methyl-1,3-butadiene	Methyl acrylate	69.5:30.5	95:5	a
2-Methyl-1,3-butadiene	Acrolein	59:41	96:4	b
1,2-Diphenyl-1,3-butadiene	β-Nitrostryene	75:25[e]	0:100[e]	c
1-Phenyl-2-methyl-1,3-butadiene	β-Nitrostryene	100:0[e]	0:100[e]	c
		Ortho:meta	Ortho:meta	
1-Methyl-1,3-butadiene	Methyl acrylate	90:10	98:2	a
2-Methylfuran	Ethyl propiolate		Ortho regioisomer formed >98%	d
2-Phenylfuran	Ethyl propiolate		Ortho regioisomer was only cycloaddition product observed	d

[a] T. Inukai and T. Kojima, *J. Org. Chem.*, 36, 924 (1971). [b] K. L. Williamson and Y. L. Hsu, *J. Am. Chem. Soc.*, 92, 7385 (1970). [c] P. C. Jain, Y. N. Mukerjee, and N. Anad, ibid., 96, 2996 (1974). [d] A. W. McCulloch and A. G. McInnes, *Can. J. Chem.*, 49, 3152 (1971). [e] Nitro group is meta or para to 2 substituent of the diene.

Table III
INDO Frontier Orbital Coefficients of 1-Substituted Furans



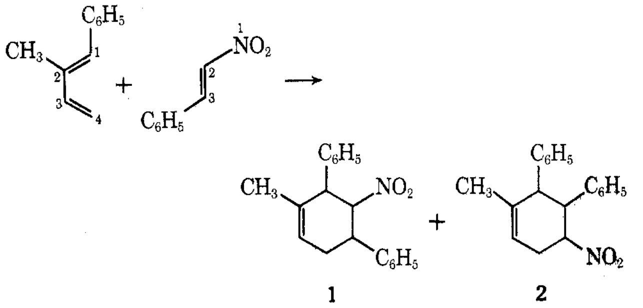
Registry no.	Substituent	P_z coefficients of HOMO[a] C-1	C-2	C-3	C-4	P_z coefficients of LUMO[a] C-1	C-2	C-3	C-4
534-22-5	CH_3	0.546	0.352	0.441	0.540	0.500	0.290	0.392	0.539
17113-33-6	C_6H_5	0.468	0.276	0.418	0.449	0.324	0.103	0.375	0.326

[a] These are absolute values. The other atomic orbital coefficients are zero for HOMO and LUMO.

the HOMO and LUMO eigenvectors of certain molecules depend on the type of calculation employed. In this work, we have used mainly the eigenvectors from INDO and CNDO/2 calculations because of their strong theoretical base[8,12] and earlier successful correlation with experimental results.[1a] Furthermore, other investigators[2a,4] have found that various semiempirical molecular orbital methods agree on the relative magnitudes of the frontier orbital coefficients of monosubstituted 1,3-butadienes for substituents other than electron withdrawing. Our molecular orbital methods do agree on the relative HOMO coefficients of 2-chloro-1,3-butadiene.

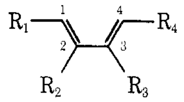
A different case is the reaction of 1-methyl-1,3-butadiene with methyl acrylate, where the terminal HOMO coefficients of the diene are of nearly the same magnitude, thereby favoring neither regioisomer. In such cases the regioselectivity is determined by the secondary orbital interactions and regioselectivity will always increase with catalysis. This increase was observed in this reaction (Table II). Another example of this case is the catalyzed reaction of 1-phenyl- and 1-methylfuran with ethyl propiolate. The terminal HOMO coefficients have nearly the same magnitudes (Table III) and the regioisomer favored by the secondary orbital interactions makes up >98% of the cycloaddition product.

A more dramatic example of the importance of secondary orbital interactions in determining the regioselectivity is the reaction between 1-phenyl-2-methyl-1,3-butadiene and β-nitrostyrene.[13] In this case the terminal HOMO coefficients of the diene have a significantly different magnitude and favor regioisomer 2 (Table IV). Secondary orbital interactions between the LUMO nitrogen coefficient of the dienophile and the HOMO coefficients of the C-2 and C-3 positions of the diene favor regioisomer **1**. Since secondary orbital interactions are weak in the uncatalyzed reaction, the terminal interactions dominate and only regioisomer 2 is observed experimentally. However, in the catalyzed reaction, only regioisomer 1 is observed owing to the greatly enhanced secondary orbital interactions. More evidence for this conclusion is that the uncatalyzed reaction gave almost equal proportions of the endo and exo adducts (nitro group) while the catalyzed reactions gave exclusively the endo adduct. Similar experimental results were obtained for the analogous reaction of 1,2-diphenyl-1,3-butadiene with β-nitrostyrene (Table II).



These experimental cases have been discussed to demonstrate this approach. There are several other theoretical combinations of the two frontier interactions which may or

Table IV
CNDO/2 HOMO and LUMO Eigenvectors of Disubstituted 1,3-Butadienes

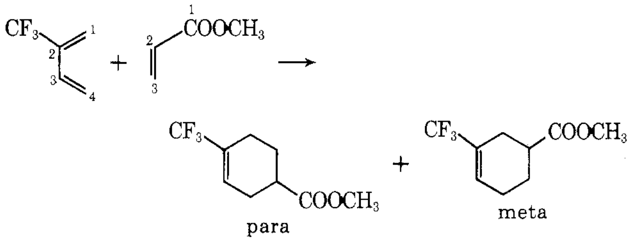


					Eigenvectors of HOMO[a]				Eigenvectors of LUMO[a]			
Registry no.	R_1	R_2	R_3	R_4	C-1	C-2	C-3	C-4	C-1	C-2	C-3	C-4
51034-43-6	Cl	H	H	CH_3	0.438	0.360	0.343	0.426	0.485	0.463	0.341	0.519
51034-44-7	H	Cl	H	CH_3	0.547	0.323	0.369	0.430	0.585	0.405	0.345	0.493
37710-49-9	H	H	Cl	CH_3	0.408	0.245	0.404	0.507	0.455	0.307	0.423	0.602
1608-27-1	C_6H_5	H	H	CH_3	0.419	0.407	0.294	0.417	0.407	0.432	0.255	0.419
21919-51-7	C_6H_5	H	CH_3	H	0.397	0.422	0.249	0.464	0.414	0.437	0.247	0.405
37580-42-0	C_6H_5	CH_3	H	H	0.433	0.433	0.208	0.388	0.415	0.443	0.247	0.411
22858-22-6	C_6H_5	H	H	Cl	0.380	0.390	0.269	0.395	0.436	0.392	0.335	0.411
54166-27-7	C_6H_5	H	Cl	H	0.380	0.422	0.228	0.438	0.420	0.408	0.281	0.470
54166-28-8	C_6H_5	Cl	H	H	0.414	0.408	0.193	0.365	0.461	0.427	0.210	0.373

[a] These are the absolute values of the P_z coefficients. The other atomic orbital coefficients are zero for the HOMO and the LUMO.

may not be observed experimentally, but the basis for rationalizing the changes in regioselectivity with catalysis is now available. The general cases are given in Table V. Finally, the effect of secondary orbital interactions on the regioselectivity will increase as the difference in the LUMO coefficient magnitudes of the diene moiety of the dienophile decreases.

Neutral Electron Demand. In the neutral electron demand reaction both frontier orbital interactions affect the regioselectivity. Upon catalysis, the HOMO diene–LUMO dienophile interaction becomes dominant; thus, the removal of the HOMO dienophile–LUMO diene interaction's effect on regioselectivity will also be important. The reaction of 2-trifluoromethyl-1,3-butadiene with methyl acrylate is an example of this removal affecting the regioselectivity. In the uncatalyzed case the HOMO dienophile–LUMO diene interaction favors the para regioisomer[14] and the HOMO diene–LUMO dienophile interaction favors the meta regioisomer. Experimental results indicate that the para regioisomer dominates slightly (Table II). Since this dominance originated from the HOMO dienophile–LUMO diene interaction, a decrease in the amount of para regioisomer is expected with catalysis. The decrease is observed experimentally with a near 50:50 ratio in the catalyzed case. This ratio is expected from examination of the terminal coefficients and secondary orbital coefficients of HOMO of the diene.



Inverse Electron Demand. The approach to predicting the effect of Lewis acid catalysis on the regioselectivity of the inverse electron demand reaction is the same as for the neutral electron demand reaction. Presently there are no experimental data available to test this approach for such reactions.[15]

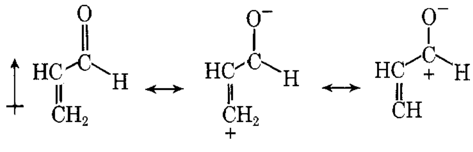
Frontier Orbital Eigenvectors of Polysubstituted Dienes. We have carried out CNDO/2 calculations on a series of disubstituted 1,3-butadienes (Table IV). The results are in accord with qualitative reasoning from summation of the individual substituent effects in the monosubstituted cases with the 1 substituent suppressing the effect of the 2 substituent somewhat. This slight dominance of the effect of the 1 substituent is expected, since the terminal coefficients of HOMO and LUMO of 1,3-butadiene are greater than the secondary orbital positions. The study also indicates that the difference in coefficient magnitudes at the secondary HOMO C-2 and C-3 positions will be a maximum for the 1,2-disubstituted case and a minimum for the 1,4-disubstituted case for a given set of substituents. Thus, for disubstituted dienes with similar terminal orbital coefficients, secondary orbital interactions will be most important in the 1,2-disubstituted case and least important in the 1,4-disubstituted case.

Dipole–Dipole Interactions. At a large distance of separation, electrostatic forces between polar reactant molecules can have a significant role in determining the orientation in the transition state. Consequently, the rationalization of preferred orientations through dipole–dipole interactions was investigated. The energy change due to dipole–dipole interactions is expressed by eq 2, where ΔE is in ki-

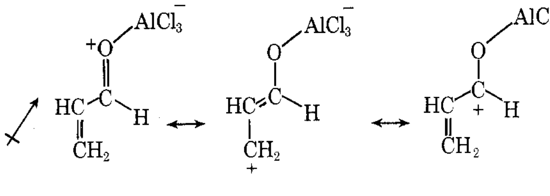
$$\Delta E = \pm\frac{14.4\mu_A\mu_B}{r^3} \qquad (2)$$

localories/mole, μ is the dipole moment in Debye units, and r is the distance of separation in angstroms.[16] The orientation in which the dipoles line up in an antiparallel is favored. The directions of the dipole moments of the dienes and dienophiles were determined from vector analysis[17]

Chart II
Valence Bond Resonance Structures of Acrolein and Lewis Acid Complexed Acrolein



Acrolein



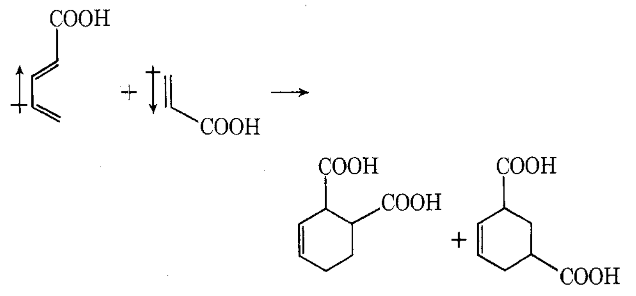
Lewis acid complexed acrolein

Table V
Effect of Lewis Acid Catalysis on the Regioselectivity of the Normal Electron Demand Diels–Alder Reaction

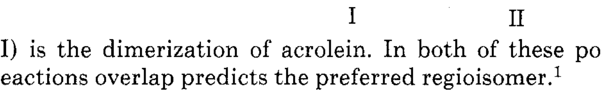
Case	Change in regioselectivity with catalysis
Terminal interactions and secondary orbital interactions favor the same regioisomer	Increased regioselectivity
Terminal interactions favor neither regioisomer and secondary orbital coefficients of the diene are significantly different	Increased regioselectivity
Secondary orbital coefficients favor neither regioisomer and the terminal coefficients of the diene are significantly different	Increased regioselectivity
Terminal interactions and secondary orbital interactions favor neither regioisomer	No change
Terminal interactions and secondary orbital interactions favor different regioisomers	1. When the difference in the magnitudes of the diene terminal coefficients is large, the terminal interactions will dominate and the regioselectivity will increase. 2. When the difference in the magnitudes of the diene terminal coefficients is small, the secondary orbital interactions will dominate and the amount of the minor regioisomer formed will increase.

and the semiempirical calculations. Lewis acid catalysis will increase the magnitude of the dipole moment, but will not change its direction (Chart II).

If dipole–dipole interactions are determining the regioselectivity of the Diels–Alder reactions in Table II, the following generalization should be observed. The Lewis acid catalyzed reaction will prefer the same regioisomer as the uncatalyzed reaction, only more so. However, this generalization is not even observed for the reactions with the polar dienes, 2-cyano-, and 2-trifluoromethyl-1,3-butadienes. More evidence against the importance of dipole–dipole interactions is obtained from the polar reaction of 1-carboxy-1,3-butadiene and acrylic acid. The dipole–dipole interaction favors the meta regioisomer while the ortho regioisomer is preferred 8.8:1. Another polar reaction in which the dipole–dipole interaction favor the unpreferred regioisomer (I) is the dimerization of acrolein. In both of these polar reactions overlap predicts the preferred regioisomer.[1]



ortho meta



I II

Conclusion

The success of this frontier orbital approach allows the prediction of the effect of Lewis acid catalysis on the regioselectivity of the uncatalyzed Diels–Alder reaction between unsymmetrically substituted dienes and dienophiles. Also, this approach indicates that secondary orbital interactions have a significant and sometimes dominant effect in determining the regioselectivity of the catalyzed Diels–Alder reaction. The individual substituents effects on the frontier orbital coefficients are additive and the coefficients of the monosubstituted dienes can be used to qualitatively determine the relative coefficient magnitudes in polysubstituted dienes. Finally, the consideration of electrostatic interactions does not improve the theory.

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References and Notes

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(2) (a) K. N. Houk, J. Sims, R. E. Duke, Jr., R. W. Strozier, and J. K. George, *J. Am. Chem. Soc.*, **95**, 7287 (1973); (b) K. N. Houk, J. Sims, C. R. Watts, and L. J. Luskus, *ibid.*, **95**, 7301 (1973), and references cited therein; (c) K. N. Houk and R. W. Strozier, *ibid.*, **95**, 4094 (1973); (d) K. N. Houk, *ibid.*, **95**, 4092 (1973).

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(5) (a) N. T. Anh and J. Seyden-Penne, *Tetrahedron*, **29**, 3259 (1973); (b) O. Eisenstein, J.-M. Lefour, and N. T. Anh, *Chem. Commun.*, 969 (1971).

(6) W. C. Herndon, *Chem. Rev.*, **72**, 157 (1972).

(7) The HOMO and LUMO coefficients of the dienes and dienophiles used in this investigation of regioselectivity were determined by the INDO,[8] CNDO/2,[8] and iterative extended Hückel[9] molecular orbital methods. A complete description of the geometries of diene and dienophiles used in the calculations is given in the first paper in this series.[1a] The experimental geometry of furan[10] with standard bond angles and bond lengths[8] for its substituents was used for the 1-substituted furans. The interpretations from the calculated eigenvectors and eigenvalues were independent of small changes in bond distances, bond angles, and rotational conformations.

(8) 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.

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(10) "Interatomic Distances", *Chem. Soc., Spec. Publ.*, **No. 11** (1958); *Suppl.*, **No. 18** (1965).

(11) Another source of the increase in regioselectivity in these cases is the decrease in the energy separation between the HOMO of the diene and the LUMO of the dienophile. As this energy separation decreases, the reaction becomes more sensitive to the substituent effect.

(12) The INDO and CNDO/2 wavefunctions are not above criticism: F. A. Van-Catledge, *J. Phys. Chem.*, **78**, 763 (1974).

(13) The CNDO/2 calculations predict that the LUMO coefficient (0.319) at

the C-2 position will be smaller than the LUMO coefficient (0.474) at the C-3 position for β-nitrostyrene.

(14) The LUMO coefficients (INDO) for 2-trifluoromethyl-1,3-butadiene are as follows: C-1, 0.626; C-2, 0.453; C-3, 0.338; C-4, 0.501.

(15) The classification of the specific uncatalyzed Diels–Alder reactions into the three general types was determined from the CNDO/2 and INDO orbital energies.

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α-Methyleneoxetane. Study of a Retro-Diels–Alder Reaction

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As a precursor to α-methyleneoxetane (**11**), the anthracene adduct **7** was prepared in a four-step sequence from the ketone **2**. Pyrolysis of **7** gave α-methyleneoxetane and anthracene, as well as the rearranged ether **8** and the olefin **15**. The structure of the rearranged ether **8**, also formed from **7** on some chromatography adsorbents or with acid, was determined with the aid of carbon-13 NMR spectroscopy and further confirmed by hydrogenation to the alcohol **9**. α-Methyleneoxetane (**11**) was characterized by spectroscopy and by its reaction with phenyllithium.

α-Methyleneoxetane (**11**) has interested us for some time because of the possibility that nucleophilic displacement on the oxetane ring[1,2] could be used to generate a specific enolate of an unsymmetrical ketone; α-methyleneoxetane might thus serve as a potential 3-ketobutyl group in the Robinson annelation reaction.[3,4] Substituted compounds having the α-methyleneoxetane ring have been prepared by several methods[2,5-7] and have been proposed as reaction intermediates.[8] In 1971, we reported a preliminary account of the first synthesis of α-methyleneoxetane (**11**),[9,10] which we obtained in low yield from a retro-Diels–Alder reaction[9-14] by pyrolysis of the anthracene adduct **7**. More recently, Haslouin and Rouessac have obtained **11** in higher yield by pyrolysis of the cyclopentadiene adduct.[11]

Since the pyrolysis of **7** gave α-methyleneoxetane in low yields only, we have investigated the composition of the nonvolatile residue from the pyrolysis experiments. In the course of this investigation we have also encountered an acid-catalyzed rearrangement of **7**. We report here a full account of the pyrolysis and rearrangement of **7**.

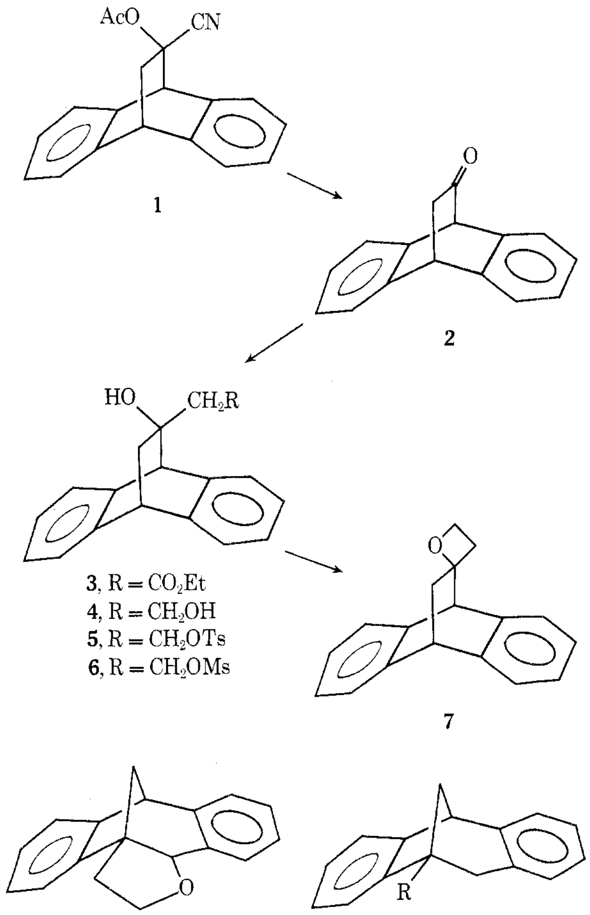
The anthracene adduct **7** was prepared as shown in Scheme I. Both the tosylate **5** and the mesylate **6** served as precursors to **7**. The purity of **7** from both routes was indistinguishable (ir, NMR, TLC, melting point); we obtained higher yields from the mesylate.

The anthracene adduct **7** was always purified by chromatography on Florisil followed by recrystallization from ether. On one occasion, chromatography yielded none of **7** but instead an isomeric compound. The rearrangement of **7** to the isomer was found to take place on only certain batches of Florisil. The same rearrangement also occurred on acidic alumina, but not on silica gel or neutral or basic alumina. In addition, treatment with *p*-toluenesulfonic acid or sulfuric acid at room temperature caused the rearrangement of **7** to its isomer.

The isomer was assigned structure **8** on the basis of its analytical and spectral data, in particular the carbon-13 NMR data. The structure was further confirmed by catalytic hydrogenation to the alcohol **9**. The chemical shifts and coupling constants in the proton NMR of **9** are very analogous to those reported for the related compound **10** prepared by Cristol.[15,16]

Pyrolyses of the anthracene adduct **7** were carried out on a small scale (50–500 mg) by heating at 330–350° in a slow stream of nitrogen for 5–25 min while collecting the volatile products in a receiver cooled in Dry Ice–acetone. The distillate, a colorless liquid, was identified as α-methyleneoxetane (**11**) by its ir, NMR, and mass spectra and its reaction with phenyllithium, which produced, after work-up, 4-phenyl-2-butanone (**12**),[17,18] 2-phenyl-3-buten-2-ol (**13**),[19,20] and 2,4-diphenyl-2-butanol (**14**).[18,21] In some pyrolyses, methyl vinyl ketone was formed as an impurity. On three occasions, the yield of α-methyleneoxetane was determined to be about 10%.[22]

Scheme I



3, R = CO$_2$Et
4, R = CH$_2$OH
5, R = CH$_2$OTs
6, R = CH$_2$OMs

8

9, R = CH$_2$CH$_2$OH
10, R = CH$_3$