Steric Control in the Diels-Alder Reaction[1)]

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The Diels-Alder reactions of polychlorocyclopentadienes with substituted ethylenes were investigated, and the rates of the reaction and the *endo* : *exo* adduct distributions were determined. The introduction of a chlorine atom at the C_5 position of cyclopentadiene resulted in an enhanced *endo* preference for substituents in the adducts, despite the depressed reactivity of the diene. This is contrary to what is to be expected from the so-called "selectivity-reactivity relationship in the Diels-Alder reaction." The results in this work were explained in terms of steric interaction between the C_5-chlorine atom of the diene and the substituent of dienophiles.

Many investigators have been interested in *endo* selectivity in the Diels-Alder reaction from both experimental and theoretical points of view. Many factors have been considered to be responsible for the stereochemistry of the reaction.[2-7)] However, the elucidation of the steric factor seems to remain incomplete. Early, Martin, and Hill[3)] ascribed the deviation from the *endo* rule[2a,3)] mainly to a repulsive interaction between the methylene group of cyclopentadiene and substituent(s) of dienophile. This concept has also been employed widely in other reactions.[4)] Kobuke *et al.*[6)] pointed out the importance of the dispersion force rather than the steric factor in the same reaction.

In the course of our investigation of the correlation between the selectivity and the reactivity in the Diels-Alder reaction,[7)] we found a significant deviation when hexachlorocyclopentadiene was employed as a diene. The reaction was found to give *endo* adducts preferentially, although low *endo* adduct distributions were predicted from the correlation.[7)] This paper will be concerned with the enhanced *endo* epimer preference of the Diels-Alder reaction of polychlorocyclopentadienes. The role of steric interaction will be discussed in connection with the selectivity-reactivity correlation in the Diels-Alder reaction.

Results and Discussion

The rates and the epimer distributions in the Diels-Alder reactions of 1,2,3,4-tetrachloro- (**1a**) and hexachlorocyclopentadiene (**1c**) with methyl acrylate and styrene were examined by means of GLC. The results are tabulated in Table 1. We already pointed out in the previous paper[7)] that the more reactive addenda there are, the more selective the Diels-Alder reaction, where secondary orbital interaction plays an important role. However, Reactions 2 and 3 in Table 1 gave rather high *endo* epimer distributions in spite of the lower reactivity of the substrates. This anormalous behavior is shown definitely in Fig. 1 as a significant deviation from the selectivity-reactivity correlation (Points 2 and 3), while no such deviation was observed in the reaction of tetrachlorocyclopentadiene (Point 1). These facts are likely to indicate the relative importance of steric interaction between the chloromethylene group of **1c** and the substituent of a dienophile; the electronic effect or the secondary orbital interaction plays a subordinate role. Accordingly, we examined more systematically the steric control for the *endo*

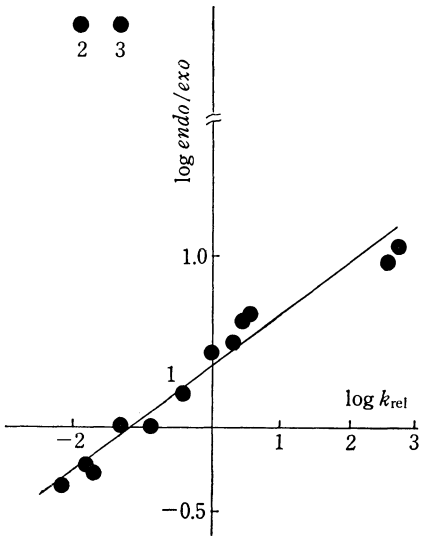

Fig. 1. A correlation of selectivity (log *endo*/*exo*) and reactivity (log k_{rel}) in the Diels-Alder reaction. Numerals denote the reaction numbers cited in Table 1; for the other points (not numbered), see Ref. 7.

TABLE 1. RATES AND *endo* SELECTIVITIES FOR THE REACTION OF **1a** AND **1c** WITH METHYL ACRYLATE AND STYRENE AT 40 °C

Reaction No.	Diene	Dienophile	Rate const[a)] (l/mol, s)	k_{rel}[b)]	*endo* Selectivity[a)] (%)
1	**1a**	Methyl acrylate	1.89×10^{-5}	3.57×10^{-1}	60.1
2	**1c**	Methyl acrylate	6.04×10^{-7}	1.14×10^{-2}	100
3	**1c**	Styrene	2.12×10^{-6}	4.00×10^{-2}	100

a) Determined by means of GLC. b) Relative rates to the reaction of cyclopentadiene with methyl acrylate; see Ref. 7.

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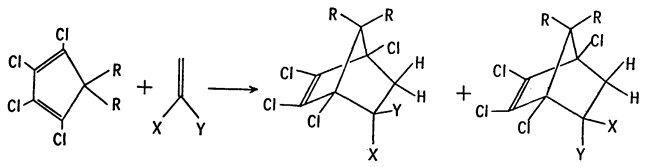
selectivity in the Diels-Alder reaction.

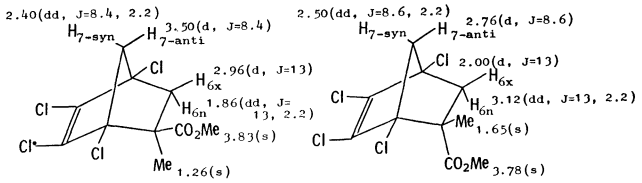
The following sets of reactions were carried out in *p*-xylene at 90 °C: diene; **1a** and **1c**: dienophile; monosubstituted ethylenes (methyl acrylate, acrylic acid, acrylonitrile, vinyl acetate, and styrene) and 1,1-disubstituted ethylenes (corresponding alkyl-substituted derivatives). The reactions proceeded smoothly when monosubstituted ethylenes were employed as dienophiles. However, the reactions of **1c** with 1,1-disubstituted ethylenes were not very fast; even after fifteen days at 90 °C the yields of the products were about 30% (the starting materials were recovered). In all the case, the reaction mixtures were readily separated to the *exo* and *endo* isomers by means of GLC. The *endo* isomer distribution was determined by means of GLC or NMR. The *endo* : *exo* isomer ratio was almost independent of the reaction times. The results are tabulated in Table 2, together with the reported data of the reactions of 1,2,3,4,5-pentachlorocyclopentadiene (**1b**).[8] Since the reaction of **1b** gave a mixture of *anti-endo*, *syn-endo*, and *syn-exo* isomers, the 7-*syn*-chloro-*endo*/7-*syn*-chloro-*exo* ratios are also given in Table 2.



Diene Dienophile *exo*- (**x**) *endo*- (**n**)
(**1a**) R=H X=H, Me, Bu
(**1b**) R=H, Cl Y=CO_2Me, CO_2H, CN,
(**1c**) R=Cl OAc, Ph

Scheme 1.

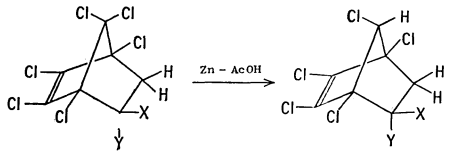
The configuration of the isomeric adducts was deduced by means of NMR analysis, taking into account the following characteristic signals of norbornene derivatives. The shielding effect of the double bond in 5-substituted 2-norbornene leads the proton signals



Scheme 2. Chemical shift in ppm, coupling constant in Hz.

of the 5-*endo* substituents to a higher field than those of the corresponding *exo* substituents. A long-range coupling over the planar W-letter configuration is present between H_{7-syn} and $H_{5n,6n}$. An *exo*-oriented Y makes the difference in the chemical shift between H_{7-syn} and H_{7-anti} larger than an *endo*-oriented Y does. A typical example is shown in Scheme 2 for the adducts of **1a** with methyl methacrylate (**2x** and **2n**).

5-*endo*-Methyl protons in **2x** and *endo*-5-methoxycarbonyl methyl protons in **2n** absorb at a higher field than the corresponding protons of their isomers. The signal of H_{6n} is split into a double doublet by the long-range coupling with H_{7-syn} (J=2.2 Hz) as well as by the coupling with H_{6x}. The configurations of the isomers of the other Diels-Alder adducts were similarly analyzed. The chemical shift and the splitting pattern of these compounds were similar to those of



3n X=H, Y=CO_2Me **9n** X=H, Y=CO_2Me
4n X=H, Y=CO_2H **10n** X=H, Y=OAc
5n X=H, Y=OAc **11n** X=H, Y=Ph
6n X=H, Y=Ph **12n** X=Me, Y=OAc
7n X=Me, Y=OAc **13n** X=Me, Y=CN
8n X=Me, Y=CN

Scheme 3.

Table 2. *endo* Selectivity in the Diels-Alder reactions of polychlorocyclopentadienes with various dienophiles

Dienophile		Diene				
		(**1a**)[a]		(**1b**)[a]	(**1c**)[a]	
X[a]	**Y**[a]	Yield of adduct (%) [reaction time, h]	*endo* Selectivity (%)	*endo* Selectivity (%)[b]	Yield of adduct (%) [reaction time, h]	*endo* Selectivity (%)
H	OAc	56 [24]	75.5 (3.08)[c]	92.8 (6.28)[d]	72 [40]	100
H	CO_2CH_3	75 [15]	60.7 (1.54)[c]	89.8 (3.59)[d]	72 [54]	100
H	CO_2H	86 [24]	66.7 (2.00)[c]	—	85 [40]	100
H	CN	61 [24]	53.7 (1.16)[c]	86.8 (1.14)[d]	65 [40]	94.2
H	Ph	59 [60]	78.8 (3.72)[c]	100 (2.92)[d]	95 [40]	100
Me	OAc	17 [40]	57.1	—	15 [240]	100
Me	CO_2CH_3	80 [40]	41.8	—	10 [240]	95
Bu	CO_2CH_3	57 [40]	33.9	—	37 [300]	87
Me	CN	83 [40]	23.0	—	25 [240]	18.3
Me	Ph	64 [70]	64.3	—	22 [240]	94.2

a) See Scheme 1. b) Ref. 8. c) *endo*/*exo* Ratios. d) 7-*syn*-Chloro-*endo*/7-*syn*-chloro-*exo* isomer ratios.

the reported compounds.[8-11]

On the other hand, in the reactions of **1c** with methyl acrylate, acrylic acid, vinyl acetate, styrene, and isopropenyl acetate, only ones (**3n**—**7n**) of the epimeric adducts were produced (Scheme 3). The configurations of these adducts were determined by zinc–acetic acid reduction.[12] The procedure is known to give the corresponding 1,2,3,4-*syn*-7-pentachloronorbornene derivatives stereoselectively. The reduction products, **9n**—**11n**, were proved to be identical with the respective known compounds by a comparison with their NMR spectra.[8] That is, all of the adducts, **3n**—**6n**, were found to have the *endo* configuration. The configuration of **4n** was determined after it had been converted into **3n** by diazomethane.

The configuration of **12n** was deduced on the basis of the following NMR spectral evidence. The replacement of a 7-*anti*-chlorine atom by a hydrogen atom must affect the chemical shift of 5-*exo*-methyl protons more markedly than that of 5-*endo*-methyl protons. This concept was exemplified by the fact that, of the two epimeric adducts of **1c** with methacrylonitrile, the 5-*endo*-cyano-5-*exo*-methyl epimer (**8n**) revealed its methyl signal at δ 1.98, while the 5-*endo*-methyl-5-*exo*-cyano epimer (**8x**) did so at δ 1.47. Upon the above-cited reduction, **8n** gave **13n**, in which the methyl group resonated at δ 1.71. Similarly, **8x** gave **13x**, with its methyl signal at δ 1.42. That is, the replacement of a 7-*anti*-chlorine atom by a hydrogen atom led the 5-*exo*-methyl signal to a field higher by 0.27 ppm, but had little effect on the 5-*endo*-methyl signal. The chemical-shift difference of the methyl signal of **7n** (δ 2.00) and that of **12n** (δ 1.80) manifested an *exo* configuration for these methyl groups. Accordingly, **7n** was determined to be the 5-*endo*-acetoxy-5-*exo*-methyl epimer.

As is shown in Table 2, the introduction of succesive chlorine atoms at the C_5 position of cyclopentadiene resulted in enhanced *endo* adduct distributions for the reactions of polychlorocyclopentadienes with monosubstituted ethylenes. According to the "Diels-Alder selectivity-reactivity relationship,"[7] the less reactive diene, **1c**, may be anticipated to reveal a lower *endo* selectivity than **1a**. However, this was not the case. The *endo* selectivity for the Diels-Alder reactions of cyclopentadiene has been thought, in general, to be caused by dipole-dipole interaction, attractive force, and other ineractions. However, in the present case, the dienes have chlorine atoms at the C_5 position, so the steric situation should be some what different from the usual Diels-Alder reactions. That is, *exo*-orienting substituent in a transition state should experience rather strong steric crowding. The high *endo* epimer distributions observed for the reactions of **1b** and **1c** suggest that the substituents of the dienophiles are forced to occupy the sterically less hindered *endo* position. In addition, the *endo* : *exo* ratios for **1a** and the 7-*syn*-chloro-*endo* : 7-*syn*-chloro-*exo* ratios for **1b** change almost in parallel with the change in the substituent of dienophiles. Furthermore, no 7-*anti*-chloro-*exo* isomers were found in the adducts of **1b** with monosubstituted ethylenes.[8] These facts clearly indicate the existence of steric repulsion between the *anti* chlorine atom and the *exo* substituent in the transition state. This can be further explained by inspecting the results obtained from the reactions of **1a** and **1c** with 1,1-disubstituted ethylenes. Here, two substituents, X and Y, occupy competitively the *endo* position in the transition state. Table 2 shows that the amounts of the *endo* adducts increase remarkably when the methylene hydrogen atoms of **1a** are replaced by chlorine atoms. Methacrylonitrile reveals a lower *endo*-CN preference in the reaction with **1c**. This is in good accord with Mark's consideration that the sterically least demanding cyano group is forced to the rather unfavored *exo* position when it is in competition with a bulkier group.[13] In addition, such steric crowding in the transition state will be responsible for the lower reactivity of **1c** toward 1,1-disubstituted ethylenes, as is shown in Table 2.

In conclusion, in the Diels-Alder reactions of polychlorocyclopentadienes with substituted ethylenes the steric requirement of bulkier substituents should be considered as one of the predominant factors in determining the *endo* selectivity and should cause the deviation from the selectivity-reactivity relationship.

Experimental

The NMR spectra were recorded on a JEOL PS-100 spectrometer, using TMS as the internal standard. The analytical determination by GLC was performed on a JEOL 20 K gas chromatograph.

Materials. Hexachlorocyclopentadiene (**1c**) was commercially obtained and was distilled; bp 116 °C/17 Torr. The preparation and purification of other diene and dienophiles were reported previously.[7]

The Diels-Alder Reaction and Analytical Procedure. In a typical run, a mixture of 7.3×10^{-3} M of a dienophile, 2.8×10^{-2} M of a diene, and 2 ml of *p*-xylene was sealed in a glass ampoule maintained at 90±0.1 °C. The reaction time was changed from 15 to 72 h for the reactions with 1,2,3,4-tetrachlorocyclopentadiene (**1a**) and from 40 to 300 h for the reactions of hexachlorocyclopentadiene (**1c**) according to the reactivity of the dienophiles. The Diels-Alder adducts were analyzed by means of GLC and NMR, after passage to a bed of silica gel, if neccesary. Stainless steel columns (2 m) packed with 7% Silicon QF-1 (Column A), 5% PEG 20 M (Column B), and 5% Silicon DC550 (Column C) on a Diasolid L were used. For the adducts of **1a**, *endo* isomers showed longer retention times, while for the adducts of **1c** they showed shorter retention times.

Kinetics. Stock solutions of a diene and a dienophile in butyl chloride were prepared and stored in a freezer. Aliquots were taken from the stock solutions and mixed for

Table 3. Data for kinetic measurements

Reaction No.[a]	Initial concentration (×10 M)		GLC column[b]	GLC internal standard
	Diene	Dienophile		
1	2.33	2.20	D	**12n**
2	0.890—2.15	1.64—32.8	E	*o*-Terphenyl
3	0.890—2.15	3.22—16.8	E	*o*-Terphenyl

a) Reaction numbers cited correspond to those in Table 1. b) D, 1 m PEG 20 M (1%); E, 1 m Apiezone Grease L (5%).

each kinetic run. Analysis was done by means of GLC. The initial concentrations of the diene and the dienophile, the column specifications, and the internal standards for quantitative GLC analyses are shown in Table 3. All the reactions studied were clearly second-order and gave a single product or a mixture of *endo* and *exo* isomeric products.

Reaction of **1a** *with Methyl Acrylate.* The Diels-Alder adducts, 1,2,3,4-tetrachloro-5-*endo*-methoxycarbonylbicyclo-[2.2.1]hept-2-ene (**14n**) and its 5-*exo* isomer (**14x**), were separated by the use of Column A at 160 °C (retention times: **14n**, 8.5 min; **14x**, 6.3 min). Mp: **14n**, 86—87 °C; **14x**, 61.5—62.5 °C. NMR (δ): **14n**, 3.78 (3H, s, CO_2CH_3), 3.40 (1H, dd, J=4 and 8 Hz, 5-*exo*-H), 2.52 (2H, bs, 7-*syn*-H and 7-*anti*-H), 2.40—2.50 (2H, m, 6-*endo*-H and 6-*exo*-H); **14x**, 3.83 (3H, s, CO_2CH_3), 2.92 (1H, m, J=2, 4, and 8 Hz, 5-*endo*-H), 3.32 (1H, d, J=8 Hz, 7-*anti*-H), 2.58 (1H, dd, J=4 and 12 Hz, 6-*exo*-H), 2.24—2.32 (2H, m, 6-*endo*-H and 7-*syn*-H). Found: **14n**, C, 36.89; H, 2.79; Cl, 49.05%; **14x**, C, 37.29; H, 2.69; Cl, 48.88%. Calcd for $C_9H_8O_2Cl_4$: C, 37.27; H, 2.78; Cl, 48.99%.

Reaction of **1a** *with Acrylic Acid.* The isomeric distribution was determined by means of the NMR spectra. The Diels-Alder adducts, 1,2,3,4-tetrachloro-5-*endo*-carboxybicyclo-[2.2.1]hept-2-ene (**15n**) and its 5-*exo* isomer (**15x**), were fractionated by recrystallization from benzene–hexane. They were then esterified by diazomethane, and the products were identified by means of GLC with **14n** and **14x** respectively. Mp: **15n**, 161 °C; **15x**, 127—129 °C. NMR (δ): **15n**, 9.30 (1H, s, CO_2H), 3.44 (1H, dd, J=4 and 8 Hz, 5-*exo*-H), 2.41—2.48 (4H, m, other protons); **15x**, 10.45 (1H, s, CO_2H), 3.12 (1H, d, J=8 Hz, 7-*anti*-H), 2.92 (1H, m, J=1, 4, and 8 Hz, 5-*endo*-H), 2.26—2.60 (3H, m, other protons). Found: **15n**, C, 34.57; H, 1.94; Cl, 51.20%; **15x**, C, 35.00; H, 2.18; Cl, 51.22%. Calcd for $C_8H_6O_2Cl_4$: C, 34.82; H, 2.19; Cl, 51.40%.

Reaction of **1a** *with Vinyl Acetate.* The Diels-Alder adducts, 1,2,3,4-tetrachloro-5-*endo*-acetoxybicyclo[2.2.1]hept-2-ene (**16n**) and its 5-*exo* isomer (**16x**), were separated by the use of Column B at 150 °C (retention times: **16n**, 16.3 min; **16x**, 14.1 min). Mp: **16n**, 52—53 °C; **16x**, colorless liquid. NMR (δ): **16n**, 5.54 (1H, dd, J=2 and 8 Hz, 5-*exo*-H), 2.78 (1H, dd, J=8 and 12 Hz, 6-*exo*-H), 2.50—2.58 (2H, bs, 7-*syn*-H and 7-*anti*-H), 2.10 (3H, s, $OCOCH_3$), 1.84 (1H, dd, J=3 and 12 Hz, 6-*endo*-H); **16x**, 5.02 (1H, m, J=1, 3, and 8 Hz, 5-*endo*-H), 2.87 (1H, d, J=8 Hz, 7-*anti*-H), 2.56—2.66 (2H, m, 6-*exo*-H and 7-*syn*-H), 2.17 (3H, s, $OCOCH_3$), 2.02 (1H, dd, J=3 and 12 Hz, 6-*endo*-H). Found: **16n**, C, 37.43; H, 3.05%; **16x**, C, 37.08; H, 2.66%. Calcd for $C_9H_8O_2Cl_4$: C, 37.27; H, 2.78%.

Reaction of **1a** *with Acrylonitrile.* The Diels-Alder adducts, 1,2,3,4-tetrachloro-5-*endo*-cyanobicyclo[2.2.1]hept-2-ene (**17n**) and its 5-*exo* isomer (**17x**), were separated by the use of Column A at 160 °C (retention times: **17n**, 13.5 min; **17x**, 9.7 min). Mp: **17n**, 75—76 °C; **17x**, 92—93 °C. NMR (δ): **17n**, 3.50 (1H, dd, J=4 and 10 Hz, 5-*exo*-H), 2.74 (1H, dd, J=10 and 12 Hz, 6-*exo*-H), 1.50 (2H, bs, 7-*syn*-H and 7-*anti*-H), 1.34 (1H, dd, J=4 and 12 Hz, 6-*endo*-H); **17x**, 3.02 (1H, m, J=2, 5, and 9 Hz, 5-*endo*-H), 2.86 (1H, d, J=8 Hz, 7-*anti*-H), 2.53—2.74 (3H, m, 7-*syn*-H, 6-*endo*-H, and 6-*exo*-H). Found: **17n**, C, 37.58; H, 1.71; Cl, 55.53%; **17x**, C, 37.37; H, 1.71; Cl, 55.18%. Calcd for $C_8H_5NCl_4$: C, 37.44; H, 1.98; Cl, 55.20%.

Reaction of **1a** *with Styrene.* The Diels-Alder adducts, 1,2,3,4-tetrachloro-5-*endo*-phenylbicyclo[2.2.1]hept-2-ene (**18n**) and its 5-*exo* isomer (**18x**), were separated by the use of Column A at 180 °C (retention times: **18n**, 10.2 min; **18x**, 9.1 min). Mp: **18n**, 64—65 °C; **18x**, colorless liquid. NMR (δ): 6.96—7.28 (5H, m, Ph), 3.64 (1H, dd, J=4 and 8 Hz, 5-*exo*-H), 2.32—2.76 (4H, m, other protons); **18x**, 7.30 (5H, s, Ph), 3.10 (1H, m, J=1, 5, and 8 Hz, 5-*endo*-H), 2.80 (1H, d, J=8 Hz, 7-*anti*-H), 2.40—2.76 (3H, m, other protons). Found: **18n**, C, 50.84; H, 3.31%; **18x**, C, 50.85; H, 2.95%. Calcd for $C_{13}H_{10}Cl_4$: C, 50.68; H, 3.27%.

Reaction of **1a** *with Methyl Methacrylate.* The Diels-Alder adducts, 1,2,3,4-tetrachloro-5-*endo*-methoxycarbonyl-5-*exo*-methylbicyclo[2.2.1]hept-2-ene (**2n**) and its 5-*exo*-methoxycarbonyl-5-*endo*-methyl isomer (**2x**), were separated by the use of Column A at 160 °C (retention times: **2n**, 8.7 min; **2x**, 7.0 min) after passage through a bed of silica gel (using benzene–hexane as the eluent). Mp: **2n**, 58.5—59.5 °C; **2x**, 64.5—65.5 °C. The NMR data of these compounds are shown in Scheme 2. Found: **2n**, C, 39.41; H, 3.19%; **2x**, C, 39.23; H, 3.17%. Calcd for $C_{10}H_{10}O_2Cl_4$: C, 39.51; H, 3.32%.

Reaction of **1a** *with Methyl 2-Butylacrylate.* The Diels-Alder adducts, 1,2,3,4-tetrachloro-5-*endo*-methoxycarbonyl-5-*exo*-butylbicyclo[2.2.1]hept-2-ene (**19n**) and its 5-*exo*-methoxycarbonyl-5-*endo*-butyl isomer (**19x**), were separated by the use of Column A at 180 °C (retention times; **19n**; 21.1 min; **19x**, 13.8 min). Mp: **19n**, 77—80 °C; **19x**, colorless liquid. NMR (δ): **19n**, 3.78 (3H, s, CO_2CH_3), 3.02 (1H, dd, J=2 and 12 Hz, 6-*endo*-H), 2.72 (1H, d, J=8 Hz, 7-*anti*-H), 2.46 (1H, dd, J=2 and 8 Hz, 7-*syn*-H), 1.98 (1H, d, J=12 Hz, 6-*exo*-H), 0.96—1.60 (9H, m, Bu); **19x**, 3.87 (3H, s, CO_2CH_3), 3.17 (1H, d, J=8 Hz, 7-*anti*-H), 2.98 (1H, d, J=12 Hz, 6-*exo*-H), 2.34 (1H, dd, J=2 and 12 Hz, 7-*syn*-H), 1.90 (1H, dd, J=2 and 12 Hz, 6-*endo*-H), 0.92—1.55 (9H, m, Bu). Found: **19n**, C, 44.95; H, 4.63%; **19x**, 45.28; H, 4.63%. Calcd for $C_{13}H_{16}O_2Cl_4$: C, 45.11; H, 4.66%.

Reaction of **1a** *with Isopropenyl Acetate.* The isomer distribution was determined by means of GLC using Column A (retention times: 1,2,3,4-tetrachloro-5-*endo*-acetoxy-5-*exo*-methylbicyclo[2.2.1]hept-2-ene (**20n**), 8.2 min; and its 5-*exo*-acetoxy-5-*endo*-methyl isomer (**20x**), 7.2 min). However, the pure isomers could not be obtained because their retention times were too close to each other. NMR (δ, characteristic signals): **20n**, 1.76 (s, 5-CH_3), 1.92 (s, $OCOCH_3$); **20x**, 1.44 (s, 5-CH_3), 2.04 (s, $OCOCH_3$). For the isomer mixture, Found: C, 39.57; H, 3.26%. Calcd for $C_9H_8O_2Cl_4$: C, 39.51; H, 3.32%.

Reaction of **1a** *with Methacrylonitrile.* The Diels-Alder adducts, 1,2,3,4-tetrachloro-5-*endo*-cyano-5-*exo*-methylbicyclo-[2.2.1]hept-2-ene (**21n**) and its 5-*exo*-cyano-5-*endo*-methyl isomer (**21x**), were separated by the use of Column A at 155 °C (retention times: **21n**, 12.0 min; **21x**, 7.7 min). Mp: **21n**, 99—100 °C; **21x**, colorless liquid. NMR (δ): **21n**, 2.70 (1H, dd, J=2 and 12 Hz, 6-*endo*-H), 2.60 (2H, m, 7-*syn*-H and 7-*anti*-H), 2.27 (1H, d, J=12 Hz, 6-*exo*-H), 1.75 (3H, s, CH_3); **21x**, 3.01 (1H, d, J=10 Hz, 7-*anti*-H), 2.86 (1H, d, J=13 Hz, 6-*exo*-H), 2.64 (1H, dd, J=3 and 10 Hz, 7-*syn*-H), 2.10 (1H, dd, J=3 and 13 Hz, 6-*endo*-H), 1.42 (3H, s, CH_3). Found: **21n**, C, 39.89; H, 2.55%; **21x**, C, 39.76; H, 2.49%. Calcd for $C_9H_7NCl_4$: C, 39.89; H, 2.60%.

Reaction of **1a** *with* α*-Methylstyrene.* The isomeric distribution was determined by means of GLC using Column A at 180 °C (retention times: 1,2,3,4-tetrachloro-5-*endo*-phenyl-5-*exo*-methylbicyclo[2.2.1]hept-2-ene (**22n**), 8.8 min and its 5-*exo*-phenyl-5-*endo*-methyl isomer (**22x**), 7.8 min). However, the pure isomers could not be obtained because their retention times were too close to each other. NMR (δ, characteristic signals): **22n**, 1.76 (s, CH_3); **22x**, 1.45

(s, CH_3). For the isomer mixture, Found: C, 52.75; H, 3.81%. Calcd for $C_{14}H_{10}Cl_4$: C, 52.21; H, 3.76%.

Reaction of ***1c*** *with Methyl Acrylate.* The GLC, TLC, and NMR all indicated the presence of a single product, 1,2,3,4,7,7-hexachloro-5-*endo*-methoxycarbonylbicyclo[2.2.1]-hept-2-ene (**3n**); bp 140—145 °C/7 Torr. NMR (δ): 3.65 (1H, dd, J=4 and 7 Hz, 5-*exo*-H), 2.60—2.76 (2H, m, 6-*endo*-H and 6-*exo*-H), 3.82 (3H, s, CO_2CH_3). Found: C, 30.13; H, 1.91; Cl, 59.55%. Calcd for $C_9H_6O_2Cl_6$: C, 30.12; H, 1.69; Cl, 59.28%.

Reaction of ***1c*** *with Acrylic Acid.* The NMR indicated the presence of a single product, 1,2,3,4,7,7-hexachloro-5-*endo*-carboxybicyclo[2.2.1]hept-2-ene (**4n**); mp 142—145 °C. This product was esterified to **3n** by diazomethane. NMR (δ): 11.36 (1H, s, CO_2H), 3.70 (1H, dd, J=4 and 8 Hz, 5-*exo*-H), 2.78 (1H, dd, J=8 and 12 Hz, 6-*exo*-H), 2.62 (1H, dd, J=4 and 12 Hz, 6-*endo*-H). Found: C, 27.84; H, 1.08; Cl, 61.58%. Calcd for $C_8H_4O_2Cl_6$: C, 27.86; H, 1.17; Cl, 61.69%.

Reaction of ***1c*** *with Vinyl Acetate.* The GLC, TLC, and NMR all indicated the presence of a single product, 1,2,3,4,7,7-hexachloro-5-*endo*-acetoxybicyclo[2.2.1]hept-2-ene (**5n**); mp 42.5—43.0 °C. NMR (δ): 5.64 (1H, dd, J=3 and 8 Hz, 5-*exo*-H), 3.10 (1H, dd, J=8 and 13 Hz, 6-*exo*-H), 2.05 (3H, s, $OCOCH_3$), 1.95 (1H, dd, J=3 and 13 Hz, 6-*endo*-H). Found: C, 29.89; H, 1.55; Cl, 59.49%. Calcd for $C_9H_6O_2Cl_6$: C, 30.12; H, 1.69; Cl, 59.28%.

Reaction of ***1c*** *with Styrene.* The GLC, TLC, and NMR all indicated the presence of a single product, 1,2,3,4,7,7-hexachloro-5-*endo*-phenylbicyclo[2.2.1]hept-2-ene (**6n**); mp 74—75 °C. NMR (δ): 6.96—7.40 (5H, m, Ph), 3.90 (1H, dd, J=4 and 12 Hz, 5-*exo*-H), 2.84 (1H, dd, J=8 and 12 Hz, 6-*exo*-H), 2.42 (1H, dd, J=4 and 12 Hz, 6-*endo*-H). Found: C, 41.53; H, 1.92; Cl, 56.17%. Calcd for $C_{13}H_8Cl_6$: C, 41.42; H, 2.14; Cl, 56.44%.

Reaction of ***1c*** *with Acrylonitrile.* The Diels-Alder adducts, 1,2,3,4,7,7-hexachloro-5-*endo*-cyanobicyclo[2.2.1]-hept-2-ene (**23n**) and its 5-*exo*-isomer (**23x**), were separated by the use of Column A at 165 °C (retention times: **23n**, 9.8 min; **23x**, 15.7 min). Mp: **23n**, 141—143 °C; **23x**, 72—75 °C. NMR (δ): **23n**, 3.62 (1H, dd, J=4 and 8 Hz, 5-*exo*-H), 2.86 (1H, dd, J=8 and 12 Hz, 6-*exo*-H), 2.32 (1H, dd, J=4 and 12 Hz, 6-*endo*-H); **23x**, 3.06 (1H, dd, J=4 and 8 Hz, 5-*endo*-H), 2.76 (1H, dd, J=4 and 12 Hz, 6-*exo*-H), 2.42 (1H, dd, J=8 and 12 Hz, 6-*endo*-H). Found: **23n**, C, 29.49; H, 0.86; Cl, 64.84%; **23x**, C, 30.35; H, 0.98; Cl, 63.92;. Calcd for $C_9H_3NCl_6$: C, 29.49,; H, 0.93; Cl, 65.29%.

Reaction of ***1c*** *with Methyl Methacrylate.* Since the GLC peaks of the Diels-Alder adducts, 1,2,3,4,7,7-hexachloro-5-*endo*-methoxycarbonyl-5-*exo*-methylbicyclo[2.2.1]hept-2-ene (**24n**) and its 5-*exo*-methoxycarbonyl-5-*endo*-methyl isomer (**24x**), did not resolve satisfactorily, the isomer distribution was determined by the integration of the NMR spectra. A mixture of **24n** and **24x**; mp 68—70 °C. NMR (δ, characteristic signals): **24n**, 3.79 (s, CO_2CH_3), 1.80 (s, 5-CH_3); **24x**, 3.85 (s, CO_2CH_3), 1.38 (s, 5-CH_3). For the same mixture, Found: C, 32.82; H, 2.17%. Calcd for $C_{10}H_8O_2Cl_6$: C, 32.21; H, 2.16%.

Reaction of ***1c*** *with Methyl 2-Butylacrylate.* Since the GLC peaks of the Diels-Alder adducts, 1,2,3,4,7,7-hexachloro-5-*endo*-methoxycarbonyl-5-*exo*-butylbicyclo[2.2.1]hept-2-ene (**25n**) and its 5-*exo*-methoxycarbonyl-5-*endo*-butyl isomer (**25x**), did not resolve satisfactorily, the isomer distribution was determined by the integration of the NMR spectra. NMR (δ, characteristic signals): **25n**, 3.78 (s, CO_2CH_3), 3.18 (d, J=12 Hz, 6-*endo*-H), 2.44 (d, J=12 Hz, 6-*exo*-H); **25x**, 3.96 (s, CO_2CH_3), 3.39 (d, J=12 Hz, 6-*exo*-H), 1.95 (d, J=12 Hz, 6-*endo*-H). Found: C, 37.62; H, 3.11; Cl, 51.53%. Calcd for $C_{13}H_{14}O_2Cl_6$: C, 37.62; H, 3.40; Cl, 51.27%.

Reaction of ***1c*** *with Isopropenyl Acetate.* The GLC and NMR indicated the presence of a single product, 1,2,3,4,7,-7-hexachloro-5-*endo*-acetoxy-5-*exo*-methylbicyclo[2.2.1]hept-2-ene (**7n**); colorless liquid. NMR (δ): 2.85 (2H, s, 6-*endo*-H and 6-*exo*-H), 2.02 (3H, s, $OCOCH_3$), 2.00 (3H, s, CH_3). Found: C, 32.51; H, 2.17; Cl, 57.11%. Calcd for $C_{10}H_8O_2Cl_6$: C, 32.21; H, 2.16; Cl, 57.05%.

Reaction of ***1c*** *with Methacrylonitrile.* The Diels-Alder adducts, 1,2,3,4,7,7-hexachloro-5-*endo*-cyano-5-*exo*-methylbicyclo[2.2.1]hept-2-ene (**8n**) and its 5-*exo*-cyano-5-*endo*-methyl isomer (**8x**), were separated by the use of Column A at 180 °C (retention times: **8n**, 7.0 min; **8x**, 8.7 min). Mp: **8n**, 185—188 °C; **8x**, 144—145 °C. NMR (δ): **8n**, 2.80 (2H, s, 6-*endo*-H and 6-*exo*-H), 1.98 (3H, s, CH_3); **8x**, 3.12 (1H, d, J=12 Hz, 6-*exo*-H), 2.12 (1H, d, J=12 Hz, 6-*endo*-H), 1.47 (3H, s, CH_3). Found: **8n**, C, 31.84; H, 1.36; Cl, 62.49%; **8x**, C, 32.00; H, 1.40; Cl, 62.42%. Calcd for $C_9H_5NCl_6$: C, 31.80; H, 1.48; Cl, 62.59%.

Reaction of ***1c*** *with α-Methylstyrene.* The Diels-Alder adducts, 1,2,3,4,7,7-hexachloro-5-*endo*-phenyl-5-*exo*-methylbicyclo[2.2.1]hept-2-ene (**26n**) and its 5-*exo*-phenyl-5-*endo*-methyl isomer (**26x**), were separated by the use of Column A at 180 °C (retention times: **26n**, 19.0 min; **26x**, 21.5 min). Mp: **26n**, 67—68 °C; **26x**, colorless liquid. NMR (δ): **26n**, 7.22 (5H, s, Ph), 3.12 (1H, d, J=14 Hz, 6-*exo*-H), 2.64 (1H, d, J=14 Hz, 6-*endo*-H), 1.90 (3H, s, CH_3); **26x**, 7.20—7.80 (5H, m, Ph), 3.50 (1H, d, J=13 Hz, 6-*exo*-H), 2.10 (1H, d, J=13 Hz, 6-*endo*-H), 1.38 (3H, s, CH_3). Found: **26n**, C, 42.92; H, 2.46; Cl, 54.11%; **26x**, C, 43.01; H, 2.71; Cl, 54.64%. Calcd for $C_{14}H_{10}Cl_6$: C, 43.21; H, 2.58, Cl, 54.48%.

Zinc-Acetic Acid Reductions of ***3n—8n.*** Williamson's procedure[12] was used, and the main products were collected by preparative gas chromatography (Column C at 170 °C). 1,2,3,4-*syn*-7-Pentachloro-5-*endo*-methoxycarbonylbicyclo-[2.2.1]hept-2-ene (**9n**), mp 58—59 °C (yield, 66%); lit,[8] 59—60 °C. 1,2,3,4-*syn*-7-Pentachloro-5-*endo*-acetoxybicyclo-[2.2.1]hept-2-ene (**10n**), mp 82—84 °C (yield, 57%); lit,[8] 83.5—84 °C. 1,2,3,4-*syn*-7-Pentachloro-5-*endo*-phenylbicyclo[2.2.1]hept-2-ene (**11n**), mp 61—63 °C (yield, 40%); lit,[8] 62—66 °C. 1,2,3,4-*syn*-7-Pentachloro-5-*endo*-cyano-5-*exo*-methylbicyclo[2.2.1]hept-2-ene (**13n**), mp 101—102 °C (yield, 91%). NMR (δ): 4.37 (1H, s, 7-*anti*-H), 2.78 (1H, d, J=13 Hz, 6-*endo*-H), 2.27 (1H, d, J=13 Hz, 6-*exo*-H), 1.71 (3H, s, CH_3). 1,2,3,4-*syn*-7-Pentachloro-5-*exo*-cyano-5-*endo*-methylbicyclo[2.2.1]hept-2-ene (**13x**), mp 112—114 °C (yield, 81%). NMR (δ): 4.66 (1H, s, 7-*anti*-H), 2.90 (1H, d, J=12 Hz, 6-*exo*-H), 2.17 (1H, d, J=12 Hz, 6-*endo*-H), 1.42 (3H, s, CH_3). Found: **13n**, C, 35.67; H, 2.06%; **13x**, C, 35.55; H, 2.11%. Calcd for $C_9H_6NCl_5$: C, 35.39; H, 1.98%. 1,2,3,4-*syn*-7-Pentachloro-5-*endo*-acetoxy-5-*exo*-methylbicyclo[2.2.1]hept-2-ene (**12n**), mp 74—75 °C (yield, 30%). NMR (δ): 4.30 (1H, s, 7-*anti*-H), 2.72 (1H, d, J=13 Hz, 6-*exo*-H), 2.42 (1H, d, J=13 Hz, 6-*endo*-H), 1.98 (3H, s, $OCOCH_3$), 1.80 (3H, s, CH_3). Found: C, 35.74; H, 2.85%. Calcd for $C_{10}H_9O_2Cl_5$: C, 35.48; H, 2.68%.

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