An Investigation of the *endo* Product Selectivity in the Diels-Alder Reaction[1]

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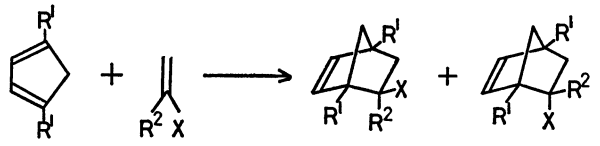
The Diels-Alder reactions of cyclopentadienes with a variety of substituted ethylenes were carried out, and their reaction rates and the *endo* : *exo* isomer ratios of the products were determined. It was shown that the faster reaction is characterized by a higher *endo* isomer distribution and the existence of a linear correlation between the reaction rate and the *endo* isomer distribution. The results were interpreted in terms of the concept of secondary orbital interaction in the transition state.

Many investigators have been interested in the *endo* addition rule of the Diels-Alder reaction[2] since Alder expressed it as the "maximum accumulation of unsaturation."[3] The *endo* selectivity of the reaction has been discussed mainly in terms of dipole—dipole[4] or secondary orbital[5] interactions, steric[2a] and electronic[6] effects, dispersion force,[7] and favorable geometry for interacting orbitals[8] on both experimental and theoretical grounds. There have been a large number of studies of the *endo* selectivity of the reaction, but little has been done to investigate it from the viewpoint of the reactivity of dienophiles.

In the some Lewis acid-catalyzed Diels-Alder reactions, it has been reported that the dienophiles complexed with the catalysts show an enhanced *endo* selectivity in comparison with that of the uncomplexed ones in spite of the higher reactivities of the formers.[9,10] There seems to be a particular parallelism between the enhanced selectivity and the higher reactivity in the Diels-Alder reaction. In order to get a better insight into the mechanism of the Diels-Alder reaction, a detailed examination of this phenomenon is essential. Therefore, this work will be concerned with an investigation of the correlation between the *endo* selectivity and the reaction rate of the Diels-Alder reaction. For this purpose, the reactions of cyclopentadienes with various substituted ethylenes were examined (Scheme 1).



(**1**) Diene Dienophile *exo* (**2x**) *endo* (**2n**)

(**1a**) R^1=H R^2=H, Me, Et, *n*-Bu
(**1b**) R^1=C_6H_5 X=CO_2Me, CHO, COMe, COEt, CO-*n*-Pr, CO-*iso*-Pr, COCl, COBr, maleic anhydride and *N*-phenylmaleimide.
(**1c**) R^1=*p*-Cl-C_6H_4

Scheme 1.

Results and Discussion

The following sets of Diels-Alder reactions were carried out: Dienes; cyclopentadiene (**1a**), diphenyl- and di-*p*-chlorophenylcyclopentadiene (**1b**, **1c**): Dienophiles; acrylic acid derivatives, vinyl ketones, acrolein, and maleic acid derivatives. All the reactions were carried out at 25° C and 35 °C. The second-order rate constants were determined by following the reaction by means of glpc and spectrophotometry. A competitive reaction method was employed for the estimation of the rate constants of **1a** with vinyl ketones and methyl 2-alkylacrylates. The results are tabulated in Tables 1 and 2. The isomer distributions of the reactions were analyzed by means of glpc and NMR. Control experiments showed that no *endo-exo* interconversion operated under the present reaction conditions and during the analytical procedure.

The isomeric adducts were isolated by means of glpc and tlc, and their configurations were confirmed by means of NMR analysis, taking into account the fact that the shielding effect of the double bond in 5-substituted 2-norbornene leads the signal of the *endo*-5-methyl proton to a higher field than that of the *exo*-5-methyl proton. The chemical shifts and the splitting patterns of the adducts were similar to those

TABLE 1. SECOND-ORDER RATE CONSTANTS FOR THE REACTIONS OF CYCLOPENTADIENES WITH VARIOUS DIENOPHILES AT 35 °C

No.	Diene	Dienophile	Solvent	k_2 (1 mol^{-1} s^{-1})[a]
1	cyclopentadiene	*N*-phenylmaleimide	dioxane	1.30×10^{-1} [b]
2	cyclopentadiene	maleic anhydride	dioxane	1.22×10^{-1} [b]
3	cyclopentadiene	acryloyl bromide	benzene	3.09×10^{-2} [c]
4	cyclopentadiene	acryloyl chloride	benzene	2.00×10^{-2} [c]
10	cyclopentadiene	methyl acrylate	*n*-butyl chloride	5.30×10^{-5} [c]
11	1,4-diphenylcyclopentadiene	methyl acrylate	chloroform	6.94×10^{-6} [d]
12	1,4-di-*p*-chlorophenyl-cyclopentadiene	methyl acrylate	chloroform	2.55×10^{-6} [d]

a) Values are average of two or more runs. Estimated errors are about 10% for the reactions 3 and 4, and about 5% for the reactions 10—12. b) Calculated from the reported data, see ref. 21. c) Determined by means of glpc. d) Determined by spectrophotometry.

Table 2. Relative rates and *endo*-isomer distributions in the Diels-Alder reactions of cyclopentadienes with various dienophiles in benzene

No.	Diene[a] R^1	Dienophile[a] R^2	Dienophile[a] X	Relative rate[b]	*endo*-Adduct[c] (%)
1	H	*N*-phenylmaleimide		2.45×10^{3}	>99.5[d]
2	H	maleic anhydride		2.30×10^{3}	99.5
3	H	H	COBr	5.83×10^{2}	92.2
4	H	H	COCl	3.77×10^{2}	90.7
5	H	H	CO-*iso*-Pr	3.20	82.1
6	H	H	CO-*n*-Pr	2.40	80.5
7	H	H	COEt	2.28	82.8
8	H	H	COMe	2.28	82.3
9	H	H	CHO	2.00	75.0
10	H	H	CO_2Me	1.00	73.7
11	Ph	H	CO_2Me	1.30×10^{-1}	51[d]
12	*p*-Cl-Ph	H	CO_2Me	4.81×10^{-2}	50[d]
13	H	Me	CO_2Me	1.65×10^{-2}	35.3[e]
14	H	Et	CO_2Me	1.62×10^{-2}	37.0[e]
15	H	*n*-Bu	CO_2Me	7.78×10^{-3}	30.6[e]

a) See Scheme 1. b) Relative to the reaction 10. The values for the reactions 1, 4, 11, and 12 were calculated from Table 1. The others were determined by competitive reactions with methyl acrylates. Analysis based on glpc. c) Determined by glpc. The values are accurate to within 0.2%. d) Determined by NMR. The values are accurate to within 1%. e) In methylene chloride.

reported for related compounds.[11]

Cyclopentadienes were employed as the diene components in order to avoid the uncertainty which is unavoidable in the reactions of acyclic dienes because of their *cis-trans* isomerization. The dienophiles employed were characterized by their carbonyl function so that the reactions to be compared would have similar character.

As may be seen in Table 2, a higher *endo* isomer distribution appeared when a more reactive dienophile was used. Although it is difficult to treat the reactivity of a dienophile in a quantitative sense, the logarithms of the apparent relative rate constants were employed as a provisional measure of the reactivity of the dienophile. In Fig. 1, the logarithms of the *endo* : *exo* isomer ratios, a measure of the *endo* selectivity, are plotted against the logarithms of the relative rates of the reactions. A fair correlation is found between the rates and the *endo* selectivity.

The fact that a more reactive addend has a higher *endo* selectivity seems to be contrary to the so-called selectivity-reactivity relationship in polar reactions.[12] Kojima and Inukai[13] have observed a similar phenomenon in the aluminum chloride-catalyzed Diels-Alder reactions. They have also pointed out the major role of the electrophilicity of dienophiles for the observed inter- and intramolecular selectivities.

Recently we ourselves reported on the pressure effect of the Diels-Alder reaction.[14] From an examination of the activation volumes of the reactions, it was deduced that a faster Diels-Alder reaction proceeds through a tighter transition state. The tighter transition state implies the existence of a stronger secondary orbital interaction as well as a closer proximity of the reacting species. The extent of stabilization due to secondary orbital interaction must be responsible

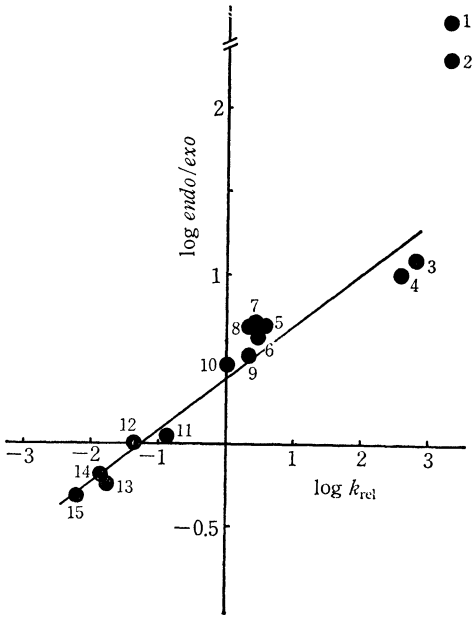


Fig. 1. A correlation of log (*endo*/*exo*) with log k_{rel}. The numerals correspond to the reaction number in Table 2.

for the determination of the *endo*: *exo* isomer ratio. The correlation shown in Fig. 1 indicates that the more reactive dienophile is characterized by the possibility of the stronger secondary orbital interaction.

The introduction of an alkyl group into the dienophile resulted in a decrease in the *endo* isomer distribution to less than 50%. However, even in these cases the correlation still holds, as is shown in Fig. 1.[15] Naturally, the alkyl group in the dienophile may depress its reactivity for electronic (inductive) and steric reasons.

A steric repulsion can operate between the alkyl group and the methylene group of cyclopentadiene in the *endo* transition state. These effects will make the *endo* transition state looser, and will result in a decrease in the amount of the *endo* isomer.

Thus, Fig. 1 substantiates the existence of a correlation between the *endo* selectivity and the relative rates in a given set of Diels-Alder reactions. Although it has been well-known in the field of synthetic organic chemistry that the faster Diels-Alder reactions preferentially yield a large amount of *endo* isomers, it should be emphasized that the linear correlation holds over a wide range of the reactivities of dienophiles.

Some anomalous deviation is seen in Fig. 1. That is, in the reactions of maleic anhydride or maleimide with cyclopentadiene, higher selectivities were observed than those expected from their relative rates. This possibly results from the two-fold interaction between the π-orbits of carbonyl groups and cyclopentadiene, as was pointed out in our previous report.[14] In the reaction of cyclopentadiene with maleic anhydride and maleimide, the transition-state geometry is quite favorable for secondary orbital interaction because of the cyclic feature of the dienophile. This must also be responsible for the observed higher *endo* selectivity in these two cases.

Experimental

All the NMR spectra were recorded on a JEOL PS-100 spectrometer, using TMS as the internal standard. The chemical shifts were expressed in δ-values. The analytical determination by glpc was performed by means of JEOL JGC-20K and Perkin-Elmer model 800 gas-chromatographs. The preparative glpc was performed by means of JEOL JGC-1100 gas-chromatograph. The UV spectra were recorded on a Shimadzu UV-200 spectrometer.

Materials. Methyl vinyl ketone[16] (bp 81 °C); ethyl vinyl ketone[17] (bp 102—103 °C); *n*-propyl vinyl ketone[17] (bp 35—36 °C/22 mmHg); isopropyl vinyl ketone[17] (33—35 °C/30 mmHg); acryloyl chloride[18] (bp 74—75 °C); acryloyl bromide[18] (bp 99—100 °C); methyl 2-*n*-butyl acrylate[19] (bp 69—70 °C/25 mmHg) and 1,4-diphenylcyclopentadiene-1,3 (**1b**)[20] (mp 161—162 °C) were prepared by the methods reported in the literature. 1,4-Di-(*p*-chlorophenyl)cyclopentadiene-1,3 (**1c**) was prepared from ethyl 3-(*p*-chlorophenyl)-propionate and *p*-chloroacetophenone[20]; mp 167—168 °C. Found: C, 71.37; H, 4.15%. Calcd for $C_{21}H_{12}O_2Cl_2$: C, 71.09; H, 4.21%. The other dienophiles were commercially available and were redistilled when necessary.

Product Analysis. In a typical run, a mixture of 2.5×10^{-3} M of a dienophile, 2.5×10^{-3} M of a diene, and 2 ml of a solvent was sealed in a glass ampoule and immersed in a thermostatted bath. The reaction time was changed from three hours to several days according to the reactivity of the addends and the temperature. The Diels-Alder adducts were analyzed by means of glpc and NMR. Stainless steel columns (2 m) packed with 5% PEG (column A), 5% TCPE (column B), 5% PEGS (column C), and 5% Silicon SE-30 (column D) on Diasolid L were used.

*Reactions of **1a** with Alkyl Vinyl Ketones.* The Diels-Alder adducts were separated by means of glpc (column A). All the adducts were colorless liquids. Retention times: 5-*endo*-acetylbicyclo[2.2.1]hept-2-ene (**3n**), 5.2 min; 5-*exo*-acetylbicyclo[2.2.1]hept-2-ene (**3x**), 4.0 min at 130 °C: 5-*endo*-propionylbicyclo[2.2.1]hept-2-ene (**4n**), 6.8 min; 5-*exo*-propionylbicyclo[2.2.1]hept-2-ene (**4x**), 5.2 min at 130 °C: 5-*endo*-*n*-butyrylcyclo[2.2.1]hept-2-ene (**5n**), 3.8 min; 5-*exo*-*n*-butyrylbicyclo[2.2.1]hept-2-ene (**5x**), 3.0 min at 160 °C: 5-*endo*-isobutyrylbicyclo[2.2.1]hept-2-ene (**6n**), 4.0 min; 5-*exo*-isobutyrylbicyclo[2.2.1]hept-2-ene (**6x**), 3.0 min at 160 °C.

NMR spectra (characteristic signals): **3n**, 2.00(CH_3); **3x**, 2.10 (CH_3); **4n**, 1.01 ($\mathbf{CH_3}CH_2$-), 2.44($CH_3\mathbf{CH_2}$-); **4x**, 1.06($\mathbf{CH_3}CH_2$-), 2.50($CH_3\mathbf{CH_2}$-): **5n**, 0.88($\mathbf{CH_3}CH_2CH_2$-), 2.30($CH_3CH_2\mathbf{CH_2}$-); **5x**, 0.90 ($\mathbf{CH_3}CH_2CH_2$-), 2.34($CH_3CH_2\mathbf{CH_2}$-): **6n**, 0.98, 1.04 (($\mathbf{CH_3}$)$_2$CH-); **6x**, 1.06, 1.18 (($\mathbf{CH_3}$)$_2$CH-).

Elementary analysis: Found: **5n**, C, 80.24; H, 9.76%; **5x**, C, 80.24; H, 10.03%: **6n**, C, 80.38; H, 9.91%; **6x**, 80.18; H, 9.66%. Calcd for $C_{10}H_{16}O$: C, 80.44; H, 9.83%.

*Reactions of **1a** with Methyl Acrylate and Methyl 2-Alkylacrylates.* The Diels-Alder adducts were separated by means of glpc (columns A and B). All the adducts were colorless liquids. Retention times: 5-*endo*-carbomethoxybicyclo[2.2.1] hept-2-ene (**7n**), 3.1 min; 5-*exo*-carbomethoxybicyclo[2.2.1]hep -2-ene (**7x**), 2.7 min at 150 °C (column A): 5-*endo*-carbomethoxy-5-*exo*-methylbicyclo[2.2.1] hept-2-ene (**8n**), 2.9 min; 5-*exo*-carbomethoxy-5-*endo*-methylbicyclo-[2.2.1]hept-2-ene, (**8x**), 2.6 min at 110 °C (column B): 5-*endo*-carbomethoxy-5-*exo*-ethylbicyclo[2.2.1]hept-2-ene (**9n**), 3.2 min; 5-*exo*-carbomethoxy-5-*endo*-ethylbicyclo[2.2.1]-2-ene (**9x**), 2.7 min at 120 °C (column B): 5-*endo*-carbomethoxy-5-*exo*-*n*-butylbicyclo[2.2.1]hept-2-ene (**10n**), 4.3 min; 5-*exo*-carbomethoxy-5-*endo*-*n*-butylbicyclo[2.2.1]hept-2-ene (**10x**), 3.7 min at 126 °C (column B).

NMR spectra (characteristic signals): **7n**, 3.57 (CO_2CH_3); **7x**, 3.63 (CO_2CH_3): **8n**, 3.56 (CO_2CH_3), 1.38 (CH_3); **8x**, 3.65 (CO_2CH_3), 1.08 (CH_3): **9n**, 3.55 (CO_2CH_3), 0.82 ($\mathbf{CH_3}CH_2$-); **9x**, 3.65 (CO_2CH_3), 0.72 ($\mathbf{CH_3}CH_2$-): **10n**, 3.56 (CO_2CH_3), 0.90 ($\mathbf{CH_3}(CH_2)_3$-); **10x**, 3.68 (CO_2CH_3), 0.88 ($\mathbf{CH_3}(CH_2)_3$-).

Elementary analysis: Found: **10n**, C, 74.73; H, 9.72%; **10x**, C, 75.23; H, 9.77%. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68%.

*Reaction of **1a** with Acrolein.* The Diels-Alder adducts, 5-*endo*-formylbicyclo[2.2.1]hept-2-ene (**11n**) and 5-*exo*-formylbicyclo[2.2.1]hept-2-ene (**11x**), were separated by means of glpc (column A, at 125 °C; retention times: **11n**, 2.7 min; **11x**, 2.3 min). These are colorless liquids. NMR spectra (characteristic signals); **11n**, 9.32 (CHO): **11x**, 9.76 (CHO).

*Reactions of **1a** with Acryloyl Halides.* After the reactions were completed, the products were esterified with methanol containing lutidine in a sealed ampoule at room temperature, and subsequently analyzed by glpc (column A). The added litidine had no effect on the *endo* : *exo* isomer ratios. The esterified products were identified as **7n** and **7x** by comparing the retention time and the NMR spectra with those of authentic samples.

*Reactions of **1b** and **1c** with Methyl Acrylate.* The Diels-Alder adducts, 1,4-diphenyl-5-*endo*-carbomethoxybicyclo-[2.2.1]hept-2-ene (**12n**) and 1,4-diphenyl-5-*exo*-carbomethoxybicyclo[2.2.1]hept-2-ene (**12x**); 1,4-di(*p*-chlorophenyl)-5-*endo*-carbomethoxybicyclo[2.2.1]-hept-2-ene (**13n**) and 1,4-di-(*p*-chlorophenyl)-5-*exo*-carbomethoxybicyclo[2.2.1]hept-2-ene (**13x**) were separated by means of preparative tlc. The *endo* : *exo* isomer ratios were determined by integration on the NMR spectra. **12n**, oily liquid, NMR: 7.28 (Ph), 6.35 (CH=CH), 3.37(CO_2CH_3), 3.24(5-*exo*-H), 2.40(6-*endo*-H), 2.00(6-*exo*-H), 1.96(7-*anti*- and 7-*syn*-H): **12x**, mp 63—65 °C, NMR; 7.30(Ph), 6.35(CH=CH), 3.08(CO_2CH_3), 2.76(7-*anti*-H), 2.68(5-*endo*-H), 2.40(6-*exo*-H), 1.88(7-*syn*-H), 1.80(6-*endo*-H): **13n**, mp 88 °C, NMR; 7.28(Ph), 6.28(CH=CH), 3.48

(CO_2CH_3), 3.32(5-*exo*-H), 2.36(6-*exo*-H), 2.04—1.72 (other protons): **13x**, mp 96—97 °C, NMR; 7.30(Ph), 6.30(CH=CH), 3.20(CO_2CH_3), 2.75(7-*anti*-H), 2.72(5-*endo*-H), 2.38(6-*exo*-H), 1.96—1.70 (6-*endo*- and 7-*syn*-H).

Elementary analysis: Found: **12n**, C, 83.02; H, 6.69%: **12x**, C, 82.78; H, 6.62%. Calcd for $C_{21}H_{20}O_2$: C, 82.86; H, 6.62%. Found: **13n**, C, 67.41; H, 4.68%: **13x**, C, 67.38; H, 5.02%. Calcd for $C_{21}H_{18}Cl_2O_2$: C, 67.57; H, 4.86%.

Reactions of ***1a*** *with Maleic Anhydride and* N-*Phenylmaleimide.* The isomer distribution of the reaction of **1a** with maleic anhydride was determined by means of glpc (column D). Retention time: bicyclo[2.2.1]hept-5-ene-*endo*-2,3-dicarboxylic anhydride (**14n**), 3.9 min; bicyclo[2.2.1]hept-5-ene-*exo*-2,3-dicarboxylic anhydride (**14x**), 3.2 min at 150 °C. However, a small portion (0.15%) of **14n** was isomerized to **14x** in the glpc condition. Accordingly, the value of the isomer ratio was corrected by this figure. **14n**, mp 163—164 °C; NMR, 6.32(CH=CH), 3.40—3.70 (1—4-H's), 1.30—1.90 (other protons). **14x**; although no attempt to isolate **14x** was made, the structure of **14x** was confirmed by an isomerization experiment according to Craig's method.[22] NMR (including 70% of **14n**), 2.92 (2- and 3-H).

The adduct of **1a** with *N*-phenylmaleimide (**15n**), mp 144 °C; NMR, 7.10—7.64 (Ph), 6.28 (CH=CH), 3.28—3.64 (1—4-H's), 1.50—1.90 (other protons). The isomer distribution was determined by means of comparing the NMR data with those of **14**. An inspection of the NMR of the adduct with *N*-phenylmaleimide showed an *endo* isomer distribution of more than 99.5%.

Kinetic Experiments (a) The Reactions of ***1a*** *with Acryloyl Halides.* The initial concentrations were 0.0620—0.0842 M for the acryloyl halides, 0.0442 M for **1a**, and 0.0178 M for the internal standard (2,4-dichlorotoluene). The reaction mixture was maintained at 35±0.02 °C. Portions of the sample were withdrawn at appropriate time intervals and quenched with a large excess of methanol containing lutidine. After three hours, the solutions were analyzed by means of glpc. By following the amount of the esters, **7n** and **7x**, the second-order rate constants were calculated.

(b) The Reactions of ***1b*** *and* ***1c*** *with Methyl Acrylate.* The initial concentrations were $5.11—5.81\times10^{-4}$ M for the dienes and $7.07—10.1\times10^{-2}$ M for the dienophile. By following the disappearance of **1b** (or **1c**) spectrophotometrically, the pseudo-first-order rate constants were calculated (λ_{max}=353 nm for **1b** and 360 nm for **1c**).

The competitive reaction technique employed was the same as that used in the aromatic substitution reactions. The relative rates were calculated using the following formula:

$$k_1/k_2 = \{\log C_1^\circ - \log (C_1^\circ - X_1)\}/\{\log C_2^\circ - \log (C_2^\circ - X_2)\}$$

where C_1° and C_2° refer to the initial concentrations of dienophiles and where X_1 and X_2 refer to the final concentrations of the products. Analysis was performed by means of glpc, using appropriate internal standards. In most of the experiments, the competitive reaction of cyclopentadiene with the methyl acrylate—other dienophile pair was employed. However, the relative rate of methyl methacrylate was not obtained because of the coincidental overlap of the glpc peaks of the two reaction products. The relative rate of methyl methacrylate was calculated from the rate of methyl methacrylate relative to that of acrylonitrile and the rate of the latter relative to that of methyl acrylate. The results are shown in Table 3.

Table 3. Relative rates of the Diels-Alder reactions of cyclopentadiene with methyl acrylate (MeA), methyl methacrylate (MeMA), and acrylonitrile (AN)

Diene (mmol/l)	MeA (MeMA)[a] (mmol/l)	AN (mmol/l)	Relative rate
214	74.4	145	1.07[b]
325	46.9	136	1.02[b]
354	46.9	136	1.00[b]
627	(441)[a]	204	1.58×10^{-2} [c]
710	(430)[a]	192	1.63×10^{-2} [c]
720	(291)[a]	187	1.66×10^{-2} [c]

a) The values in parenthese are the concentration of MeMA. b) k_{AN}/k_{MeA}. c) k_{MeMA}/k_{AN}.

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