Notes

A CNINDO Investigation of Diene Reactivity in the Diels–Alder Reaction between 1-(*p*-Substituted phenyl)-1,3-butadienes and Maleic Anhydride

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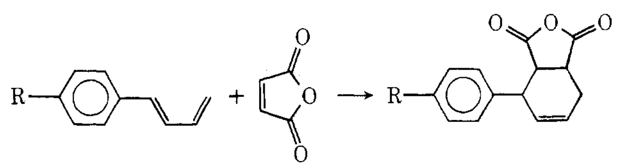
Many investigators[2-4] have indicated the importance of the energy of the highest occupied molecular orbital (HOMO) and of the lowest unoccupied molecular orbital (LUMO) in determining diene reactivity in the Diels–Alder reaction. Sustmann and Schubert[4] have recently shown a correlation of the HOMO diene-LUMO dienophile energy separation with the logarithm of the rate constant for the normal electron demand Diels–Alder reaction. However, their study used many open-chain dienes for which the relative concentrations of the cisoid conformational isomers are not known.[5] In this report we have investigated the diene reactivity of the 1-(*p*-substituted phenyl)-1,3-butadiene system in order to obtain a more precise evaluation of the effect of the energy of the HOMO and other diene molecular properties on the rate of the Diels–Alder reaction. The concentrations of the cisoid conformations of the dienes in this study should all be the same.

Earlier we had shown that the CNDO/2 and INDO methods (CNINDO)[6] can be used to predict with reasonable success the regioselectivity of the Diels–Alder reaction between unsymmetrically substituted dienes and dienophiles.[7] Therefore, in this study CNINDO calculations were utilized to investigate the diene reactivity in the Diels–Alder reaction between 1-(*p*-substituted phenyl)-1,3-butadienes and maleic anhydride. The molecular orbital calculations were performed with standard bond angles and bond lengths.[8] The conformation of the dienes used in these calculations was the cisoid planar.[7,9] We found that the interpretations from the CNINDO calculated eigenvectors and eigenvalues were independent of small changes in bond angles, bond lengths, and rotational conformations.[10]



R = H, CH_3, OCH_3, Cl, NO_2

An examination of this reaction using Sustmann's model for substituent effects[12] and HOMO and LUMO energies from the CNINDO calculations was carried out. We found that the energy difference between the HOMO of the diene and the LUMO of maleic anhydride was considerably smaller than the corresponding difference between the HOMO of maleic anhydride and the LUMO of the diene in all cases. This is the orbital arrangement[12] of a normal electron demand Diels–Alder reaction and indicates a charge donation[3a] from the diene to maleic anhydride in the transition state of this Diels–Alder reaction. The direction of this charge donation is in agreement with the observed substituent effect.[13]

A molecular property of the dienes which should be a good parameter for comparing the relative abilities of the dienes to donate electron density is the total p_z density of the butadiene moiety (Table I). We have found a linear relationship[14] between the total p_z density of the butadiene moiety and the logarithm of the relative rate[13] at 25°. A least-squares regression analysis of the relationship gave correlation coefficients of 0.899 (CNDO/2) and 0.980 (INDO). This poorer correlation of theory with experimental data for the CNDO/2 method was due to the inclusion of the data for the chlorine substituent. A possible explanation for the correlation is that the donor–acceptor interaction between the diene and the dienophile provides a mechanism through which the electron density of the diene is reduced in the transition state. Thus, when the HOMO of the diene and LUMO of the dienophile are not too different, the decrease in the electronic repulsions of the electron-rich diene through delocalization becomes an important rate-enhancing factor. By similar analysis, the delocalization of the electron density of the electron-poor diene to the dienophile becomes a rate-retarding factor.

The proposed substituent effect[12] on the energy of the HOMO of the diene is that electron-donating groups increase the energy of the HOMO and electron-withdrawing groups decrease its energy. This trend is observed in our calculations (Table I). Also, from frontier orbital theory, one would expect more stabilization of the transition state as the energy of the HOMO of the diene increases for a normal electron demand Diels–Alder reaction. This effect is observed in the linear relationship which we found between the energy of the HOMO of the diene and the logarithm of the relative rates of reaction[13] at 25°. A least-squares regression analysis of this relationship gave correlation coefficients of 0.962 (CNDO/2) and 0.989 (INDO).

Frontier electron density has been used by many inves-

Table I
Molecular Properties of 1-(*p*-Substituted phenyl)-1,3-butadienes

Registry no.	Para substituent	Log k/k_H[a]	Energy of the HOMO,[b] au: INDO	Energy of the HOMO,[b] au: CNDO/2	Total p_z density of butadiene moiety: INDO	Total p_z density of butadiene moiety: CNDO/2	Terminal FED[c]: INDO	Terminal FED[c]: CNDO/2
30448-78-3	OCH_3	0.4216	−0.364	−0.388	4.012	4.012	0.226	0.243
33356-85-3	CH_3	0.0453	−0.377	−0.397	4.004	4.005	0.290	0.283
1515-78-2	H	0.0	−0.387	−0.408	4.001	4.001	0.337	0.338
33356-84-2	Cl	−0.2321		−0.411		3.983		0.266
20264-89-5	NO_2	−0.5607	−0.413	−0.433	3.981	3.980	0.355	0.347

[a] Reference 12. [b] π molecular orbital. [c] The terminal frontier electron density is the sum of the squares of the p_z coefficients of the HOMO at the terminal carbon positions of the diene. The other atomic orbital coefficients are zero for HOMO.

tigators[2,3c,7,15] to predict the preferred regioisomers in the Diels–Alder reaction. A simple second-order perturbation treatment[16] predicts a decrease in the rate of reaction as the terminal frontier electron density decreases (assuming that frontier orbital energies are constant). The calculations, however, show a decrease in the terminal frontier electron density of the dienes as the logarithm of the relative rate of reaction increases (Table I).[17] This lack of correlation between the terminal frontier electron densities of the dienes and the logarithm of the relative rates is not unexpected when one considers the large change ($\sim$30 kcal) in the energy of the diene HOMO. Consequently, the terminal electron densities of the dienes are not useful in predicting diene reactivity in such cases.

In conclusion, the linear relationships between the energy of HOMO of the diene and the logarithm of the relative rates of reaction and between the total p_z density of the butadiene moiety and the logarithm of the relative rates of reaction indicate that these molecular properties do have a significant effect on the stability of the transition state of this normal electron demand Diels–Alder reaction. Subsequently, the relative reactivities of the dienes can be predicted from either the HOMO energy or the total p_z density of the butadiene moiety. Though the terminal frontier electron densities of the dienes are useful for determining regioselectivity, they were not found to be useful for predicting relative diene reactivity in cases where the energy of the diene HOMO varied significantly.

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Registry No.—Maleic anhydride, 108-31-6.

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(9) The maleic anhydride molecule was assumed to be planar with a plane of symmetry bisecting the COC angle of the ring. No significant change in the energies of HOMO and LUMO was found by varying this angle between 104 and 109°.

(10) We have found that the relationship between the CNINDO energy of the highest occupied molecular orbital and the experimental ionization potential for dienes and dienophiles with electron-donating substituents (OCH_3, CH_3) and conjugating substituents (C_6H_5) is satisfactory. The general qualitative trend of the experimental ionization potential is correctly represented by the CNINDO methods in these systems. However, for electron-withdrawing substituents such as CHO and CN, the theory predicts π HOMO values which are higher than that of ethylene, while the experimental values[2a] are lower. These observations are in agreement with Bloor and Breen's CNDO study of monosubstituted benzenes.[11] Thus, we expect that the qualitative trend observed in the CNINDO HOMO energies of the 1-(*p*-substituted phenyl)-1,3-butadienes will be real. Also, the CNINDO HOMO energies of the transoid and cisoid conformations of the dienes studied varied by less than 0.1 ev. This gives some justification to the widely accepted use of experimental ionization potentials to determine the energies of the HOMO of the cisoid conformations of open-chain dienes.

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(17) The same trend was found with the total frontier electron density of the HOMO for the butadiene moiety of the molecule.

Polyphenylated Cyclobuten-4-ones from Squaryl Dichloride

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The high-yield synthesis of 1,2-diphenylcyclobutene-3,4-dione (**1**) from squaryl dichloride in benzene solution under Friedel-Crafts conditions was reported in a recent communication.[1] At the low temperatures ($\sim$10°) employed in that work, the reaction did not proceed substantially beyond the stage of **1** despite a benzene/squaryl dichloride molar ratio of nearly 43 and a moderate excess of Lewis acid ($AlCl_3$, freshly sublimed, 2.26 mol per mol of dichloride).

We now report that, at higher temperatures, the dichloride reacts with more than 2 mol of benzene. As a result, one observes drastically lowered yields, or even complete disappearance, of **1** in favor of the successor species **2**, 1,2,3,3-tetraphenylcyclobuten-4-one, whose yield in the previous work[1] had amounted to a mere 1%. In addition, the enolone **3**, 1-hydroxy-2,3,3-triphenylcyclobuten-4-one, arises in appreciable yields, and small quantities of the naphthol **4**, resulting from thermal electrocyclic ring opening[2] of **2** and intramolecular cyclization of the intermediary vinyl ketene species, are also formed. For example, at the reflux temperature of the benzene medium (24 hr), with catalyst ($AlCl_3$, freshly sublimed) and reactant concentrations the same as in the preceding investigation,[1] squaryl dichloride was found to convert to **2** and **3** in 53 and 27% yields, respectively; furthermore, **4** was separated in 1.5% yield.