

Inverse Secondary Deuterium Kinetic Isotope Effect in Diels–Alder Reaction of Orthonaphtho [3.3] orthoanthracenophane with Maleic Anhydride

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Inverse Secondary Deuterium Kinetic Isotope Effect in Diels-Alder Reaction of Orthonaphtho[3.3]orthoanthracenophane with Maleic Anhydride

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The Diels-Alder reactions of rigid [3.3]orthoanthracenophanes **1** and **2** with maleic anhydride and deuterium-labeled maleic anhydride- d_2 , were studied. In the reaction of naphthophane **1**, a large inverse secondary kinetic isotope effect (SDKIE) ($k_{H_2}/k_{D_2}=0.78$) was observed, while benzophane **2** shows a SDKIE similar to that of anthracene itself ($k_{H_2}/k_{D_2}=0.95$ and 0.96).

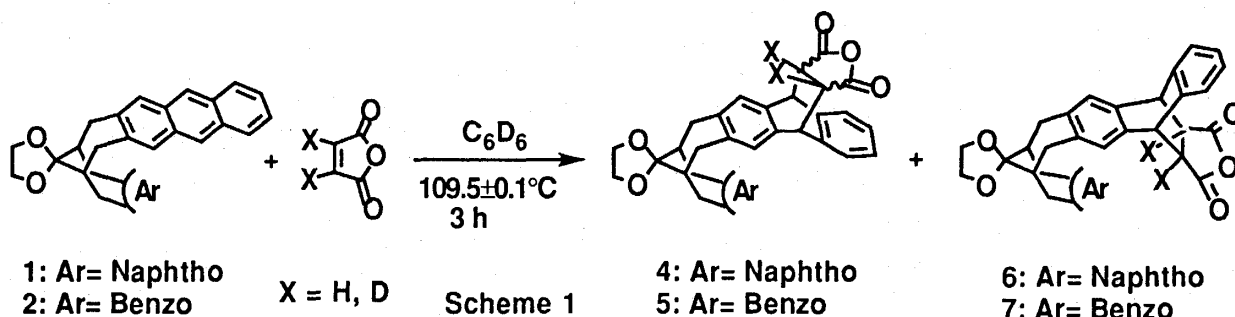
Introduction

[3.3]Orthoanthracenophanes **1** and **2** are rigid structures with layered aromatic systems. Recently it was reported that Diels-Alder (D-A) reactions of **1** and **2** with maleic anhydride (MA) and maleimide show a high inside-face selectivity. This is especially true for reactions of **1**.¹⁾ Secondary deuterium kinetic isotope effects (SDKIE) (k_{H_2}/k_{D_2}) have been an important tool in the study of the mechanism of D-A reactions.²⁾ In order to more fully elucidate the interesting reactivity of phanes **1** and **2**, they were reacted with MA and deuterium-labeled MA- d_2 .³⁾ The effect of the underlying

naphtho- and benzo-units in these systems on the D-A reaction was evaluated by SDKIE.

Results and Discussion

The reactions of **1-2** and anthracene **3** with MA or MA- d_2 were carried out in benzene- d_6 at 109.5 ± 0.1 °C (Scheme 1).^{4,5)} The outside-adducts **4-5** and inside-adducts **6-7** are not interconvertible under the reaction conditions, showing that the rate of retro-reaction is negligibly small. The reactions were analyzed as being of second-order. The rate constants and the values of k_{H_2}/k_{D_2} in the D-A reactions are given in Table 1.



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Dedicated to Professor Hitoshi Takeshita on the occasion of his retirement.

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Table 1 Inverse Secondary Kinetic Isotope Effects in Diels-Alder Reaction of 1-3 with MA

Reaction	k (mmol ⁻¹ min ⁻¹)	Reaction	k (mmol ⁻¹ min ⁻¹)	k_{H_2} / k_{D_2}
1 + MA	0.680 ± 0.016	1 + MA- <i>d</i> ₂	0.871 ± 0.028	0.78
2 + MA	0.337 ± 0.013	2 + MA- <i>d</i> ₂	0.353 ± 0.008	0.95
3 + MA	0.190 ± 0.008	3 + MA- <i>d</i> ₂	0.198 ± 0.004	0.96

In the D-A reaction with MA,phanes 1 and 2 are more reactive than 3. This fact seems to reflect a through-space electronic interaction between the anthracene unit and the underlying aromatic rings in the phane structure. The interaction is more significant in naphthophane 1 than in the benzophane 2. Also 1 reacts faster than 2 with both MA and MA-*d*₂. The composition monitored by ¹H NMR spectroscopy shows that the π-facial selectivities of 1 and 2 in the reaction with MA-*d*₂ are identical with those in the reaction with MA.

The reaction of anthracene 3 with MA and MA-*d*₂ shows $k_{H_2}/k_{D_2} = 0.96$, which is close to the value reported previously.⁹ A similar k_{H_2}/k_{D_2} (0.95) is found for the reactions of benzophane 2. On the other hand, naphthophane 1 shows a remarkably large inverse SDKIE ($k_{H_2}/k_{D_2} = 0.78$). Both the inside- and outside-face additions are affected equally, although a more precise analysis is needed to more exactly determine the SDKIE for the outside-face addition.

The above facts could be explained by considering a product-like, late transition state in the addition of naphthophane 1 and a reactant-like, early transition state in the addition of 2 and 3, as a D-A reaction via a reactant-like transition state is known to give a smaller k_H/k_D than a reaction via a product-like transition state.⁶ This different behavior of 1 and 2 may indicate that the electronic interaction between the aromatic ring-systems perturbs the aromatic stabilization of the anthraceno-unit more in 1 than in 2. Further investigations are in progress.

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- MA-*d*₂⁷⁾ was recrystallized from ether and sublimed twice. Deuterium content (92.3%) was determined on the basis of the ¹H NMR spectrum of its maleanilic-*d*₂ acid derivative.
- An equimolar mixture of dienes 1-3 and MA or MA-*d*₂ in benzene-*d*₆ in a sealed NMR sample tube was heated and the reaction was monitored by using 500 MHz ¹H NMR and analyzed as a second-order reaction. The equation of the reaction rate is given as $d[C_{diene}]/dt = k[C_{diene}][C_{Cenc}] = k[C_{diene}]^2$. The singlet peaks of protons H₉ and H₁₀ (δ = 7.76, 8.02, and 8.18 ppm) of the anthracene ring of dienes 1-3 were used as the internal reference peak (relative peak height is 1.00). The relative peak height *H* of protons H₉ and H₁₀ of 9,10-dihydro-9,10-ethanoanthracene ring of the adduct is given in terms of $C_x/(C_0 - C_x)$, in which C_0 is a concentration (mmol) of a diene at time zero and C_x is a concentration (mmol) of an adduct at time *t*. From the graphical plot of t (min) versus $(C_0 - C_x)^{-1} = (1+H)/C_0$, the second-order rate constant *k* and its standard deviation were determined by least square calculation.
- After 3h, conversions of 1-3 are 17-40%. The ratios of 4/6 and 5/7 are 4:6 and 2:8, respectively.
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