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A SIMPLE MODEL FOR PREDICTING THE EFFECT OF SUBSTITUENTS ON THE RATES OF THERMAL PERICYCLIC REACTIONS

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Abstract—An operationally useful model is proposed for predicting the qualitative effect of substituents on the rates of thermal pericyclic reactions. The method provides a unified interpretation of several previously unrelated experimental observations. It also enables the prediction of substituent effects in pericyclic reactions for which experimental data are not yet available.

The utility of pericyclic reactions in the synthesis of complex molecules is becoming increasingly apparent. In particular the predictable stereochemical course[1] for such reactions is of enormous value in the design of synthetic strategies. Unfortunately, one currently has little control over the rates of pericyclic reactions, in part because they are notoriously insensitive to solvent effects.[2] Thus a desired transformation may require temperatures too high for the survival of sensitive functional groups, or, on the other hand, an undesired transformation may be so facile that it becomes a major competing side reaction.

One approach to solving this problem would be to control the reaction rate by selection of substituents with appropriate electronic properties. In a multistep synthesis the position of a given substituent is usually predetermined by its eventual location (albeit in modified form) in the final product; consequently substituent position cannot reasonably be considered an operational variable. By contrast control of the electronic properties of a substituent is quite straightforward. Thus electron donors and acceptors may be interconverted by change of oxidation state (amines $\rightleftharpoons$ nitro groups, sulfides $\rightleftharpoons$ sulfones, alcohols $\rightleftharpoons$ carbonyl compounds) while interconversion of acceptor carbonyl compounds and conjugating alkenes may be achieved through Wittig reaction and ozonolysis respectively.

The profound influences of certain types of substituent on the rates of pericyclic reactions have recently been elegantly demonstrated.[3,4] However, a simple theory which would enable one to employ such effects in a predictable way appears to be lacking. In general terms one would like to know the optimum electronic properties of a substituent at a given position in order to maximize (or minimize) the rate of an ensuing pericyclic reaction. It is the purpose of this paper to attempt to derive an operationally useful basis for such predictions. A deliberately simple theoretical model is employed in order that results may be obtained without resorting to extensive computations. However, the qualitative conclusions drawn should not vary when more rigorous molecular orbital methods are used.

The theoretical model. It is intuitively reasonable that the degree of conjugation of substituent orbitals with those of the carbon framework will change as a pericyclic reaction proceeds from reactant(s) to transition state. In particular one would expect increased delocalization in the transition state since, by definition, a pericyclic reaction proceeds through a transition state involving a cycle of completely conjugated orbitals. The simple model presented below is based on the assumption that this change in degree of delocalization is the sole determinant of the substituent influence on reaction rate.

As a model for the transition state of each reaction the corresponding completely conjugated cyclic hydrocarbon is used (e.g. benzene for the Cope rearrangement). This is in the spirit of Dewar's analysis of pericyclic reactions[5] and closely parallels the Berson–Salem treatment of subjacent orbital effects.[6] In those cases where the cycle of orbitals in the transition state involves an odd number of phase changes the corresponding Möbius[7] hydrocarbon has been employed (e.g. Möbius cyclobutadiene as a model for the conrotatory ring opening of cyclobutene). The energy levels of the Möbius hydrocarbon are readily deduced by changing the sign of the appropriate pair of off-diagonal elements in the secular determinant. Total π-electron energies of the reactant(s) and model transition state are calculated by the simple Hückel molecular orbital method. (In many cases the results are known and tabulated,[8,9] and hence no calculation is required.)

In order to deduce qualitative substituent effects one needs only to know whether a particular type of substituent, say a π-electron donor, will increase or decrease the reaction rate. Given this information it seems reasonable to assume that the relative effectiveness of specific π-donors will follow the usual order (perhaps reflected by σ_R values[10]): e.g. $K^{+-}O- > Li–O- > Me_2N- > MeO- \gg Me-$. It therefore seems appropriate to replace all of these substituents by a model for the purposes of the calculations. We have chosen to use a carbon bearing a doubly occupied $2p\pi$ orbital.[11] Similarly π-electron acceptors such as tricoordinate boron and nitro groups are represented by an empty $p\pi$ orbital on carbon, while conjugating but non-polar substituents are represented by a vinyl group. The commonly used carbonyl substituents may be expected to exhibit properties intermediate between those calculated for an acceptor and a conjugating group.

These suggested analogies receive considerable support from the apparent success of the model in reproducing experimental results. Furthermore there is good qualitative agreement with the results obtained by Epiotis using a more sophisticated approach.[12]

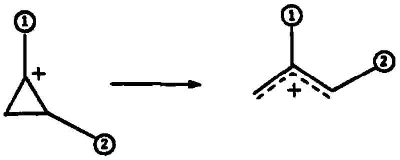
RESULTS

Reactions are classified according to the ring size of the cyclic array of orbitals overlapping in the transition state. Substituents are classified as acceptor (Acc), donor (Don), conjugating (Con) or no substituent (O). When the ring is even-membered, addition of a single atom substituent generates an odd-alternant hydrocarbon which must have a non-bonding molecular orbital. This orbital will be empty when the substituent is an acceptor but doubly occupied when it is a donor; however, being non-bonding, the orbital makes no contribution to the total π-electron energy of the system. The calculations consequently predict identical behavior for donors and acceptors in such cases. In a sense this result is an artifact of the model since use of a heteroatom substituent would enable one to distinguish the effects of donors and acceptors. However, in a more important sense the prediction is genuine since in these cases both types of substituent would be expected to accelerate the reaction or both types would be expected to retard the reaction. In the interests of keeping the model as simple as possible donors and acceptors are thus combined in a single class of polar (Pol) substituents for such cases.

The total π electron energy of a particular reactant as calculated by the Hückel method will be of the form $n\alpha + x\beta$ while for the model transition state the result would be $n\alpha + y\beta$. In the following tables the values of x and y are recorded under columns R and TS respectively. Under column Δ are presented the relative "activation energies" computed by taking the difference $y - x$ and expressing the result in absolute β units with respect to an arbitrary zero for the unsubstituted case. Thus reactions with a negative number in the Δ column are predicted to have a higher rate than the unsubstituted reference.

The tables assembled at the end of each section summarize the results by listing the predicted order of decreasing rates for substituents at a given position. Where possible, comparisons are made between theoretical predictions and experimental facts.

Three membered rings. (a) Cyclopropyl cation to allyl cation, disrotatory.

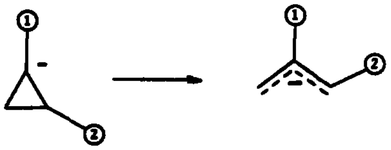


		R	TS	Δ
1	Acc	0.000	4.340	−0.340
	Don	2.000	4.962	1.038
	Con	2.828	6.429	0.399
	O	0.000	4.000	0.000
2	Acc	0.000	4.340	−0.340
	Don	0.000	4.962	−0.962
	Con	2.000	6.429	−0.429
	O	0.000	4.000	0.000

	Order of decreasing rates 1	2	3	·4
1	Acc	O	Con	Don
2	Don	Con	Acc	O

Since the ring-opening of unsubstituted cyclopropyl cation is an extremely rapid reaction,[13] the observation of a substituent effect is likely to take the form of a rate retardation, predicted to occur with donor or conjugating substituents at the 1 position. This prediction receives experimental support from the observation that solvolysis of 1-cyclopropylcyclopropyl tosylate affords predominantly ring-closed products.[14] (Cyclopropane can presumably be considered to be a conjugating substituent.[14])

(b) Cyclopropyl anion to allyl anion, conrotatory.

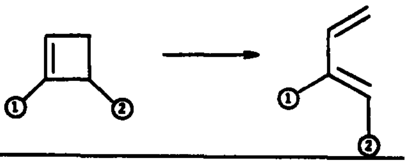


		R	TS	Δ
1	Acc	2.000	4.962	1.038
	Don	0.000	4.340	−0.340
	Con	2.828	6.429	0.399
	O	0.000	4.000	0.000
2	Acc	0.000	4.962	−0.962
	Don	0.000	4.340	−0.340
	Con	2.000	6.429	−0.429
	O	0.000	4.000	0.000

	Order of decreasing rates 1	2	3	4
1	Don	O	Con	Acc
2	Acc	Con	Don	O

In contrast to the cyclopropyl cation to allyl cation reaction, ring-opening of cyclopropyl anion is quite sluggish. In fact, experiments suggest that the reaction will be observed only if "... at least one anion stabilizing substituent [is] located at each terminus of the allyl anion."[15] Rephrasing, the ring-opening is accelerated by acceptor substituents at the 2 position, as predicted by the model.

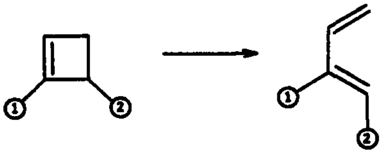
Four membered rings. (a) Cyclobutene to butadiene, conrotatory.



		R	TS	Δ
1	Pol	2.828	6.293	0.192
	Con	4.472	8.055	0.074
	O	2.000	5.657	0.000
2	Pol	2.000	6.293	−0.638
	Con	4.000	8.055	−0.398
	O	2.000	5.657	0.000

	Order of decreasing rates 1	2	3
1	O	Con	Pol
2	Pol	Con	O

(b) Cyclobutene to butadiene, disrotatory.



		R	TS	Δ
1	Pol	2.828	5.596	−0.768
	Con	4.472	6.603	−0.131
	O	2.000	4.000	0.000
2	Pol	2.000	5.596	−1.596
	Con	4.000	6.603	−0.603
	O	2.000	4.000	0.000

	Order of decreasing rates 1	 2	 3
1	Pol	Con	O
2	Pol	Con	O

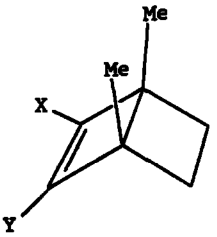
One of the more intriguing results of the calculations is the prediction that any substituent at the 1 position of a cyclobutene should decrease the rate of conrotatory ring-opening but increase the rate of disrotatory ring-opening. This prediction appears to receive experimental verification, as shown in Tables 1 and 2.

Table 1. Activation energies for conrotatory ring-opening of substituted cyclobutenes[16,17]

Compound	E_a kcal/mol
Cyclobutene	32.5
1-Chlorocyclobutene	33.6
1-Cyanocyclobutene	33.6
1-Ethylcyclobutene	34.8
1-Methylcyclobutene	35.1

Table 2. Activation energies for disrotatory ring-opening of substituted cyclobutenes[18]

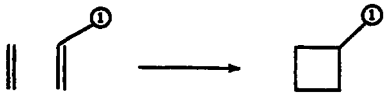
Compound	E_a kcal/mol
1	36.8
2	32.3
3	30.8
4	28.4



1: X = Y = Me; **2**: X = Me, Y = CO_2Me
3: X = C_6H_5, Y = CO_2Me; **4**: X = Y = CO_2Me

It is of interest that substituent effects are predicted to be much larger for the forbidden (disrotatory) reaction than for the allowed reaction. This is a general phenomenon and is in accord with the calculations of Epiotis.[12]

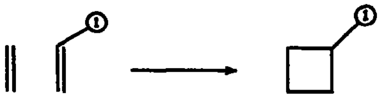
(c) 2+2 Cycloaddition, $\pi^2s^+\pi^2s$



		R	TS	Δ
1	Pol	4.828	5.596	−0.768
	Con	6.472	6.603	−0.131
	O	4.000	4.000	0.000

	Order of decreasing rates 1	 2	 3
1	Pol	Con	O

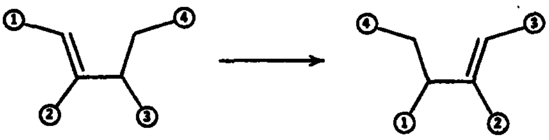
(d) 2+2 Cycloaddition, $\pi^2s+\pi^2a$



		R	TS	Δ
1	Pol	4.828	6.293	0.192
	Con	6.472	8.055	0.074
	O	4.000	5.657	0.000

	Order of decreasing rates 1	 2	 3
1	O	Con	Pol

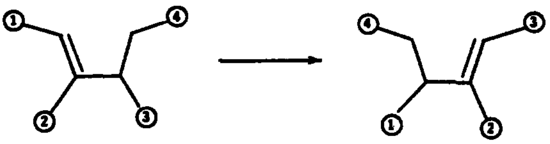
(e) [1,3] Sigmatropic shift, suprafacial retention and antarafacial inversion.



		R	TS	Δ
1, 2	Pol	2.828	5.596	−0.768
	Con	4.472	6.603	−0.131
	O	2.000	4.000	0.000
3, 4	Pol	2.000	5.596	−1.596
	Con	4.000	6.603	−0.603
	O	2.000	4.000	0.000

	Order of decreasing rates 1	 2	 3
1, 2	Pol	Con	O
3, 4	Pol	Con	O

(f) [1,3] Simatropic shift, suprafacial inversion and antarafacial retention.

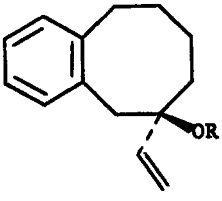


		R	TS	Δ
1,2	Pol	2.828	6.293	0.192
	Con	4.472	8.055	0.074
	O	2.000	5.657	0.000
3,4	Pol	2.000	6.293	−0.636
	Con	4.000	8.055	−0.398
	O	2.000	5.657	0.000

	Order of decreasing rates		
	1	2	3
1,2	O	Con	Pol
3,4	Pol	Con	O

[1,3] Sigmatropic shifts, whether proceeding by the allowed or forbidden pathways, are calculated to be subject to rate acceleration by polar substituents on the migrating group. This prediction appears to receive support from the work of Franzus *et al.*[4] who found that the potassium salt of 7-norbornadienol undergoes a [1,3] sigmatropic shift with an activation energy of ≤19 kcal/mol, fully 30 kcal/mol lower than the activation energy for the corresponding reaction of unsubstituted norbornadiene.[19] An example of acceleration of a [1,3] sigmatropic shift by an amide ion on the migrating group has been reported.[20]

The calculations lead to the prediction that polar substituents at the 3 and 4 positions should be equally effective in accelerating the reaction. It would clearly be an important test of the model to look for an unusually facile [1,3] shift in a system bearing a polar substituent at the 3 position. In fact, there is a literature example of just such a reaction; ring expansion of **5** to **6** occurs at 350°C when R = Me_3Si but room temperature when R = K.[21]



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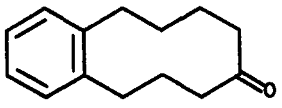
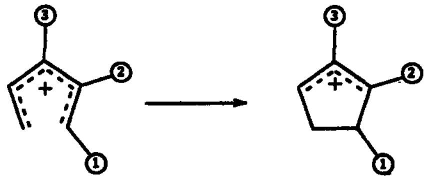


6

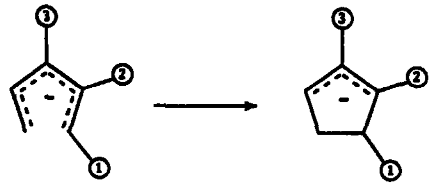
Five membered rings. (a) Pentadienyl cation to cyclopentenyl cation, conrotatory.



		R	TS	Δ
1	Acc	6.098	6.958	0.148
	Don	6.988	7.466	0.530
	Con	8.055	8.917	0.146
	O	5.464	6.472	0.000
2	Acc	6.155	6.958	0.205
	Don	6.155	7.466	−0.303
	Con	7.878	8.917	−0.031
	O	5.464	6.472	0.000
3	Acc	5.864	6.958	−0.086
	Don	6.899	7.466	0.441
	Con	8.000	8.917	0.091
	O	5.464	6.472	0.000

	Order of decreasing rates			
	1	2	3	4
1	O	Acc, Con	Acc, Con	Don
2	Don	Con	O	Acc
3	Acc	O	Con	Don

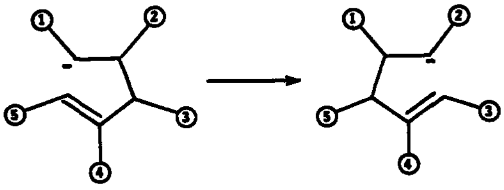
(b) Pentadienyl anion to cyclopentenyl anion, disrotatory.



		R	TS	Δ
1	Acc	6.988	7.466	0.530
	Don	6.098	6.958	0.148
	Con	8.055	8.917	0.146
	O	5.464	6.472	0.000
2	Acc	6.155	7.466	−0.303
	Don	6.155	6.958	0.205
	Con	7.878	8.917	−0.031
	O	5.464	6.472	0.000
3	Acc	6.899	7.466	0.441
	Don	5.864	6.958	−0.086
	Con	8.000	8.917	0.091
	O	5.464	6.472	0.000

	Order of decreasing rates			
	1	2	3	4
1	O	Con, Don	Con, Don	Acc
2	Acc	Con	O	Don
3	Don	O	Con	Acc

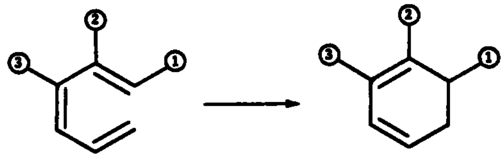
(c) [2,3] Sigmatropic shift, $\pi^2s + \sigma^2s + \omega^2s$



		R	TS	Δ
1	Acc	4.000	7.466	1.006
	Don	2.000	6.958	−0.486
	Con	4.828	8.917	0.383
	O	2.000	6.472	0.000
2, 3	Acc	2.000	7.466	−0.994
	Don	2.000	6.958	−0.486
	Con	4.000	8.917	−0.445
	O	2.000	6.472	0.000
4, 5	Acc	2.828	7.466	−0.166
	Don	2.828	6.958	0.342
	Con	4.472	8.917	0.027
	O	2.000	6.472	0.000

	Order of decreasing rates			
	1	2	3	4
1	Don	O	Con	Acc
2, 3	Acc	Don	Con	O
4, 5	Acc	O	Con	Don

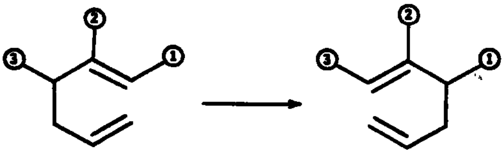
Six membered rings. (a) Z-Hexatriene to cyclohexadiene, disrotatory.



		R	TS	Δ
1	Pol	8.055	8.720	0.347
	Con	9.518	10.425	0.105
	O	6.988	8.000	0.000
2	Pol	7.727	8.720	0.019
	Con	9.409	10.425	−0.004
	O	6.988	8.000	0.000
3	Pol	7.878	8.720	0.170
	Con	9.446	10.425	0.033
	O	6.988	8.000	0.000

	Order of decreasing rates		
	1	2	3
1	O	Con	Pol
2	O, Con	O, Con	Pol
3	O	Con	Pol

(b) Cope rearrangement, $\sigma^2s + \pi^2s + \pi^2s$

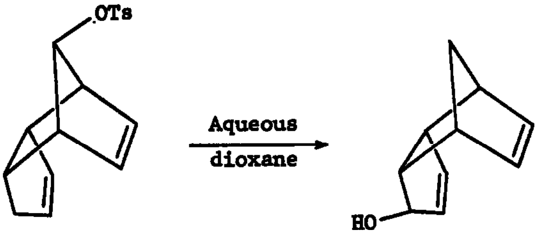


		R	TS	Δ
1, 2	Pol	4.828	8.720	0.108
	Con	6.472	10.425	0.047
	O	4.000	8.000	0.000
3	Pol	4.000	8.720	−0.720
	Con	6.000	10.425	−0.425
	O	4.000	8.000	0.000

	Order of decreasing rates		
	1	2	3
1, 2	O	Con	Pol
3	Pol	Con	O

One of the primary stimuli for the present work was the report by Evans and Golob[3] that a suitably placed alkoxide substituent could increase the rate of a Cope rearrangement by a factor of up to 10^{17} (probably corresponding to a reduction in activation energy of ~23 kcal/mol). This result is now understandable within the framework of the model.

The Cope rearrangement also serves as another very important test case for the calculations. As mentioned above, the model predicts similar behavior for acceptor and donor substituents in several reactions. This prediction is verified for the Cope rearrangement; thus in 1972 Breslow and Hoffman[22] reported the facile solvolytic Cope rearrangement of the tricyclic molecule 7. The carbonium ion generated by solvolysis of 7 can be seen to be the counterpart of Evans' 1,5-hexadiene in which the donor alkoxide has been replaced by an acceptor cation.



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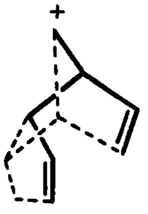
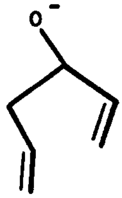


Breslow

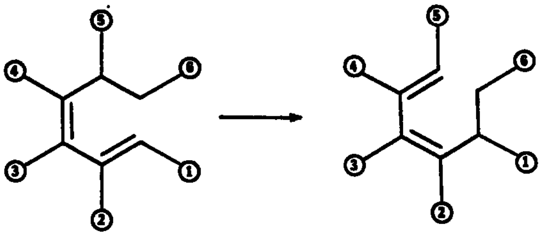


Evans

The importance of increased delocalization in the transition state was recognized by Breslow and Hoffman.[22]

It is important to emphasize that the model transition state used in these calculations is appropriate only for the completely concerted reaction; incursion of other mechanisms may produce unexpected results. For example the Cope rearrangement of 1,5-hexadiene is modestly accelerated by a phenyl substituent at the 2 position. This result has been interpreted in terms of a cyclohexane-1,4-diyl intermediate in the reaction.[23]

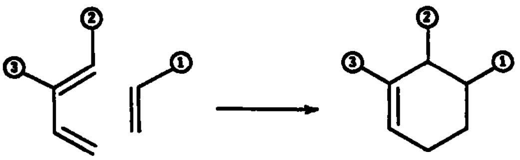
(c) [1,5] Sigmatropic shift, $\sigma^2s + \pi^2s + \pi^2s$



		R	TS	Δ
1,4	Pol	5.464	8.720	0.272
	Con	6.988	10.425	0.091
	O	4.472	8.000	0.000
2,3	Pol	5.226	8.720	0.034
	Con	6.899	10.425	0.002
	O	4.472	8.000	0.000
5,6	Pol	4.472	8.720	−0.720
	Con	6.472	10.425	−0.425
	O	4.472	8.000	0.000

	Order of decreasing rates		
	1	2	3
1,4	O	Con	Pol
2,3	O, Con	O, Con	Pol
5,6	Pol	Con	O

(d) Diels–Alder reaction, single substituent, $\pi^2s + \pi^4s$.

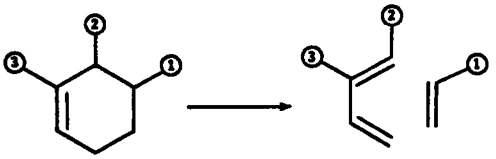


		R	TS	Δ
1	Pol	7.300	8.720	0.108
	Con	8.944	10.425	0.047
	O	6.472	8.000	0.000
2	Pol	7.464	8.720	0.272
	Con	8.988	10.425	0.091
	O	6.472	8.000	0.000
3	Pol	7.226	8.720	0.034
	Con	8.899	10.425	0.002
	O	6.472	8.000	0.000

	Order of decreasing rates		
	1	2	3
1	O	Con	Pol
2	O	Con	Pol
3	O, Con	O, Con	Pol

The first apparent failure of the model comes with the single substituent Diels–Alder reaction. In view of the fact that donor and acceptor substituents are not differentiated for this reaction, there is clearly no way to reproduce the experimental fact that acceptor substituents on the dienophile accelerate the reaction while donor substituents retard it. This differentiation between polar substituents is apparently a second order effect, explicable in other terms.[24]

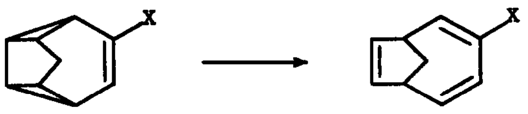
(e) Retro-Diels–Alder reaction, single substituent, $\sigma^2s + \sigma^2s + \pi^2s$.



		R	TS	Δ
1,2	Pol	2.000	8.720	−0.720
	Con	4.000	10.425	−0.425
	O	2.000	8.000	0.000
3	Pol	2.828	8.720	0.108
	Con	4.472	10.425	0.047
	O	2.000	8.000	0.000

	Order of decreasing rates		
	1	2	3
1,2	Pol	Con	O
3	O	Con	Pol

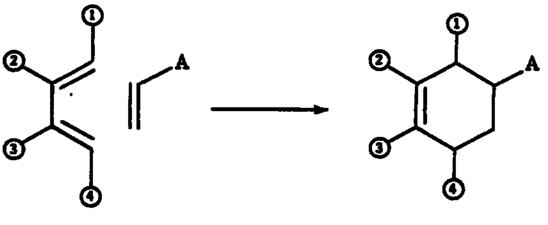
The predicted retardation of a retro-Diels–Alder reaction by a substituent at the 3 position has been observed by Miller who finds that the rate of conversion of **8b** to **9b** is markedly less than that of **8a** to **9a**.[25]



8a: X = H
8b: X = OLi

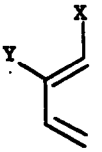
9a: X = H
9b: X = OLi

(f) Diels–Alder reaction with electron deficient dienophiles, $\pi^2s + \pi^4s$



		R	TS	Δ
1	Acc	8.292	9.364	0.348
	Don	8.292	9.954	−0.242
	Con	9.876	11.204	0.032
	O	7.300	8.720	0.000
2	Acc	8.054	9.431	0.043
	Don	8.054	9.431	0.043
	Con	9.727	11.142	0.005
	O	7.300	8.720	0.000
3	Acc	8.054	9.302	0.172
	Don	8.054	9.925	−0.451
	Con	9.727	11.190	−0.043
	O	7.300	8.720	0.000
4	Acc	8.292	9.431	0.281
	Don	8.292	9.431	0.281
	Con	9.816	11.142	0.094
	O	7.300	8.720	0.000

The delocalization effects which are at least partially masked for the single substituent Diels–Alder reaction, reappear when both diene and dienophile are substituted. Thus the predicted relative rates for reaction of an electron deficient olefin with dienes **10**–**13** is **10** > **11** > **12** > **13**, assuming MeO– to be a donor and phenyl to be conjugating.



10: X = OMe, Y = H
11: X = H, Y = C_6H_5
12: X = H, Y = H
13: X = C_6H_5, Y = H

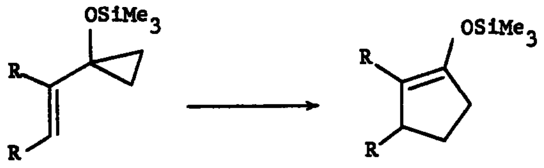
Interestingly, this is precisely the order of reactivities observed experimentally for reaction with maleic anhydride.[26]

Since product distributions are determined by relative rates, one can also deduce regiochemistry from the calculations. For both conjugating and donor substituents "ortho" products are predicted to be favored from 1-substituted dienes, while "para" products should be formed from 2-substituted dienes. These predictions are confirmed experimentally[26] and are in accord with the calculations of Houk.[27] Acceptor-substituted dienes are predicted to give "meta" products with an electron deficient dienophile. Experimentally such reactions are rare but, when they do occur, appear to prefer the "ortho, para" regime.[26] There is some indication, however, that Diels–Alder reactions of electron deficient dienes with electron deficient dienophiles are non-concerted,[28] in which case application of the model presented above would clearly be inappropriate.

DISCUSSION

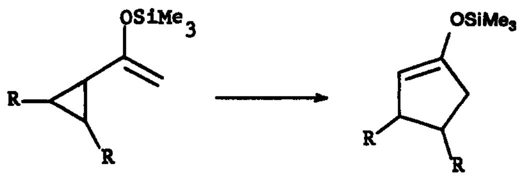
Considering the extremely simple theoretical model used in this work, its degree of success in correlating substituent effects for a wide variety of pericyclic reactions is surprisingly good.

The results appear to be sufficiently reliable for one to make synthetically useful predictions. For example, the cyclopentanone synthesis of Trost *et al.*[29,30] involves a vinyl cyclopropane rearrangement ([1,3] sigmatropic shift) on intermediates such as **14**.



14

The utility of this reaction is somewhat limited by the high temperatures involved (330°C). However, the present results suggest that if **14** were treated with potassium fluoride and 18-crown-6 or with tetrabutylammonium fluoride[31] the resulting alkoxide ion should rearrange very much more readily, possibly even at room temperature. By contrast, the formally similar cyclopentanone synthesis of Monti *et al.*[32] involving vinyl cyclopropane rearrangement of intermediates such as **15**, may actually suffer a rate retardation if the trimethylsilyl group were replaced by K^+ or Bu_4N^+ (assuming that the predominant mechanism is suprafacial inversion[33]).



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Extrapolation of the present work to multisubstituted systems should be a simple exercise. Attempts to estimate the effect of several substituents from the individual effects of each group are not recommended, however, since substituents can interact with each other in a distinctly non-additive way.[34] Rather, one should carry out the calculation on the model most appropriate for the system under study.

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