The Stereochemistry of the Diels–Alder Reaction. II. Lewis Acid Catalysis of Syn–Anti Isomerism[1]

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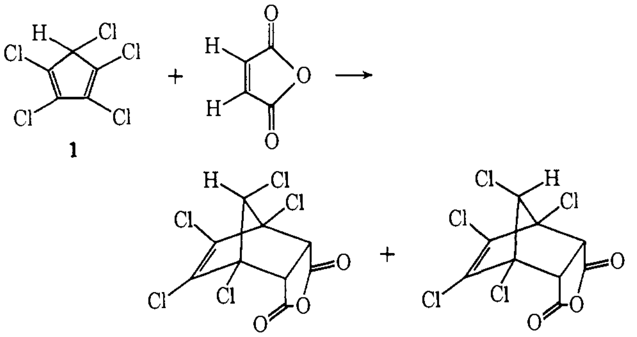
Abstract: Electronic and steric factors governing syn–anti isomerism in the Diels–Alder reaction have been investigated. Pentachlorocyclopentadiene (**1**) with many dienophiles gives bicycloheptene Diels–Alder adducts in which the predominant isomer has the chlorine atom on the bridge anti to the double bond. The amount of this isomer, which is disfavored on steric grounds, is *increased* by the addition of Lewis acids, in particular aluminum chloride. A greater percentage of this unexpected isomer is formed when the catalyst ($AlCl_3$, $TiCl_4$, BF_3) can form a complex with the dienophile (*e.g.*, maleic anhydride, methyl acrylate, acrylonitrile). The catalytic activity parallels the Lewis acid strength. These results lend further support to the hypothesis that the primary factor governing syn–anti isomerism in systems of this type is an attractive interaction due to dipole–dipole, dipole–induced dipole, and London dispersion forces between the diene and the dienophile (the polarity of which is increased on complexing with the Lewis acid). Lewis acids also increase the endo–exo ratio of the products and cause a very slight acceleration in the rate of this kinetically controlled Diels–Alder reaction.

The Diels–Alder reaction of cyclic dienes with dienophiles is governed by three "rules": the "cis principle" whereby the cis or trans stereochemistry of the diene and dienophile is retained in the product, the "endo addition rule" whereby the substituent is predominantly in the endo position in the product, and the rule of "steric approach control" whereby the diene and dienophile approach each other from their less-hindered sides.[3-5] It is this last rule which governs syn–anti isomerism and it is based simply on the logical expectation that bonding will take place most readily if no steric hindrance exists between diene and dienophile. However, until our recent work[6] no systematic study of the various factors governing syn–anti isomerism in the Diels–Alder reaction had been made.

We studied the reaction of pentachlorocyclopentadiene (**1**) with a variety of dienophiles to give **2–9a,b,c** in the relative amounts shown in Table I. In order that maleic anhydride give 90.8% of **2a** it is necessary for the potential bridge chlorine atom to be on the *inside* of the sandwich-like transition state **10** which gives rise to the product. This is contrary to the "natural expectation" of the rule of steric approach control.



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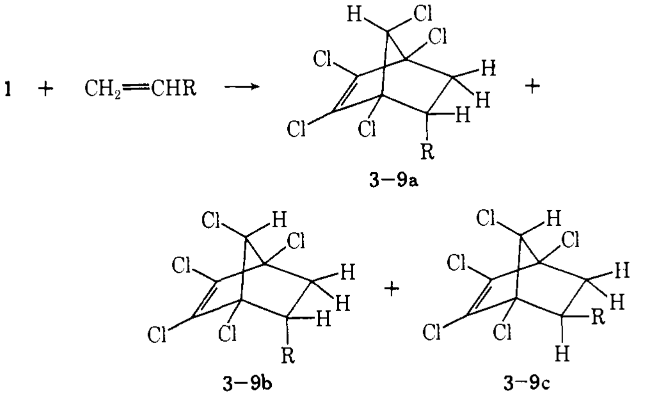
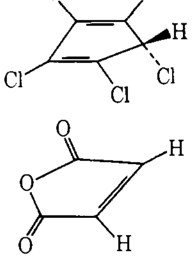
90.8%	uncatalyzed	9.2%
99%	catalyzed	1%
2a		**2b**



3–9a **3–9b** **3–9c**

R =	Anti-endo	Syn-endo	Syn-exo
-CN	**3a**	**3b**	**3c**
$-COOCH_3$	**4a**	**4b**	**4c**
$-OCOCH_3$	**5a**	**5b**	**5c**
-Br	**6a**	**6b**	**6c**
-Cl	**7a**	**7b**	**7c**
$-C_6H_5$	**8a**	**8b**	**8c**
$-CH_3$	**9a**	**9b**	**9c**



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The present work was undertaken to determine what effect, if any, Lewis acid catalysis would have on this reaction in the hope of gaining a further understanding of the molecular properties that govern syn–anti as well as exo–endo isomerism in the Diels–Alder reaction.

A remarkable acceleration of the *rate* of the Diels–Alder reaction by aluminum chloride was first recog-

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[2] Taken from the thesis of Y.-F. Li Hsu submitted to Mount Holyoke College in partial fulfillment of the requirements for the Ph.D. degree.

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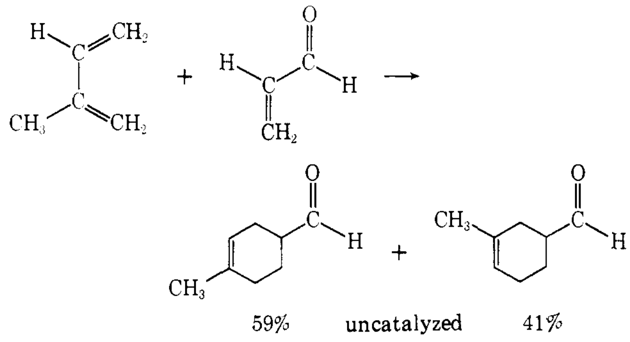
Table I. Diels-Alder Adducts of Pentachlorocyclopentadiene (**1**). Aluminum Chloride Catalyzed and Uncatalyzed Reactions

Compd no.	Dienophile	Dipole moment	Rel % of adducts Anti-endo **a**	 Syn-endo **b**	 Syn-exo **c**	 Anti-exo	React. time, hr	React. temp, °C	Yield,[a] %
2	Maleic anhydride		90.8	9.2			3	105	73
	$AlCl_3$ catalyzed[b]		99	1			2.5	100	80
3	Acrylonitrile	3.89[c]	71.7	15.1	13.2		6	100	62
	$AlCl_3$ catalyzed[b]		62.0	13.0	6.0	19.0	4.5	100	85
4	Methyl acrylate	1.67[d]	53.2	36.6	10.2		6	66	60
	$AlCl_3$ catalyzed[b]		69.1	28.5	2.4		0.75	66	77
5	Vinyl acetate	1.75[e]	47.7	45.1	7.2		8	120	73
6	Vinyl bromide	1.41[f]	48.1	35.1	16.8		18	100	90
7	Vinyl chloride	1.44[f]	45.5	40.0	14.5		26	100	97
	$AlCl_3$ catalyzed[b]		46.3	36.2	17.2		20	100	94
8	Styrene	0.56[g]	38.4	61.6			0.83	101	73
9	Propene	0.35[h]	31.3	11.7	57.0		6	100	90

[a] The remainder is primarily the dimer of **1**. [b] Approximately equal moles of aluminum chloride etherate, diene **1**, and dienophile. For exact amounts see the Experimental Section. [c] W. S. Wilcox, J. H. Goldstein, and J. W. Simmons, *J. Chem. Phys.*, **22**, 516 (1954). [d] R. J. W. LeFevre and K. M. S. Sundaram, *J. Chem. Soc.*, 3188 (1963). [e] I. Sakurada and S. Lee, *Z. Phys. Chem. Abt. B*, **43**, 245 (1939). [f] J. A. C. Hugill, I. E. Coop, and L. E. Sutton, *Trans. Faraday Soc.*, **34**, 1518 (1938). [g] W. Gallay, *Kolloid-Z.*, **57**, 1 (1931). [h] D. R. Lide and D. E. Mann, *J. Chem. Phys.*, **27**, 868 (1957).

nized by Yates and Eaton.[7] It was subsequently noted that the reaction is also catalyzed by other Lewis acids (BF_3, $TiCl_4$, $SnCl_4$) but the utility of such catalysis is hampered by the ease of polymerization of the dienes and dienophiles in the presence of the catalyst.[8] In 1964 it was reported that Lewis acids not only accelerate the rate, but also alter the isomer distribution when one is dealing with dienes and dienophiles which are both unsymmetrically substituted, *e.g.*, isoprene and acrolein.[9] Lewis acids alter the exo-endo ratio in reactions with cyclopentadiene.[10] For instance methyl acrylate gives an 80:20 ratio of endo to exo adducts in the uncatalyzed reaction but a 95:5 to 98:2 ratio when the reaction is catalyzed by Lewis acids ($AlCl_3$ etherate, BF_3 etherate, $TiCl_4$, $SnCl_4$).[10a,d]



59% uncatalyzed 41%

96% $SnCl_4 \cdot 5H_2O$ catalyzed 4%

11 **12**

There is no reason to suspect that the Lewis acid catalyzed Diels-Alder reaction involves any basic change in the mechanism of the reaction. The reaction of dimethyl fumarate with anthracene[7] and the reactions of dimethyl fumarate and maleate with cyclopentadiene[10d] and 9,10-dimethylanthracene[11] demonstrate that the stereochemical integrity of the dienophile is unaffected by the use of aluminum chloride.

Results and Discussion

Aluminum chloride increases the anti-syn ratio of isomers just as it has been shown to increase the endo-exo ratio to produce more of the seemingly less stable isomer. For instance, the uncatalyzed reaction of maleic anhydride and pentachlorocyclopentadiene[12] (**1**) gives 90.8% of the *anti*-7-chloro compound **2a**, which, as indicated above, is the unexpected isomer on steric grounds. Upon the addition of 1 equiv of aluminum chloride etherate[13] to the reactants this isomer is produced in quantitative yield.

An uncatalyzed reaction of methyl acrylate and **1** gives the three adducts **4a**, **4b**, and **4c** in the ratio[14] of 53:37:10. Boron trifluoride etherate has a negligible effect on this ratio (Table II) whereas 1 equiv of titanium tetrachloride has the same effect as 0.125 equiv of aluminum chloride etherate. A full equivalent of aluminum chloride changes the ratio to 69:29:2 by producing more of the anti-endo isomer **a** at the expense of the syn-endo and syn-exo isomers, **b** and **c**. This catalytic activity parallels the strengths of these three Lewis acids as recently determined by an nmr method.[15]

In addition to changing the product ratios aluminum chloride has two other effects on the reaction of **1** with methyl acrylate: as the amount of catalyst increases the reaction time decreases and the yields of adducts increase (Table II). Aluminum chloride forms a strong 1:1 complex[16] with methyl acrylate (*vide infra*); the catalyzed reaction of **1** takes place with this complex and is lightly faster than the uncatalyzed reaction (for reasons discussed below); since the competing reaction of **1** with itself to form dimer is not catalyzed, the yields of methyl acrylate adducts increase.

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(7) P. Yates and P. Eaton, *J. Amer. Chem. Soc.*, 82, 4436 (1960).

(8) G. I. Fray and R. Robinson, *ibid.*, **83**, 249 (1961).

(9) E. F. Lutz and G. M. Bailey, *ibid.*, **86**, 3899 (1964).

(10) (a) J. Sauer and J. Kredel, *Tetrahedron Lett.*, 731 (1966); (b) J. Sauer and J. Kredel, *Angew. Chem., Int. Ed. Engl.*, 4, 989 (1965); (c) R. F. Farmer and J. Hamer, *J. Org. Chem.*, 31, 2418 (1966); (d) T. Inukai and T. Kojima, *ibid.*, **31**, 2032 (1966).

(11) J. Sauer, D. Lang, and H. Wiest, *Chem. Ber.*, **97**, 3208 (1964).

(12) E. T. McBee and D. K. Smith, *J. Amer. Chem. Soc.*, 77, 389 (1955).

(13) W. Menzel and M. Froehlich, *Ber. Deut. Chem. Ges. B*, **75**, 1055 (1942). Aluminum chloride etherate was employed throughout this study because of the ease with which it can be purified and handled.

(14) Isomeric ratios are determined by integration of the glc curves and are considered to be accurate to *ca.* ±1%. Compounds are identified by collection and comparison of infrared spectra with authentic samples.[6]

(15) J. F. Deters, P. A. McCusker, and R. C. Pilger, Jr., *J. Amer. Chem. Soc.*, 90, 4583 (1968).

(16) For a comprehensive discussion of aluminum chloride complexes see "Friedel-Crafts and Related Reactions," Vol. I, G. A. Olah, Ed., Wiley-Interscience, New York, N. Y., 1963, p 543.

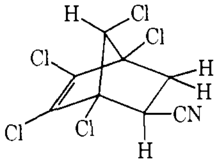
Table II. Lewis Acid Catalyzed Reaction of Pentachlorocyclopentadiene (1) with Methyl Acrylate[a]

Lewis acid	Catalyst, mmol	React. time, hr	Rel % of adducts: Anti–endo **4a**	Syn–endo **4b**	Syn–exo **4c**	Yield,[b] %
None		6	53.2	36.6	10.2	60
$BF_3 \cdot O(C_2H_5)_2$	6.5	6	53.8	37.6	8.6	59
	13.0	6	53.4	38.4	8.2	65
	19.5	4.5	53.2	38.8	8.0	60
$TiCl_4$	16	3	64.1	32.5	3.4	85
$AlCl_3 \cdot O(C_2H_5)_2$	1.63	3	64.1	32.5	3.4	82
	3.25	2	65.3	33.0	1.7	78
	6.50	1.5	66.8	30.8	2.4	83
	13.00	0.75	69.1	28.5	2.4	97

[a] 13 mmol of **1**, 16 mmol of methyl acrylate, and 50 ml of *p*-xylene heated at 66°. [b] The remainder is primarily the dimer of **1**.

To demonstrate that we are dealing with a kinetically controlled reaction, a mixture of **4a**, **4b**, and **4c** in the ratio 53.2:36.6:10.2 (*i.e.*, the products of the uncatalyzed reaction) was heated with 0.5 equiv of aluminum chloride etherate at 84° for 3 hr, conditions much more drastic than those employed for either the catalyzed or uncatalyzed reaction. The ratio of **a**:**b**:**c** was found to be unaffected by the catalyst.

The ratios of products obtained from the catalyzed and uncatalyzed reaction of vinyl chloride with **1** are very similar (Table I). By contrast, the product ratios for the acrylonitrile reaction were markedly altered by catalysis. The total per cent of *anti*-7-chloro products (81%) was greater than for the uncatalyzed reaction (71.7%), but surprisingly the reaction produced 19% of the *anti*-chloro *exo*-cyano adduct **13**. In none of the other reactions we have studied has an *anti*-7-chloro exo-substituted compound been detected. The structure proof for **13**, as for all the other compounds in this study, rests ultimately on nmr spectroscopy and is based on the well-established[17] stereospecific long-range coupling of a syn proton on the one-carbon bridge with an endo proton on the two-carbon bridge. In **13** the bridge proton couples with both the 5-endo proton (J = 0.98 Hz) and the 6-endo proton (J = 1.34 Hz).



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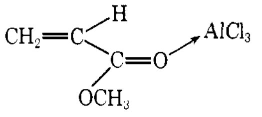
We have evidence for the formation of an aluminum chloride complex with at least one of the dienophiles. When a xylene solution of aluminum chloride etherate is mixed with a xylene solution of methyl acrylate, heat is evolved and on cooling white crystals form (mp 67° dec). These white crystals dissolve in chloroform and display in the nmr spectrum the peaks expected for methyl acrylate. Sauer has shown[10a,b] that the normal 1720-cm^{-1} carbonyl band of methyl acrylate is shifted to 1560–1640 cm^{-1} by the presence of aluminum chloride etherate, titanium tetrachloride, and stannic chloride. Esters form 1:1 complexes with aluminum chloride[18] whose infrared spectra show, in addition to lower frequency carbonyl stretch vibrations, increased acyl C–O and C–H stretch frequencies.[19] All this is consistent with a complex of this type



$$\mathrm{CH_2{=}CH{-}C(OCH_3){=}O \cdots AlCl_3}$$

in which the aluminum chloride is complexed with the carbonyl oxygen.

Rate of Reaction. It would take the reaction between anthracene and maleic anhydride 4800 hr to go to 95% completion, but upon the addition of 1 equiv of aluminum chloride the reaction is complete in 1.5 min.[7] In the present work it is seen that the rate of the catalyzed reactions of **1** is accelerated by a factor of 2 to 8 in comparison to the uncatalyzed reactions (see Table I). The reason for this great difference is that pentachlorocyclopentadiene belongs to the class of electron-deficient dienes.[5] Most Diels–Alder reactions involve electron-rich dienes and electron-poor dienophiles and the reaction is accelerated by electron-donating substituents in the diene and electron-attracting substituents in the dienophile. The highly halogenated dienes demonstrate just the opposite behavior, reacting most rapidly with electron-rich dienophiles. Diels–Alder reactions with "inverse electron demand," an idea proposed by Bachmann and Deno,[20] were first observed and investigated by Sauer[21] who found that maleic anhydride (electron-poor) reacts 47,000 times slower with hexachlorocyclopentadiene than with 9,10-dimethylanthracene but that *p*-methoxystyrene (electron-rich) reacts 31 times *faster* with the hexachlorodiene than with the 9,10-dimethylanthracene.

On this basis we might expect that the aluminum chloride catalyzed Diels–Alder reactions of **1** might proceed at a *slower* rate than the uncatalyzed reaction since the effect of aluminum chloride complexing with methyl acrylate, as an example, would be to lower the electron density in the methyl acrylate double bond. However, this does not happen. The catalyzed rereactions of **1** are slightly *faster* than the uncatalyzed reactions. It is noteworthy that aluminum chloride in our system changes the endo–exo ratio just as much as it does for the reaction of methyl acrylate with cyclopentadiene, but does not produce anything like the acceleration in rate. In other words the rate effect and the stereochemical effect must be considered separately in any rationalization of these results.

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[17] See ref 6 for numerous references.

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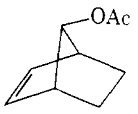
[21] J. Sauer and H. Wiest, *Angew. Chem.*, 74, 353 (1962); *Angew. Chem., Int. Ed. Engl.*, **1**, 249 (1962).

Mechanism of the Reaction. In discussing a mechanism for the Diels–Alder reaction we must consider syn–anti as well as exo–endo ratios of products and the effect of Lewis acid catalysts on these ratios. Our results show that *anti*-7-chloro isomers are favored over *syn*-7-chloro isomers in many instances (Table I) and that the percentage of anti isomers increases in the presence of Lewis acids. Two opposing factors govern this syn–anti ratio: steric effects which favor the *syn*-7-chloro isomers on the one hand and a positive attractive interaction between the C-7 chlorine and the dienophile which favors the *anti*-7-chloro isomers on the other.

It will be noted in Table I that there is a good correlation between the per cent of *anti*-7-chloro isomers, **a**, and the dipole moments of the monosubstituted dienophiles—the higher the dipole moments of the dienophile the greater the dipole interaction between the polar dienophile and the polarizable bridge chlorine atom in the transition state. When the dienophile is made even more polar by complexing with aluminum chloride (as in the case of methyl acrylate and acrylonitrile) the per cent of *anti*-7-chloro compound in the product increases. In the case of vinyl chloride, which is by no means a nonpolar molecule, the complexing with aluminum chloride is weak;[22] the polarity of the vinyl chloride is not increased and neither is the amount of *anti*-7-chloro isomer in the product.

The preferential formation of **14** reported by Winstein and Woodward[23] and the recently reported formation of **15** (in 73% yield) by Nenitzescu, *et al.*,[24] are further examples of the preferential formation of isomers not expected on steric grounds. On the other hand the addition of maleic anhydride to cycloheptatriene to give **16**[25] must be governed entirely by steric interactions.



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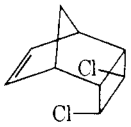

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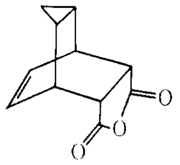

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The correlation between dienophile dipole moment and per cent of *anti*-7-chloro isomers suggests strongly that the prime factor governing syn–anti isomerism in this system is an attractive interaction between the diene and dienophile due to dipole–dipole, dipole-induced dipole, and London–dispersion forces.[6] Dipole–dipole interactions are proportional to the product of the molecular dipole moments and inversely proportional to the cube of the molecular separation. Dipole–induced dipole forces are proportional to the polarizabilities of the two molecules and inversely proportional to the sixth power of their separation and London–dispersion interactions are proportional to the product of the polarizabilities and ionization potentials and inversely proportional to the sixth power of the intermolecular separation. From these relationships we would expect the attraction between the polarizable potential bridge chlorine of the diene and a dienophile to increase if the polarity of the dienophile increased. Since these interactions are only effective at short range, being inversely proportional to the sixth power of the separation, we would expect preferential reaction on the side of the diene having the polarizable chlorine atom.

Aluminum chloride, in addition to causing an increase in the anti–syn ratio, also causes an increase in the endo–exo ratio (Table I), a catalytic effect which has been noted by others.[10] Endo substitution is favored for those dienophiles which have a substituent in conjugation with the olefinic bond (**2**, **3**, **4**, and **8** in the present study). This has been put on a quantum chemical basis by Hoffmann and Woodward[26] who demonstrated by extended Hückel calculations an energy lowering symmetry-allowed mixing of the highest occupied diene (or dienophile) orbital with the lowest unoccupied dienophile (or diene) orbital, a view subsequently substantiated by Herndon and Hall.[27] Aluminum chloride complexing of the dienophile obviously increases this π–π interaction.

The uncatalyzed reaction of **1** with a variety of dienophiles, while giving substantial amounts of the endo–anti isomers, **a**, did not give any exo–anti isomers. This we attribute to steric hindrance between the potential *anti*-7-chlorine atom and the potential exo substituent in the transition state. The catalyzed reaction of acrylonitrile did however produce 19% of the anti–exo compound **13**. This constitutes an interesting exception which we rationalize on the basis of a dipole attraction between the complexed nitrile group and the potential *anti*-7-chlorine (which is on a doubly allylic carbon atom) in the transition state, an interaction which outweighs the steric effect. Models indicate that steric hindrance between the axially symmetric nitrile and the potential bridge chlorine in the transition state is minimal. This is not true for the other dienophiles we have examined.

The close resemblance of the whole course of the catalyzed to the uncatalyzed Diels–Alder reaction in the present study indicates that the two are proceeding by substantially the same mechanism. On this basis we would rule out a long-lived zwitterionic intermediate of the type proposed by Thompson and Melillo[28] for the aluminum chloride catalyzed reaction of butadiene with 2-phenylcyclohexenone.

The syn–anti and endo–exo ratios of products obtained from the Diels–Alder reaction of pentachlorocyclopentadiene (**1**) are the result of a delicate balance between steric factors on the one hand and dipole attraction (and secondary orbital interactions for conjugated dienophiles) on the other. Lewis acids which can complex with the dienophile change this balance in a logical, if not quantitatively calculable manner. It is clear from these results that there is as yet no simple or single rationalization of the effect of Lewis acid catalysis in the Diels–Alder reaction which can be used in a generally predictive manner.

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Experimental Section

Infrared spectra were recorded as 5–10% solutions in carbon disulfide or chloroform on a Perkin-Elmer Model 137 spectrometer. An Aerograph Autoprep 705 gas chromatograph equipped with a Disc Model 224-4 integrator was used for both analytical and preparative purposes. The helium flow rate was 200 ml/min. The detector and injector were kept 30° above the column temperature. Proton magnetic resonance spectra were recorded as 30% solutions on a Varian HA-100 spectrometer. Melting points were taken on a Thomas-Hoover apparatus and are uncorrected. Microanalyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich. All commercially available materials employed in this work were distilled, recrystallized, or sublimed before they were used. All Diels–Alder reactions were terminated at the disappearance of the 13.12-μ diene band in the infrared spectrum.

Aluminum chloride etherate was prepared according to the procedure of Menzel and Froelich.[13] Aluminum chloride was sublimed under nitrogen at 170°. This (22.27 g, 0.167 mol) was slowly added to ice-cold anhydrous ether (13.3 g, 0.185 mol) keeping the temperature below 5°. After all the aluminum chloride had dissolved, aluminum chloride etherate crystallized slowly as white plates. The excess ether was removed at 27° (3 mm) and the product stored at 0° under vacuum.

Catalyzed Reaction of 1 with Maleic Anhydride. To a solution of 3.26 g (13.5 mmol) of 1,2,3,4,5-pentachlorocyclopentadiene[12] (**1**) and 1.57 g (16 mmol) of maleic anhydride in 25 ml of *p*-xylene was added a solution of 3.32 g (16.0 mmol) of aluminum chloride etherate in 25 ml of *p*-xylene under nitrogen. The reaction mixture immediately turned yellow. As the mixture was heated to 100° a white solid formed which remained during the whole reaction. The infrared spectrum indicated the completion of the reaction in 2.5 hr at which time the mixture was poured into 70 ml of 1 *M* hydrochloric acid cooled to 0° and extracted with ether. The organic layer was washed with water and saturated sodium chloride solution and dried over anhydrous sodium sulfate. The solution was concentrated under aspirator vacuum and analyzed by glc (SF-96 column, 200°). In addition to a 20% yield of the dimer of **1** two adducts were obtained in 80% yield. The first compound eluted (99%) was shown to be the *anti*-7-chloro compound **2a** by comparison of the melting point and infrared spectra[6] with an authentic sample. The second compound eluted in less than 1% yield was not identified.

In another run a mixture of 1.55 g (6.50 mmol) of **1**, 0.79 g (8.00 mmol) of maleic anhydride, and 1.66 g (8.00 mmol) of aluminum chloride etherate in 25 ml of xylene was heated for 13 hr at 70°. Working up the reaction as above gave a 79% yield of **2a** and a 21% yield of the dimer of **1**. No other compounds were detected.

Catalyzed Reactions of 1 with Methyl Acrylate. The reaction of **1** and methyl acrylate in the presence of boron trifluoride etherate, titanium tetrachloride, and aluminum chloride etherate was carried out with the results shown in Table II.

In a typical reaction a solution of 1.38 g (16 mmol) of methyl acrylate in 15 ml of *p*-xylene was added to an equal volume of a deep red solution of 3.05 g (16 mmol) of titanium tetrachloride in *p*-xylene. Red crystals formed instantly and the temperature rose to 38°. To the dark red mixture was added a solution of 3.10 g (13 mmol) of **1** in 20 ml of *p*-xylene. The reaction mixture was heated at 66° for 3 hr at which time the disappearance of the 13.13-μ diene band in the infrared spectrum indicated the completion of the reaction. The reaction mixture was poured into 80 ml of cold 1 *M* hydrochloric acid and the organic material extracted with ether. The ethereal extracts were washed with water and saturated sodium chloride solution and then dried over anhydrous sodium sulfate. Removal of the ether gave a viscous liquid shown to be 15% of the dimer of **1** and compounds **4a**, **4b**, and **4c** in the relative percentages 64.1, 32.5, and 3.4, respectively.

Demonstration of Kinetic Control. To a solution of 0.50 g (2.4 mmol) of aluminum chloride etherate in 14 ml of *p*-xylene was added 2.60 g (*ca.* 5 mmol) of a mixture of **4a**, **4b**, and **4c** in the relative percentages 53.2, 36.6, and 10.2. The reaction mixture was heated at 84° for 3 hr and worked up as above. Glc showed that these three isomers were present in exactly the same percentages as before heating with the catalyst.

Aluminum Chloride–Methyl Acrylate Complex. To a solution of 2.88 g (13.8 mmol) of aluminum chloride etherate in 50 ml of *p*-xylene was added 17.21 g (200 mmol) of methyl acrylate. The clear colorless solution was allowed to stand at room temperature for 2 days at which time long needlelike crystals had formed (mp 67°). The nmr spectrum of the crystals in hexadeuterioacetone was identical with that of methyl acrylate.

Catalyzed Reaction with Vinyl Chloride. A mixture of 1.55 g (6.5 mmol) of **1**, 1.66 g (8.0 mmol) of aluminum chloride etherate, 1.00 g (16 mmol) of vinyl chloride, 4 ml of dichloromethane, and a trace of hydroquinone was heated at 100° for 20 hr in an ampoule. The mixture was worked up and analyzed as above to give **7a**, **7b**, and **7c** in the relative percentages of 46.3, 36.2, and 17.7. There was in addition a 6% yield of dimer.

Catalyzed Reaction of 1 with Acrylonitrile. To a solution of 2.35 g (9.9 mmol) of **1** and 0.53 g (10 mmol) of acrylonitrile in 13 ml of *p*-xylene was added 2.08 g (10 mmol) of aluminum chloride etherate. The reaction mixture was heated at 100° for 4.5 hr at which time the infrared spectrum revealed the diene had been consumed. The reaction was worked up as above and analyzed by glc (QF-1 column, 210°). In addition to a 15% yield of the dimer of **1** four adducts were obtained in the relative percentages 62.0:13.0:6.0:19.0 and were shown to be, respectively, **3a**, **3b**, **3c**, and **13**. The first three were identified by comparison of their infrared spectra with authentic samples.

1,2,3,4-*anti*-7-Pentachloro-5-*exo*-cyanobicyclo[2.2.1]-2-heptene (**13**), a colorless oil, had $\lambda_{\max}^{\mathrm{CS_2}}$ 7.87, 8.47, 8.60, 9.48, 9.69, 11.81, 12.73, 13.19 μ; nmr δ 2.45 (6-exo, 1 H multiplet, J = 0.33, 4.12, −12.40 Hz), 2.79 (6-endo, 1 H multiplet, J = 1.34, 9.51, −12.40 Hz), 3.06 (5-endo, 1 H multiplet, J = 0.98, 4.12, 9.51 Hz), 4.09 (7-syn, 1 H multiplet, J = 0.33, 0.98, 1.34 Hz).

Anal. Calcd for $C_8H_4NCl_5$: C, 32.95; H, 1.38. Found: C, 32.79; H, 1.46.

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