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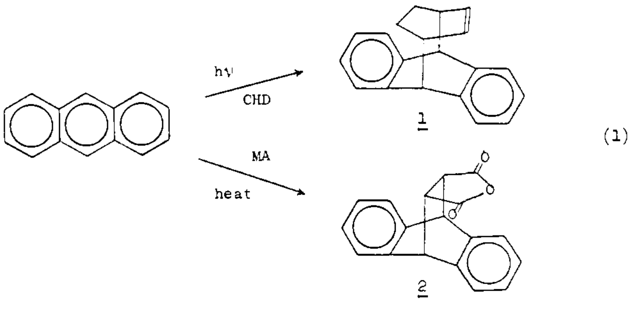
Chemistry of Exciplexes. 8.
The Role of Conservation of Orbital Symmetry in Cycloadditions of Olefins to Aromatic Hydrocarbons

Sir:

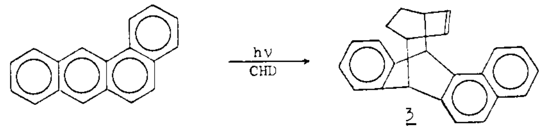
Cycloaddition reactions may proceed via a concerted or a stepwise reaction pathway.[1-6] The rule of conservation of orbital symmetry, commonly known as the Woodward–Hoffmann rule,[1] plays on important role in determining the pathway of cycloadditions. The Diels–Alder reaction in which an aromatic hydrocarbon functions as the diene component is well known.[7-10] More recently, the photocycloaddition of conjugated polyenes to aromatic hydrocarbons and their derivatives has been described.[11-14] These reactions are believed to involve concerted pericyclic bond formation and follow the precepts of the Woodward–Hoffmann rule.[15,16] In this communication, we report on the photocycloadditions favored by the higher cata-condensed polynuclear aromatic hydrocarbons with 1,3-cyclohexadiene (CHD). In these reactions, the symmetry of the relevant reactive orbitals in the arene may supersede the symmetry (when present) of the entire system conserved in the transformation. Our findings suggest that the local symmetry in the frontier orbitals about the reactive positions implicitly determines the favorable pathway of cycloaddition of unsaturated compounds to aromatic hydrocarbons.

The thermal reaction of maleic anhydride (MA) with anthracene[7] and the photocycloaddition of CHD to anthracene[13] can be examined as characteristic concerted cycloadditions (eq 1). In these reactions, reactants and products possess a plane of symmetry which is conserved throughout the transformation. As such, they are amenable to analysis using the Woodward–Hoffmann orbital symmetry approach,[1] or using Fukui's simplification of analyzing interacting fragments.[6] Consequently, the thermal reaction is interpreted as an "allowed" $[4\pi_s + 2\pi_s]$ concerted process and the photochemical reaction as an "allowed" $[4\pi_s + 4\pi_s]$ process. Furthermore, naphthalene and benzene react photochemically with CHD and(or) its derivatives to give the corresponding $[4\pi_s + 4\pi_s]$ adducts,[11-13] in accordance with the postulate of Woodward and Hoffmann and that of Fukui.



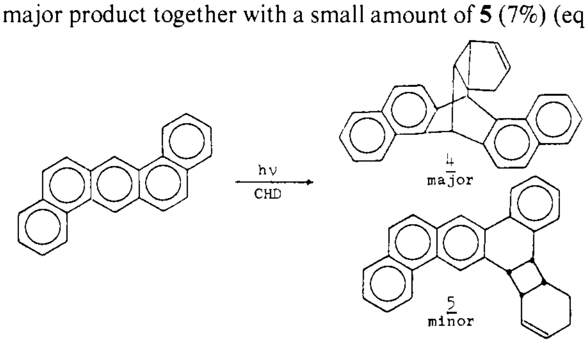
(1)

Benz[*a*]anthracene, formally lacking an element of symmetry maintained throughout the transformations, nevertheless undergoes cycloadditions which are analogous to those of anthracene. The Diels–Alder reactions have been described previously.[9,17] The major product from the photocycloaddition of benz[*a*]anthracene with CHD was assigned the structure **3** (69%, mp 152–153 °C) (eq 2) on the basis of high resolution NMR spectroscopy with spin decoupling and its conversion into a dihydro derivative.[18] This adduct has the stereochemistry predicted by the consideration of maximum secondary orbital overlap and bond order calculations. As with anthracene, the photocycloaddition of benz[*a*]anthracene with CHD affords a $[4\pi_s + 2\pi_s]$ adduct (8%, mp 141–143 °C) as a minor product.[14,19,20]



(2)

Although the reaction of dibenz[*a,h*]anthracene with MA was found to occur under forceful conditions, i.e., in boiling xylene with a large excess of the dienophile,[9,21] we found that the concerted photocycloaddition of dibenz[*a,h*]anthracene with CHD was effectively foiled. Unlike anthracene and benz[*a*]anthracene, the fluorescence of dibenz[*a,h*]anthracene was not quenched by CHD,[22] and prolonged irradiation afforded a $[4\pi_s + 2\pi_s]$ adduct, **4** (82%, mp 162–164 °C), as the major product together with a small amount of **5** (7%) (eq 3).[23]



(3)

No $[4\pi_s + 4\pi_s]$ adduct was detected in the reaction mixture.

The photochemical behavior of dibenz[*a,h*]anthracene with CHD cannot be rationalized by the simplified Woodward–Hoffmann rule, which predicts a $[4\pi_s + 4\pi_s]$ process, nor can it be explained by the method of Fukui as the result of a LUMO–LUMO interaction.[6] However, consideration of the local symmetry of the relevant orbitals involved in nascent bond formation (boxed in Figure 1) provides an insight into the observed behavior of aromatic hydrocarbons toward cycloadditions. Clearly, the local symmetry of the relevant reactive orbitals in arenes is similar to that for a typical diene (e.g., CHD) in all cases depicted, with the exception of dibenz[*a,h*]anthracene. Hence, the recognition of the local symmetry would seem to be a requisite for concerted cycloaddition(s) to be allowed at the meso positions of higher benzenoid aromatic hydrocarbons. It should be noted that, in the reaction of dibenz[*a,h*]anthracene with tetracyanoethylene, an axis of symmetry of conserved; nevertheless, no reaction is observed between these reagents under ordinary laboratory conditions.[24] Consequently, the local symmetry may be more important than the orbital symmetry of the entire system in determining an energy barrier in a concerted reaction. Fukui's method[6] of examining only the interaction of those atomic

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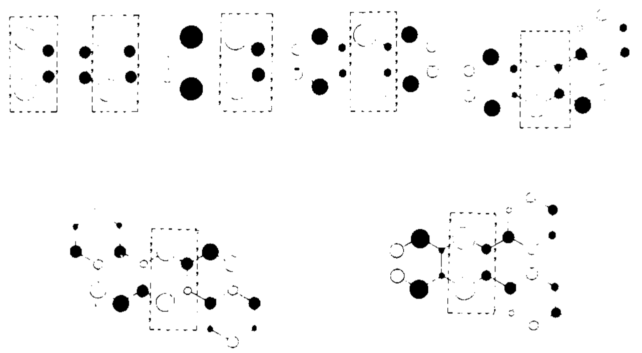
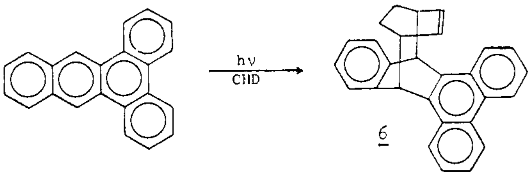


Figure 1. LUMO of 1,3-cyclohexadiene and aromatic hydrocarbons.[25,26]

orbitals undergoing bond formation also is necessarily inadequate in such cases.

As a test of our theory, we irradiated dibenz[*a,c*]anthracene in the presence of CHD; as anticipated, the major product obtained is a $[_4\pi_s + {}_4\pi_s]$ adduct, **6** (60%, mp 205-206 °C) (eq 4). Furthermore, dibenz[*a,c*]anthracene is known to undergo a thermal reaction with MA with relative facility.[9,27]



(4)

In conclusion, our results suggest that the local symmetry in the frontier orbitals as specified about the reactive positions may determine implicitly the favorable pathway of cycloaddition of unsaturated systems to aromatic compounds. The consideration of this local symmetry rather than the symmetry embracing any other (e.g., more inclusive) assembly of atoms may be used to predict the favorable reaction pathway of these and related reactions.

Acknowledgment. The authors thank the National Science Foundation and the National Institute of General Medical Sciences for the support of this work.

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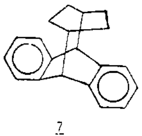

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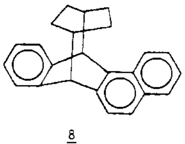

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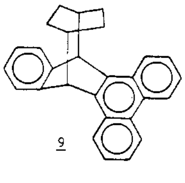

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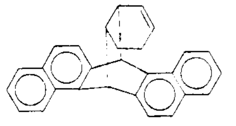

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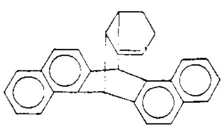

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Facile Hydroxymethylation of an Acyloxymethyl Ligand with Synthesis Gas or Hydrogen. A Model for Catalytic Reactions Yielding Methanol and Ethylene Glycol

Sir:

Conversion of CO and H_2 to organic chemicals by means of transition metal complexes is the goal of much current research, including catalytic applications,[1-3] and stoichiometric or model studies.[4-12] These investigations may lead to improved understanding of the action of metal catalysts and allow development of catalyst systems which are more active or more selective for conversion of synthesis gas to desired products. Homogeneous catalysts and complexes are generally more easily studied than heterogeneous systems, and may serve as models for the heterogeneous catalytic reduction of carbon monoxide.[13]

The probable involvement of the hydroxymethyl ligand, $-CH_2OH$, in Fischer–Tropsch and related reactions has recently been discussed.[4,13,14] However, complexes containing this ligand have been difficult to isolate, and only recently has the first stable hydroxymethyl complex of a low-valent transition metal been reported.[15] Presented herein are some initial results of studies with a metal complex bearing the acyloxymethyl ligand, $-CH_2OC(O)R$, a carboxylate ester of the hydroxymethyl ligand.[16] This ligand is stable to β-elimination (a decomposition pathway perhaps responsible for the general instability of hydroxymethyl complexes), yet should closely resemble the hydroxymethyl ligand in other reactions (e.g., alkyl migration). It therefore appears to be a useful and accurate model. Reported here is the conversion of this hydroxymethyl analogue into methyl and ethylene glycol esters by reaction with H_2 or synthesis gas, and the observation of glycolaldehyde ester, a probable intermediate in glycol ester formation. These findings are summarized in Scheme I.

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