The Stereochemistry of the Diels–Alder Reaction. *syn–anti* Isomerism[1]

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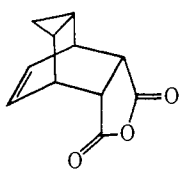
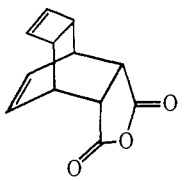
Abstract: Electronic and steric factors governing *syn–anti* isomerism in the Diels–Alder reaction have been investigated employing 1,2,3,4,5-pentachlorocyclopentadiene as the plane asymmetric dienophile. The predominance of *anti*-7-chloro isomers in many cases has been ascribed to forces arising from dipole–dipole, dipole–induced dipole, and London–dispersion interactions, the predominance of *endo* over *exo* isomers to secondary orbital interactions and the lack of *anti–exo* isomers to steric hinderance in the transition state.

Virtually every aspect of the Diels–Alder reaction has been studied during the past half-century. Its synthetic utility is unquestioned; its seeming simplicity has prompted numerous investigations into the details of its mechanism and stereochemistry.[3–6] The retention of stereochemistry in the diene and the dienophile and the predominance of *endo* addition to cyclic dienes are well-established principles.[7] Yet one aspect of this reaction has not been systematically investigated—the question of *syn–anti* isomerism.[8]

Numerous more or less isolated examples of *syn–anti* isomerism have been reported in the last few years, but no pattern to the stereochemistry of the products is discernible and no attention has been focused on this aspect of the reaction. It is generally assumed[3,5,6] that a dienophile will approach an asymmetric cyclic diene from the unhindered side to give the product with the bridge substituent *syn* to the double bond in the product. Thus the reaction of maleic anhydride with cycloheptatriene[9] and cyclooctatetraene[10] gives **1** and **2**, respectively. On the other hand 5-acetoxy-1,3-cyclopentadiene with ethylene gives **3**[11] in which the dienophile must have approached the diene from the more hindered side. Similarly 5-methyl-1,3-cyclopentadiene with N-phenylmaleimide gives equal amounts of *syn*-7- and *anti*-7-methyl adducts, **4** and **5**.[12] A number of other examples could be cited in which the proof of stereochemistry is not so rigorous as in these four examples. For example Alder and Stein reported that 5-carbomethoxy-1,3-cyclopentadiene dimerizes to give **6**[13] whereas the structure of the dimer has recently been shown to be **7**.[14] And 1,2,3,4,5-pentachlorocyclopentadiene has been claimed to give only the *syn*-7-chloro products,[15] **8**, with esters of maleic acid, a claim which we shall show is incorrect. These latter examples illustrate the primary reason that this aspect of the Diels–Alder reaction has received so little attention—the difficulty in proving the configuration at the bridge carbon atom.



1 (*syn*)



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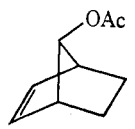
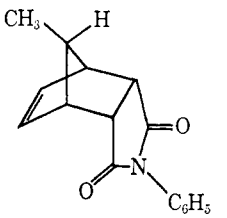
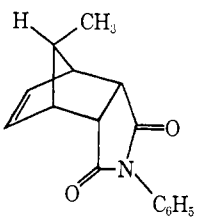


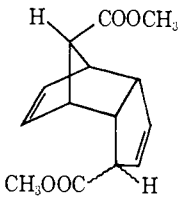
3 (*anti*)



4 (*syn*)



5 (*anti*)



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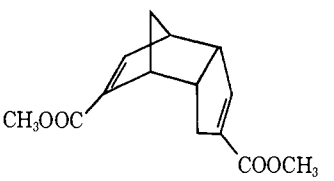

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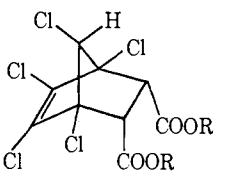

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(1) Presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1–5, 1968, and the Halocarbon Conference held at the Eastern Research Laboratory of the Dow Chemical Co., Wayland, Mass., May 5–8, 1968.

(2) Taken from the thesis of Mrs. Hsu submitted to Mount Holyoke College in partial fulfillment of the requirements for the Ph.D. degree.

(3) (a) J. Sauer, *Angew. Chem.*, 79, 76 (1967); *Angew. Chem. Intern. Ed. Engl.*, 6, 16 (1967); (b) J. Sauer, *Angew. Chem.*, 78, 233 (1966); *Angew. Chem. Intern. Ed. Engl.*, 5, 211 (1966).

(4) A. Wassermann, "Diels–Alder Reactions," Elsevier Publishing Co., New York, N. Y., 1965.

(5) A. S. Onishchenko, "Diene Synthesis," Oldbourne Press, London, 1964.

(6) J. G. Martin and R. K. Hill, *Chem. Rev.*, **61**, 537 (1961).

(7) K. Alder and G. Stein, *Angew. Chem.*, 50, 510 (1937).

(8) See p 556 of ref 6.

(9) (a) K. Alder and G. Jacobs, *Chem. Ber.*, **86**, 1528 (1953); (b) K. Alder, K. Kaiser, and M. Schumacher, *Ann.*, 602, 80 (1957); (c) M. J. Goldstein and A. H. Gewirtz, *Tetrahedron Lett.*, 4415 (1965).

(10) (a) M. Avram, G. Mateescu, and C. D. Nenitzescu, *Ann.*, **636**, 174 (1960); (b) M. Avram, E. Sliam, and C. D. Nenitzescu, *ibid.*, **636**, 184 (1960).

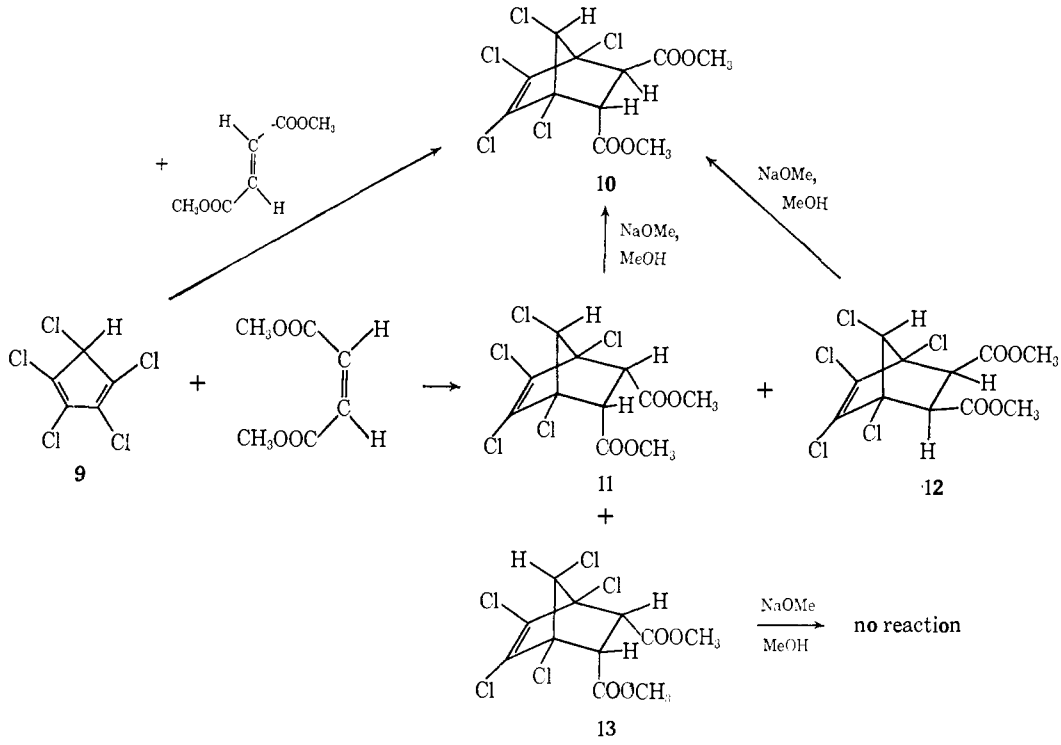
(11) S. Winstein, M. Shavatsky, C. Norton, and R. B. Woodward, *J. Am. Chem. Soc.*, 77, 4183 (1955).

(12) S. McLean and P. Haynes, *Tetrahedron*, 21, 2313 (1965).

(13) K. Alder and G. Stein, *Ann.*, **515**, 185 (1935).

(14) G. L. Dunn and J. K. Donahue, *Tetrahedron Lett.*, 3485 (1968).

(15) N. N. Mel'nikov and S. D. Volodkovich, *Zh. Obshch. Khim.*, **28**, 3317 (1958).



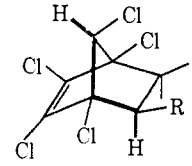
The addition of 1,2,3,4,5-pentachlorocyclopentadiene, **9**,[16] to various dienophiles gives, in many cases, predominantly the *anti*-7-chloro isomer. This isomer is *not* expected on the basis of steric effects in the transition state. We report here the results of adding **9** to eleven different dienophiles. The adducts were quantitatively analyzed and separated by preparative gas chromatography (glpc). In most cases the proof of stereochemistry at the bridge carbon atom rests on long-range nmr coupling constant data reinforced, as will be shown, by epimerization results, chromatographic behavior, and chemical shift correlations.

Results

By the addition of dimethyl maleate and fumarate to 1,2,3,4,5-pentachlorocyclopentadiene, **9**, we sought to show that this is a normal, kinetically controlled Diels–Alder reaction which obeys the "*cis*" principle[7] and the *endo* addition rule[7] even though the diene belongs in the "electron deficient" category.[3] Compound **9** is readily prepared by the catalytic or chemical reduction of commercially available hexachlorocyclopentadiene.[16] Like cyclopentadiene it dimerizes at room temperature to give a quantitative yield of dimer, mp 221°; this dimerization is the principal side reaction noted throughout this work.

The Diels–Alder reaction of **9** with a very slight excess of dimethyl fumarate in refluxing *p*-xylene under nitrogen was complete in 20 min as shown by disappearance of the intense diene band at 13.12 μ. Removal of the solvent gave a yellow-white solid which was shown by glpc to be 20% dimer and 80% of a single compound, isolated by crystallization in 76% yield, assigned structure **10**.

Reaction of dimethyl maleate under the same conditions took five times as long[17] (100 min) to give 20% dimer and roughly equal quantities[18] of three adducts isolated by column chromatography. The compound, mp 192.5–193°, was assigned the *syn*-chloro-*endo* structure, **11**, the one, mp 184–184.5°, the *syn*-chloro-*exo* structure, **12**, and the one, mp 135–137°, the *anti*-chloro-*endo* structure, **13**. The infrared spectrum of each of the four adducts (**10–13**) showed a strong carbonyl band at 5.8 μ and the highly characteristic *cis*-chlorinated double bond band at 6.30 μ. Compounds **11**, **12**, and **13** had nmr peaks at *ca.* 3.8 ppm of relative area 6 while **10** had a 3-proton peak at 3.82 and another at 3.76 ppm all assigned to the $-OCH_3$ group. Compound **10** had two one-proton doublets at 3.64 and 3.49 ppm (J = 4.82 Hz) confirming the *trans* arrangement of protons on C-5 and C-6. Compounds **11**, **12**, and **13** had singlets (area 2) at 3.8, 3.4, and 4.0 ppm in keeping with the *cis* stereochemistry of protons on C-5 and C-6. Compounds **10**, **11**, **12**, and **13** had singlets (area 1) at 5.0, 4.4, 5.5, and 4.2 ppm assigned to the single bridge proton. In **10**, **11**, and **12** the width of the peak at half-height was 0.5 Hz, in **13** 0.7 Hz. The fact that this peak was a singlet in each case rules out all compounds having the bridge proton *syn* to the double bond and a proton in the *endo* configuration on C-5 or C-6 as in **14**. If this



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configuration existed, long-range coupling over the coplanar W of the order of 1–2 Hz would be expected.

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

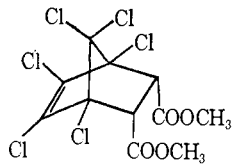
(17) A similar difference in reaction rates has been noted for the reaction of dimethyl fumarate and dimethyl maleate with cyclopentadiene (J. Sauer, H. Wiest, and M. Mielert, *Z. Naturforsch.*, 17B, 203 (1962)).

(18) In this one case the gas chromatogram was not well resolved. The addition of dimethyl maleate to cyclopentadiene gives 75% *cis-endo* product and 25% *cis-exo* product (J. Sauer, H. Wiest, and A. Mielert, *Ber.*, 97, 3183 (1964)).

This long-range coupling, for which there is now ample precedent,[19] is the key to the structure assignments made throughout this work and was found in all compounds having *syn* and *endo* protons.

Each compound was treated for 2 days with sodium methoxide in methanol. Compounds **10** and **13** were recovered unchanged and compounds **11** and **12** each gave **10**. Obviously the *anti*-chlorine in **13** inhibits epimerization of both carbomethoxy groups by steric hinderance while in **11** and **12** no such hinderance exists and the *cis* interaction of the two carbomethoxy groups can be relieved by epimerization of one ester group to give the thermodynamically stable **10**. This one experiment gives a very clear picture of the steric interactions involved in this system.

We have recently shown that 7,7-dichlorobicycloheptenes are stereoselectively reduced to 7-*syn*-chloro compounds by zinc and acetic acid or chromous acetate.[20] The reduction of **15**[21] with zinc dust in refluxing acetic acid gave **11** in 55% yield, further confirming our structure assignments.



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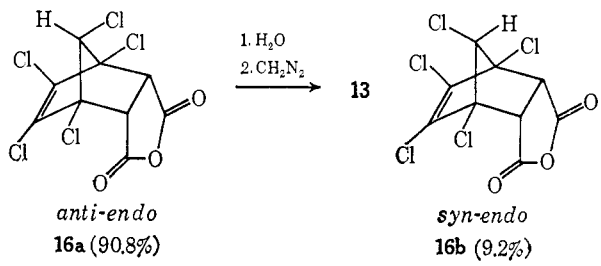
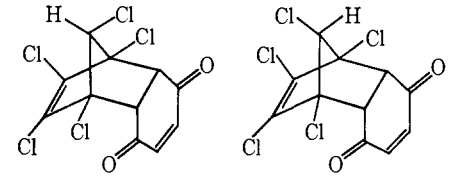
These results with dimethyl fumarate and dimethyl maleate indicate that the reaction with pentachlorocyclopentadiene, **9**, is a normal kinetically controlled Diels–Alder reaction in which the stereochemistry of the dienophile is retained and *endo* products predominate. Furthermore the predominant products are those in which the dienophile approaches the unhindered side of the diene to give products having a 7-*syn*-chlorine on the bridge, as one might expect. However, the reaction of maleic anhydride with **9** gave rather unexpected results.

When pentachlorocyclopentadiene, **9**, and a slight excess of maleic anhydride were heated at 105° in xylene there was obtained, in addition to dimer, two products **16a** and **16b**, in the ratio 90.8:9.2. That the predominant product was the unexpected *anti*-7-chloro isomer was shown by its conversion to **13** on hydrolysis and diazomethane esterification. The *endo-syn* configuration for **16b** follows from the lack of long-range coupling of the bridge proton and the protons on C-5 and C-6. Similarly *p*-benzoquinone gave only two adducts (no dimer) in 60.1 and 39.9% yield which by analogy with **16a** and **16b** as well as nmr data (see below) are assigned structures **17a** and **17b**.



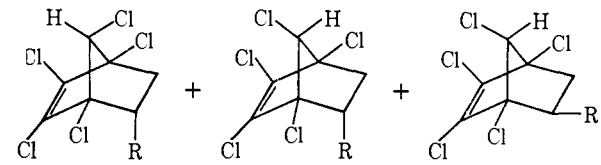
anti-endo **16a** (90.8%) — **13** — *syn-endo* **16b** (9.2%)



17a (60.1%) **17b** (39.9%)

In order to study this surprising result more carefully we added a series of monosubstituted olefins to **9** to give compounds **18–24a, b, c**

9 + CH_2=CHR →



	anti-endo	*syn-endo*	*syn-exo*
R = CN	**18a**	**18b**	**18c**
$COOCH_3$	**19a**	**19b**	**19c**
$OCOCH_3$	**20a**	**20b**	**20c**
Br	**21a**	**21b**	**21c**
Cl	**22a**	**22b**	**22c**
C_6H_5	**23a**	**23b**	**23c**
CH_3	**24a**	**24b**	**24c**

The structure proof for these compounds is best illustrated by the methyl acrylate adducts **19a, b, c**. These were prepared by reacting a slight excess of methyl acryate with **9** in xylene at 66°. The reaction was followed by infrared spectra and was complete in 6 hr; the three products were completely resolved on glpc and were collected in sufficient quantity for all analyses. The first product eluted was assigned the structure **19a**, the second which appeared a short time later was assigned structure **19c**, and the third with a rather longer retention time was assigned structure **19b**. This order of elution (**a, c, b**) prevailed for all adducts analyzed on the same chromatographic column.[22,23] All three compounds had carbonyl bands at 5.76 μ and carbon–carbon double bond bands at 6.30 μ in their infrared spectra.

We have previously analyzed the nmr spectra of **25**.[24] The spectrum of **19a** resembles that of **25** (R = COOH) very closely except that the peaks assigned to the C-6 *endo* proton are split (1.42 Hz) by coupling to the bridge proton[19] as well as being coupled to the C-5-*exo* and

(19) (a) J. Meinwald and Y. Meinwald, *J. Am. Chem. Soc.*, 85, 2514 (1963); (b) P. R. Story, L. C. Snyder, D. C. Douglass, E. W. Anderson, and R. L. Kornegay, *ibid.*, 85, 3630 (1963); (c) J. C. Davis, Jr., and T. V. Van Auken, *ibid.*, 87, 3900 (1965); (d) C. W. Jefford, B. Waegell, and K. Ramey, *ibid.*, 87, 2191 (1965); (e) J. Meinwald, Y. C. Meinwald, and T. N. Baker, III, *ibid.*, 86, 4074 (1964); (f) P. Laszlo and P. von R. Schleyer, *ibid.*, 86, 1171 (1964); (g) E. I. Snyder and B. Franzus, *ibid.*, 86, 1166 (1964); (h) P. M. Subramanian, M. T. Emerson, and N. A. LeBel, *J. Org. Chem.*, 30, 2624 (1965); (i) K. Tori, K. Aono, Y. Hata, R. Muneyuki, T. Tsuji, and H. Tanida, *Tetrahedron Lett.*, 9 (1966); (j) K. C. Ramey, D. C. Lini, R. M. Moriarty, H. Gopal, and H. G. Welsh, *J. Am. Chem. Soc.*, 89, 2401 (1967).

(20) K. L. Williamson, Y.-F. Li Hsu, and E. I. Young, *Tetrahedron*, 24, 6007 (1968).

(21) L. M. Kogan, *Zh. Org. Khim.*, 1, 458 (1965).

(22) The acetate adduct was separated on an SE-30 column, all other adducts on a QF-1 column.

(23) The relative elution time of isomers from a glpc column is related to their geometries. Generally the more symmetrical the isomer, the shorter will be its retention time. See E. L. Eliel and N. L. Allinger, "Conformational Analysis," Interscience Publishers, New York, N. Y., 1965; and C. S. Kraihanzel and M. L. Losee, *J. Am. Chem. Soc.*, 90, 4701 (1968).

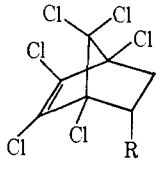
(24) K. L. Williamson, *ibid.*, 85, 516 (1963).

Table I. Diels–Alder Adducts of Pentachlorocyclopentadiene (9)

Compd no.	Dienophile	Dipole moment	Relative per cents of adducts[a] anti-endo a	syn-endo b	syn-exo c	Reaction time, hr	Reaction temp, °C	Diene:dienophile, mmoles	Yield, %
16	Maleic anhydride		90.8	9.2		3	105	13:16	73
17	*p*-Benzoquinone		60.1	39.9		2.5	112	13:16	99
18	Acrylonitrile	3.89[d]	71.7	15.1	13.2	6	100	19.8:20	62
			71.6	14.8	13.6[b]				
19	Methyl acrylate	1.67[e]	53.2	36.6	10.2	6	66	13:16	60
20	Vinyl acetate	1.75[f]	47.7	45.1	7.2	8	120	13:16	73
21	Vinyl bromide	1.41[g]	48.1	35.1	16.8	18	100	6.5:25	90
22	Vinyl chloride	1.44[g]	45.5	40.0	14.5	26	100	6.5:26	97
23	Styrene	0.56[h]	38.0	62.0		3.5	65	13:16	72
			38.4	61.6[c]		0.83	101	19.8:20.0	73
			42.2	57.8[b]		0.25	142	19.8:20.0	74
24	Propene	0.35[i]	31.3	11.7	57.0	6	100	7.8:25	90

[a] Determined by integration of glpc chromatogram. [b] Determined by integration of nmr spectrum. [c] Determined by quantitative column chromatography. [d] W. S. Wilcox, J. H. Goldstein, and J. W. Simmons, *J. Chem. Phys.*, **22**, 516 (1954). [e] R. J. W. LeFevre and K. M. S. Sundaram, *J. Chem. Soc.*, 3188 (1963). [f] I. Sakarada and S. Lee, *Z. Phys. Chem.*, **B43**, 245 (1939). [g] J. A. C. Hugill, I. E. Coop, and L. E. Sutton, *Trans. Faraday Soc.*, **34**, 1518 (1938). [h] W. Gallay, *Colloid-Z.*, **57**, 1 (1931). [i] D. R. Lide and D. E. Mann, *J. Chem. Phys.*, **27**, 868 (1957).

C-6-*exo* protons. A one-proton multiplet at 4.05 ppm split by 1.42 Hz is assigned to the bridge proton. This bridge proton also displayed small couplings to the 5- and 6-*exo* protons of 0.30 and 0.45 Hz. Compound



25, R = OAc, OH, Cl, C_6H_5, COOH, CN

19b has three quartets of equal intensities and two singlets with relative peak areas 1:3 assignable to 5-*exo*, 6-*exo*, 6-*endo*, 7-bridge, and $-OCH_3$ protons. Since no long-range coupling was observed, the bridge proton must be in the *anti* configuration. Similarly **19c** displays a single sharp peak for the bridge proton. That **19b** has the *endo* and **19c** the *exo* configuration was demonstrated by nmr and epimerization experiments.

In bicyclo[2.2.1]heptane or heptene systems 5- and 6-*exo* protons absorb at lower field strengths in the nmr than do 5- and 6-*endo* protons.[19h,j,25] Therefore compound **19b** is assigned the *endo* configuration (5- and 6-*exo* protons at 3.27 and 2.35 ppm) while **19c** is assigned the *exo* configuration (5- and 6-*endo* protons at 2.95 and 2.31 ppm). This conclusion is confirmed by epimerizing each compound with sodium methoxide in methanol at room temperature. Compound **19b** gave after 7 days a mixture containing 54% **19c** and 46% **19b** while compound **19c** gave after 10 days under the same reaction conditions 63.5% **19c** and 36.5% **19b**. As expected[26] **19c** with an *exo*-carbomethoxy group is thermodynamically more stable than **19b**. Compound **19a** was unchanged on treatment with methoxide, indicating that steric hinderance exists between the 7-*anti* chlorine atom and an *exo* substituent.

(25) R. V. Moen and H. S. Makowski, Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, Q 9.

(26) (a) K. Alder and G. Stein, *Ann.*, **514**, 211 (1934); (b) K. Alder and G. Stein, *ibid.*, **525**, 183 (1936); (c) J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, **76**, 4501 (1954); (d) C. F. Wilcox, Jr., M. Sexton, and M. F. Wilcox, *J. Org. Chem.*, 28, 1079 (1963).

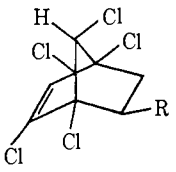
In a similar manner acrylonitrile, vinyl acetate, vinyl bromide, vinyl chloride, styrene, and propene were added to **9** with the results shown in Table I. The configurations of the protons at C-7 and C-5 were established by nmr. The 7-*syn*-chloro-*endo*-acetoxy configuration of **20b** was further confirmed by zinc/acetic acid reduction of the corresponding hexachloro compound, the complete details of which have recently been published.[20] The isomer ratios for **18a, b, c** determined by both glpc and integration of the nmr spectrum of the crude reaction mixture agreed very well (see Table I), thus indicating that the adducts are stable at the rather high temperature of the gas chromatograph and further demonstrating that these are the products of a kinetically controlled reaction.

The styrene adducts were prepared at three different temperatures. At 142° the reaction was complete in 0.25 hr; at 65° it took 3.5 hr to complete. There was a very small change in the isomer ratios over this temperature range. Each isomer was isolated and heated in xylene at 115° for 1.5 hr and recovered unchanged, proving that the products are those of kinetic and not thermodynamic control.

Discussion

In their comprehensive review of the stereochemistry of the Diels–Alder reaction, Martin and Hill[6] enunciate the principle which governs the configuration of the adducts from asymmetric dienes and dienophiles: "Those faces of the addend planes which offer the least non-bonded repulsion will be juxtaposed in the favored preliminary complexes and transition states. This rule simply enunciates the natural expectation that the dienophile should approach the less hindered side of the diene."

In one sense the present results are in agreement with this rule, but in another sense they clearly contravene it. If the addition of dienophiles to **9** were a purely random process we would expect four isomeric products, the *exo* and *endo* isomers of both the *syn*- and *anti*-7-chlorobicyclo[2.2.1]heptenes. We have never observed the *anti*-chloro-*exo* isomers, **26**. This we attribute to steric hindrance in the transition state leading to this isomer, supported by failure of **13** and **19a** to racemize to *exo* isomers. On the other hand the fact that **9** gives *pre-*



26

dominantly anti-chloro-*endo* products, **16a–19a**, in four of the nine cases we have examined is clearly at variance with the rule of steric approach control. This observation must be accounted for in any rationale of the mechanism of this reaction.

The mechanism of the Diels–Alder reaction is intimately linked with the numerous attempts to account for Alder's *endo* addition rule. This was first phrased in terms of "maximum accumulation of unsaturation" by Alder and Stein.[7] In more recent times this has been restated in quantum chemical terms by Hoffmann and Woodward,[27] who note that the *endo* transition state is stabilized, *vis à vis* the *exo* alternative, by symmetry-controlled secondary orbital interactions. This view was supported by Herndon and Hall with extended Hückel calculations,[28] but more recently these authors have concluded that such secondary orbital interactions may be relatively unimportant and that geometrical overlap relationships of the π orbitals at only the primary bonding centers need be considered.[29] Wassermann[4,30] has consistently emphasized the role of inductive forces, while Woodward and Baer[31] at one time put forward the idea that charge transfer between diene and dienophile causing electrostatic forces was the controlling factor and Berson[32] argued that *endo* addition would be favored by the attraction arising from dipole induction forces between the highly polarizable diene and the polar groups of the dienophile. He did, however, not discount the alternative postulate of some direct electronic interaction between the developing double bond in the diene and the unsaturated substituent of the dienophile—a forerunner of the Hoffmann–Woodward postulate.

In the present work we have examined a number of the physical properties of the seven monosubstituted olefins **18–24** in an effort to understand why, for example, acrylonitrile should give 72% of the *anti*-7-chloro isomer while styrene gives only 38% (Table I). Secondary orbital interactions can not be invoked; dienophiles with conjugated π electrons (*e.g.*, acrylonitrile and styrene) gave both large and small amounts of *anti*-7-chloro isomers. No steric preference is evident; however, a relationship does exist between the dipole moments of the monosubstituted olefins and the amounts of *anti*-7-chloro isomers **18a–24a** formed (Table I); the larger the dipole moment the higher the percentage of *anti* isomer. This suggests that the primary force controlling *syn–anti* isomerism in this system is produced by interactions of the van der Waals–London type.

These attractive forces have been carefully examined in studies of the vertical interactions between stacked nucleic acid bases in DNA.[33] In many ways these stacked bases resemble the transition state of the Diels–Alder reaction. The overlapping of π-electron clouds and charge-transfer complexes have been found to make a negligible contribution to the stability of the double-helical structure of DNA in comparison to interactions of the van der Waals–London type. These forces have been evaluated by DeVoe and Tinoco[34] and are considered to be the sum of contributions from dipole–dipole ($E_{\mu\mu}$), dipole–induced dipole ($E_{\mu a}$) and London/dispersion (E_L) interaction energies. The dipole–dipole

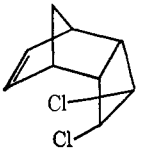
$$E_D = E_{\mu\mu} + E_{\mu a} + E_L$$

interactions are directly proportional to the product of the molecular dipole moments and inversely proportional to the cube of the molecular separation while the dipole–induced dipole is directly proportional to the polarizabilities of the two molecules and inversely proportional to the sixth power of their separation. The London/dispersion term is proportional to the product of the polarizabilities and ionization potentials and inversely proportional to the sixth power of the intermolecular separation. Pentachlorocyclopentadiene will therefore have the greatest interaction with dienophiles having the largest dipole moments. Furthermore, since chlorine has a greater polarizability than hydrogen, it is thermodynamically favored on the inside of the sandwichlike transition state, despite its larger size.[35]

Since bromine has a greater polarizability than chlorine, we might expect preferential reaction with a molecule having bromine on one side and chlorine on the other. To test this postulate we sought to prepare the adducts of 1-bromopentachlorocyclopentadiene (**27**).[36]

The bromine atom with a polarizability of 3.34 *vs.* 2.28 for chlorine would be expected to form **28** preferentially. Unfortunately **27** isomerized during the course of the reaction; the product consisted of a mixture of 1,2- and 3-bromopentachlorocyclopentadiene adducts (**28** (*syn* and *anti*), **29**, **30**), as deduced from the nmr spectrum.

Having accounted for the formation of the *anti* chloro isomers by a dipole interaction mechanism we turn our attention to isomers **18–24**, **b** and **c**, the *endo* and *exo* isomers of the *syn*-7-chloro products. We are immediately



i

(27) R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 4388 (1965).

(28) W. C. Herndon and L. H. Hall, *Theoret. Chim. Acta*, 7, 4 (1967).

(29) W. C. Herndon and L. H. Hall, *Tetrahedron Letters*, 3095 (1967).

(30) A. Wassermann, *J. Chem. Soc.*, 825, 1511 (1935); 432 (1936); *Trans. Faraday Soc.*, **35**, 841 (1939).

(31) R. B. Woodward and H. Baer, *J. Am. Chem. Soc.*, **66**, 645 (1944).

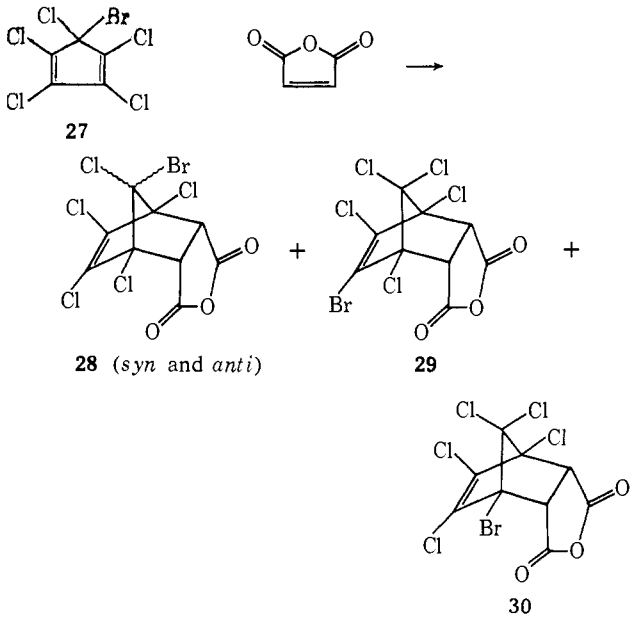
(32) J. A. Berson, A. Remanick, and W. A. Mueller, *ibid.*, 82, 5501 (1960).

(33) For a critical review, see A. Pullman and B. Pullman in "Advances in Quantum Chemistry," Vol. 4, Per-Olov Lowdin, Ed., Academic Press, New York, N. Y., 1968, p 267.

(34) H. DeVoe and I. Tinoco, Jr., *J. Mol. Biol.*, 4, 500 (1962).

(35) *cis*-3,4-Dichlorocyclobutene and cyclopentadiene give i in 73% yield (M. Avram, I. G. Dinulescu, Gh. D. Mateescu, and C. D. Nenitzescu, *Rev. Roum. Chim.*, **13**, 505 (1968)), an observation explicable in terms of the mechanism proposed here. See also W. C. Herndon and J. M. Manion, *J. Org. Chem.*, **33**, 4504 (1968), for a discussion of steric effects in the retro-Diels–Alder reaction involving a nonpolarizable 7-*anti*-methyl group.

(36) Dr. Victor Mark, Hooker Chemical Co., Niagara Falls, N. Y., private communication.



27

28 (*syn* and *anti*) 29

30

struck by the fact that the ratios of these *endo* and *exo* isomers to each other are very similar to the *endo–exo* ratios for the adducts of the same dienophiles to cyclopentadiene (Table II).

Table II. Comparison of *endo–exo* Ratios for Pentachlorocyclopentadiene and Cyclopentadiene

Compd no.	Dienophile	Pentachlorocyclopentadiene *endo*:*exo* b:c	Cyclopentadiene *endo*:*exo*
16	Maleic anhydride	100:0	100:0[a]
17	*p*-Benzoquinone	100:0	100:0[b]
18	Acrylonitrile	54:46	60:40[c]
19	Methyl acrylate	78:22	76:24[d]
20	Vinyl acetate	86:14	81:19[e]
21	Vinyl bromide	68:32	Mostly *endo*[f]
22	Vinyl chloride	74:26	Mostly *endo*[f]

[a] K. Alder and G. Stein, *Ann.*, **514**, 1 (1934). [b] A. Wassermann, *J. Chem. Soc.*, 828 (1935). [c] K. Alder, K. Heimbach, and R. Reubke, *Ber.*, **91**, 1516 (1958). [d] A. C. Cope, E. Ciganek, and W. A. LeBel, *J. Am. Chem. Soc.*, **81**, 2799 (1959). [e] J. D. Roberts, F. O. Johnson, and R. A. Carboni, *ibid.*, **76**, 5692 (1954). [f] J. D. Roberts, E. R. Trumball, Jr., W. Bennett, and R. Armstrong, *ibid.*, **72**, 3116 (1950).

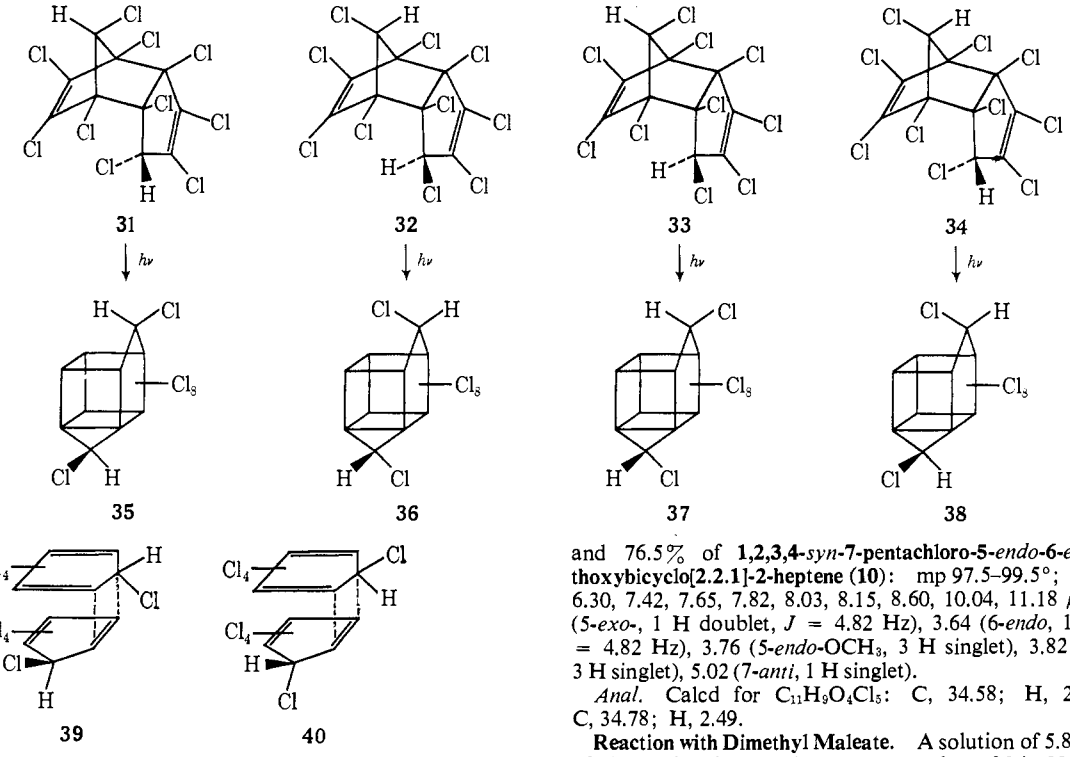
The pattern of these *endo*:*exo* ratios clearly does not parallel the dipole moments of the dienophiles, nor does it depend upon steric requirements, *e.g.*, the propene adduct is mostly *exo* while the vinyl bromide adduct is mostly *endo* yet the van der Waals radii of these two groups are roughly the same (2.0 and 1.95 Å, respectively). The explanation seems to lie right where Alder and Stein[7] and more recently Hoffmann and Woodward[27] put it—secondary orbital interactions between the developing double bond in the diene and the unsaturated substituent of the dienophile, for it will be noted that *endo* isomers predominate where the possibility for such interactions is strongest. For instance it could reasonably be argued that the phenyl group has the greatest steric bulk of the substituents studied, yet it gives 100% of the *endo* isomer. Similarly acrylonitrile, methyl acrylate, and vinyl acetate, all having π electrons in their substituents, give predominantly *endo* products. Perhaps interactions between the diene and the d electrons of the halogen in the vinyl bromide and vinyl chloride adducts accounts for the predominance of *endo* products in these two cases. At any rate the methyl group of propene, containing no d or π electrons and being of low polarizability, gives predominantly the thermodynamically more stable *exo* isomer.

Dipole interactions explain the occurrence of *anti*-7-chloro isomers, steric hinderance explains the lack of *exo* isomers in this series, and secondary orbital interactions seem to account for the *endo*:*exo* ratios observed in the *syn*-7-chloro isomers. In this one system, the adducts of pentachlorocyclopentadiene, the important mechanisms proposed for the Diels–Alder reaction seem to be on common ground.[35] The differences in activation energy represented by the different isomers formed in this reaction are quite small, often less than 1 kcal/mole; the ability to study these subtle differences is why the Diels–Alder reaction will continue to hold the attention of curious chemists.

The Dimer. Pentachlorocyclopentadiene (**9**) dimerizes slowly at room temperature and fairly rapidly at 150°. In his original report of the synthesis of **9** McBee said that the dimer could be isolated in 94% yield, mp 220–221°. He did not speculate on the structure. The formation of this dimer occurred in most of the reactions we studied. When allowed to occur in an nmr tube, the dimerization led to the gradual disappearance of the 4.73 ppm singlet of **9** and the growth of two new singlets (width at half-height 0.2 Hz) of equal intensity at 4.86 and 4.96 ppm. No other peaks could be detected in the nmr spectrum. Glpc of the dimer gave only one peak; infrared spectra of the crude and recrystallized dimer were the same; both indicate homogeneity of the compound.

If the dimerization of pentachlorocyclopentadiene were a random process, we would expect eight stereoisomers to be formed. Even when we rule out the four *exo* isomers, there exists the possibility of forming the four *endo* isomers **31**–**34**, yet we find *only one* compound formed on dimerization.

Irradiation of an acetone solution of this dimer for 2 hr gives an easily sublimed cage compound, mp 372° dec, in 80% yield. The formation of this compound immediately rules out all *exo* isomers and the nmr (sharp singlet, width at half-height 0.3 Hz, 4.56 ppm) shows that it must be either **35** or **36**. This latter conclusion is probably not obvious from the formulas, but both protons in **35** and both protons in **36** are in identical chemical environments and would be expected to give only one line (although probably not with the same chemical shift). In compound **37** each proton is in a different chemical environment and would be expected to give two lines in the nmr spectrum. Compound **38** bears an enantiomeric relationship to **37**. Compound **35** would arise from transition state **39** in which both chlorine atoms are on the inside and compound **36** would arise from the sterically favored transition state **40**. Transition state **39** is favored by dipole–dipole and London interactions as discussed above. It is a transition state of this type in which maleic anhydride combines with **9** to give a 91% yield of the *anti*-chloro compound **16a**. On the other hand transition state **39** gives rise to a compound, **31**, which has both an *anti* chlorine atom and two *exo* chlorine atoms, which we would ex-



pect to be thermodynamically unstable relative to **32**. Also hexachlorocyclopentadiene does not form a thermal dimer. Despite the fact that this is the most stereospecific reaction we have observed with pentachlorocyclopentadiene we have not been able to distinguish chemically between the two alternative structures **31** and **32**; crystallographic studies are in progress.

Experimental Section

Infrared spectra were recorded as 5–10% solutions in carbon disulfide or chloroform on a Perkin-Elmer Model 137 spectrometer. Ultraviolet spectra were recorded on a Perkin-Elmer Model 202 spectrometer in chloroform solutions. An Aerograph Autoprep Model 705 gas chromatograph equipped with a Disc Model 224-4 integrator was employed for both analytical and preparative purposes. Aluminum columns (20 ft × 3/8 in. or 10 ft × 3/8 in.) packed with 30% QF-1 on 45/60 Chromosorb W, 30% SE-30 on 60/80 mesh Chromosorb P, or 20% SF-96 silicon oil on 80/100 Chromosorb W were used. The flow rate of helium was 200 ml/min. Temperatures of the detector and the injector were kept 30° above that of the column. Proton magnetic resonance spectra were recorded as 30% solutions on a Varian HA-100 spectrometer in this laboratory and a Varian A-60 spectrometer at University of Massachusetts. Tetramethylsilane was used as an internal reference. Melting points were taken on a Thomas–Hoover apparatus and were uncorrected. Microanalyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich. All commercially available materials employed in this study 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.

1,2,3,4,5-Pentachlorocyclopentadiene (9) was prepared by the stannous chloride dihydrate reduction of hexachlorocyclopentadiene according to the procedure of McBee[16] in 60% yield: bp 50° (0.10 mm); mp 1.5–2.0°; $\lambda_{max}^{CS_2}$ 6.28, 8.13, 8.45, 13.12, 14.51 μ; nmr δ 4.73 (singlet). The reported yield is 51%, bp 68–78° (1.5 mm).[16]

Reaction with Dimethyl Fumarate. A solution of 13.0 g (90.2 mmoles) of dimethyl fumarate and 20.06 g (84.5 mmoles) of **9** in 150 ml of *p*-xylene was refluxed under nitrogen for 20 min. The disappearance of the diene peak at 13.12 μ was used to follow the reaction. Removal of the solvent under reduced pressure gave 32 g of a yellow-white solid shown by glpc (QF-1 column, 250°) to contain three components. Crystallization from *n*-hexane gave 11.3% of the dimer of **9**, 0.64% of unreacted dimethyl fumarate, and 76.5% of **1,2,3,4-*syn*-7-pentachloro-5-*endo*-6-*exo*-dicarbomethoxybicyclo[2.2.1]-2-heptene (10)**: mp 97.5–99.5°; $\mu_{max}^{CS_2,CHCl_3}$ 5.82, 6.30, 7.42, 7.65, 7.82, 8.03, 8.15, 8.60, 10.04, 11.18 μ; nmr δ 3.49 (5-*exo*-, 1 H doublet, J = 4.82 Hz), 3.64 (6-*endo*, 1 H doublet, J = 4.82 Hz), 3.76 (5-*endo*-OCH_3, 3 H singlet), 3.82 (6-*exo*-OCH_3, 3 H singlet), 5.02 (7-*anti*, 1 H singlet).

Anal. Calcd for $C_{11}H_9O_4Cl_5$: C, 34.58; H, 2.38. Found: C, 34.78; H, 2.49.

Reaction with Dimethyl Maleate. A solution of 5.8 g (40 mmoles) of dimethyl maleate and 9.3 g (39 mmoles) of **9** in 80 ml of *p*-xylene was refluxed until the 13.12-μ diene band was gone (100 min). Removal of the solvent under reduced pressure gave 12.08 g of a yellow-white solid. Glpc (QF-1 column, 215°) showed in addition to the dimer of **9** (20%) and starting materials, three products in roughly equal quantities. These compounds were separated by chromatography on alumina, eluting with ligroine/benzene mixtures (dimer came off in ligroine). The third compound eluted was **1,2,3,4-*syn*-7-pentachloro-5-*endo*-6-*endo*-dicarbomethoxybicyclo[2.2.1]-2-heptene (11)**: mp 192.5–193°; $\lambda_{max}^{CS_2}$ 5.72, 6.23, 6.97, 7.45, 7.75, 7.89, 8.52, 9.73, 10.43, 11.45 μ; nmr δ 3.77 (5,6-*endo*-OCH_3, 6 H singlet), 3.82 (5,6-*exo*-, 2 H singlet), 4.42 (7-*anti*, 1 H singlet).

Anal. Calcd for $C_{11}H_9O_4Cl_5$: C, 34.58; H, 2.38. Found: C, 34.66; H, 2.45.

The second compound eluted was **1,2,3,4-*syn*-7-pentachloro-5-*exo*-6-*exo*-dicarbomethoxybicyclo[2.2.1]-2-heptene (12)**: mp 184–184.5°; $\lambda_{max}^{CS_2}$ 5.75, 6.24, 7.02, 7.43, 7.50, 7.72, 7.88, 8.53, 8.72, 9.55, 9.79, 10.58, 11.15, 11.45 μ; nmr δ 3.43 (5,6-*endo*, 2 H singlet), 3.77 (5,6-*exo*-OCH_3, 6 H singlet), 5.53 (7-*anti*, 1 H singlet).

Anal. Calcd for $C_{11}H_9O_4Cl_5$: C, 34.58; H, 2.38. Found: C, 34.66; H, 2.45.

The first compound eluted was **1,2,3,4-*anti*-7-pentachloro-5-*endo*-6-*endo*-dicarbomethoxybicyclo[2.2.1]-2-heptene (13)**: mp 135–137°, $\lambda_{max}^{CS_2}$ 5.72, 6.28, 7.00, 7.40, 7.54, 7.80, 7.93, 8.50, 9.02, 9.40, 9.80, 10.43, 10.70, 11.22, 12.20 μ; nmr δ 3.78 (5,6-*endo*-OCH_3, 6 H singlet), 4.02 (5,6-*exo*, 2 H singlet), 4.22 (7-*syn*, 1 H singlet).

Anal. Calcd for $C_{11}H_9O_4Cl_5$: C, 34.58; H, 2.38. Found: C, 34.68; H, 2.49.

Epimerization of 10, 11, 12, 13. Each compound (0.10 g, 0.26 mmole) was separately treated with a solution of 0.02 g (0.9 mg-atom) of sodium in 7 ml of anhydrous methanol for 2 days at room temperature. After work-up in the usual way the crude product was reesterified by dissolving in 3 ml of anhydrous methanol to which 9 drops of concentrated sulfuric acid was added and refluxing for 1.5 hr. After pouring into 20 ml of water the compound was extracted with ether, and the ether extracts were washed, dried, and evaporated to give the product. Compound **10** gave unreacted starting material in 73.9% yield, mp 93–97°; compound **11** gave 0.057 g (57% yield) of a viscous residue having an infrared spectrum identical with that of **10**; compound **12** gave 54% of material having an infrared spectrum identical with that of **10**; and compound **13** gave back unchanged starting material as judged by the infrared spectrum.

Reduction of 1,2,3,4,7,7-Hexachloro-5-*endo*-6-*endo*-dicarbomethoxybicyclo[2.2.1]-2-heptene (15). This compound was reduced according to the procedure of Williamson, *et al.*[20] To a magnetically stirred, refluxing solution of 8.0 g (19 mmoles) of **15**, mp 78–79°, in 50 ml of glacial acetic acid was added 6.28 g (96 mg-

atoms) of zinc dust through Gooch tubing over a 45-min period. After an additional 4 hr of stirring and refluxing the mixture was cooled and diluted with 100 ml of water, then extracted with three 50-ml portions of ether. The ether extracts were washed with water, 10% sodium carbonate solution, water, and saturated sodium chloride solution, and then dried over anhydrous sodium sulfate. Removal of the ether gave 3.65 g of a white solid which on glpc was found to be a mixture of five compounds in the ratio of 2:1:12:2:5. The third compound, 55% of the mixture, had mp 192–193° and was found to be identical with **11** by comparison of the infrared spectra. The fifth compound eluted, 22% of the mixture, is presumed to be 1,2,3,4-tetrachloro-7-acetoxy-5-*endo*-6-*endo*-dicarbomethoxybicyclo[2.2.1]-2-heptene and had mp 188–188.5°; $\lambda_{max}^{CS_2}$ 5.73, 7.02, 7.98, 8.45, 8.90, 9.28, 9.90 μ; nmr δ 2.21 (7-$OCOCH_3$, 3 H singlet), 3.70 (5,6-*endo*-OCH_3, 6 H singlet), 3.82 (5,6-*exo*-, 2 H singlet), 5.10 (7-H, 1 H singlet).

Anal. Calcd for $C_{13}H_{12}O_6Cl_4$: C, 38.19; H, 2.98. Found: C, 38.26; H, 3.06.

Reaction with Maleic Anhydride. In a flask equipped with thermometer and condenser with attached calcium chloride drying tube was placed 3.10 g (13 mmoles) of **9** and 1.57 g (16 mmoles) of maleic anhydride in 50 ml of *p*-xylene. The reaction mixture was heated at 105° for 3 hr at which time disappearance of the 13.12-μ diene band indicated the completion of the reaction. Glpc (SF-96 column, 200°) of the crude reaction mixture showed the presence of two compounds in 73% yield.

1,2,3,4-*anti*-7-Pentachloro-5-*endo*-6-*endo*-dicarboxylic acid anhydride (16a) was the first compound eluted (57 min retention time, 90.8%): mp 209–210°; $\lambda_{max}^{CHCl_3}$ 5.39, 5.60, 6.31, 9.41, 10.67, 11.07 μ; nmr δ 4.39 (5,6-*exo*, 2 H doublet, J = 0.55 Hz), 4.89 (7-*syn*, 1 H triplet, J = 0.55 Hz).

Anal. Calcd for $C_9H_3O_3Cl_5$: C, 32.13; H, 0.90. Found: C, 31.90; H, 1.05.

1,2,3,4-*syn*-7-Pentachloro-5-*endo*-6-*endo*-dicarboxylic acid anhydride (16b) was the second compound eluted (72 min retention time, 9.2%): mp 215–217°; $\lambda_{max}^{CHCl_3}$ 5.39, 5.61, 6.31, 9.22, 9.70, 10.62. 11.16 μ; nmr δ 4.51 (5,6-*exo*, 2 H singlet), 5.38 (7-*anti*, 1 H singlet).

Anal. Calcd for $C_9H_3O_3Cl_5$: C, 32.13; H, 0.90. Found: C, 31.84; H, 1.01.

Conversion of 16a to 13. The *anti*-7-chlorodicarboxylic acid anhydride, **16a**, mp 209–210°, was hydrolyzed to the diacid which started to melt and dehydrate at 170°, solidified and remelted at 209–210°; $\lambda_{max}^{CHCl_3}$ 2.85–3.80, 5.80, 6.29, 7.10, 8.69 μ. This diacid (0.25 g, 0.71 mmole) in 1 ml of ether was treated with an ethereal solution of diazomethane until the yellow color persisted. Evaporation of the ether and crystallization from hexane gave 0.20 g (74%) of a diester, mp 137–138.5°, shown by comparison of infrared spectra to be identical with the *anti*-7-chloro diester, **13**.

Reaction with *p*-Benzoquinone. A solution of 3.10 g (13 mmoles) of **9** and 1.74 g (16 mmoles) of *p*-benzoquinone in 50 ml of *p*-xylene was heated at 112° for 2.5 hr. Removal of the *p*-xylene under reduced pressure gave a quantitative yield of a mixture of adducts shown by integration of the nmr spectrum to be present in the ratio 60.1:39.9. Dimer was not present. Fractional crystallization of the mixture from chloroform–hexane gave first the major product, ***endo*-1,4,5,8,9,10-hexahydro-5,8-methano-5,6,7,8-*anti*-11-pentachloro-1,4-diketonaphthalene (17a)**: yellow crystals, mp 182–188°; $\lambda_{max}^{CHCl_3}$ 6.02, 6.33, 9.16, 9.40, 11.24, 11.69 μ; nmr δ 3.77 (9,10 *exo*, 2 H doublet, J = 0.43 Hz), 4.16 (11-*syn*, 1 H triplet, J = 0.43 Hz), 6.75 (2,3-vinyl, 2 H singlet).

Anal. Calcd for $C_{11}H_5O_2Cl_5$: C, 38.14; H, 1.45. Found: C, 38.06; H, 1.40.

***endo*-1,4,5,8,9,10-Hexahydro-5,8-methano-5,6,7,8-*syn*-11-pentachloro-1,4-diketonaphthalene (17b)** was the minor product, isolated as yellow crystals: mp 127–138°; $\lambda_{max}^{CHCl_3}$ 6.02, 6.33, 9.16, 9.40, 9.64, 9.80, 11.34, 11.70, 11.84 μ; nmr δ 3.67 (9,10-*exo*, 2 H singlet), 4.45 (11-*anti*, 1 H singlet), 6.75 (2,3-vinyl, 2 H singlet).

Anal. Calcd for $C_{11}H_5O_2Cl_5$: C, 38.14; H, 1.45. Found: C, 38.05; H, 1.39.

Reaction with Acrylonitrile. A solution of 4.71 g (19.8 mmoles) of **9** and 1.06 g (20 mmoles) of acrylonitrile in 25 ml of *p*-xylene was heated at 100° for 6 hr. Removal of the solvent at reduced pressure gave 5.88 g of a mixture of compounds shown by integration of the nmr spectrum to contain three adducts in the ratio 71.6:13.6:14.8 (62% yield) and dimer (38% yield). Quantitative analysis and separation of the mixture were effected by glpc (QF-1 column, 210°).

1,2,3,4-*anti*-7-Pentachloro-5-*endo*-cyanobicyclo[2.2.1]-2-heptene (18a) was the first compound eluted (127 min retention time, 71.7%). The white crystals (from chloroform–hexane) had mp 97.5–100.5°; $\lambda_{max}^{CS_2}$ 4.48, 6.30, 7.86, 7.95, 10.76, 11.33, 12.88, 13.17 μ; nmr δ 2.21 (6-endo, 1 H multiplet, J = 1.49, 4.27, −12.59 Hz), 2.79 (6-*exo*, 1 H multiplet, J = 0.21, 9.83, −12.59 Hz), 3.61 (5-*exo*-, 1 H multiplet, J = 0.42, 4.27, 9.83 Hz), 4.06 (7-*syn*, 1 H multiplet, J = 0.21, 0.42, 1.49 Hz).

Anal. Calcd for $C_8H_4NCl_5$: C, 32.95; H, 1.38. Found: C, 32.80; H, 1.45.

1,2,3,4-*syn*-7-Pentachloro-5-*endo*-cyanobicyclo[2.2.1]-2-heptene (18b) was the third compound eluted (193 min retention time, 15.1%). The white crystals (from chloroform–hexane) had mp 126–127°; $\lambda_{max}^{CS_2}$ 4.51, 6.30, 7.80, 7.94, 8.03, 11.22, 11.53, 12.34, 13.37 μ; nmr δ 2.32 (6-*endo*, 1 H quartet, J = 4.45, −12.71 Hz), 2.70 (6-*exo*, 1 H quartet, J = 9.43, −12.71 Hz), 3.50 (5-*exo*, 1 H quartet, J = 4.55, 9.43 Hz), 4.28 (7-*anti*, 1 H singlet).

Anal. Calcd for $C_8H_4NCl_5$: C, 32.95; H, 1.38. Found: C, 33.15; H, 1.43.

1,2,3,4-*syn*-7-Pentachloro-5-*exo*-cyanobicyclo[2.2.1]-2-heptene (18c) was the second compound eluted (144 min retention time, 13.2%). The white crystals (from hexane) had mp 115–116°, $\lambda_{max}^{CS_2}$ 4.51, 6.30, 7.79, 7.92, 9.94, 10.08, 10.31, 11.12, 11.32, 11.68, 13.83 μ; nmr δ 2.53 (6-*endo*, 1 H quartet, J = 10.00, 12.53 Hz), 2.56 (6-*exo*, 1 H quartet, J = 4.40, −12.53 Hz), 3.12 (5-*endo*, 1 H quartet, J = 4.40, 10.00 Hz), 4.53 (7-*anti*, 1 H singlet).

Anal. Calcd for $C_8H_4NCl_5$: C, 32.95; H, 1.38. Found: C, 32.94; H, 1.40.

Reaction with Methyl Acrylate. A solution of 3.10 g (13 mmoles) of **9** and 1.38 g (16 mmoles) of methyl acrylate in 50 ml of *p*-xylene was heated at 66° for 6 hr. Removal of the solvent at reduced pressure gave a mixture of adducts (60% yield) and dimer (40% yield). The mixture was analyzed and separated by glpc (QF-1 column, 205°).

1,2,3,4-*anti*-7-Pentachloro-5-*endo*-carbomethoxybicyclo[2.2.1]-2-heptene (19a) was the first compound eluted (139 min retention time, 53.2%). The white crystals (from chloroform–hexane) had mp 45.5–47.5°; $\lambda_{max}^{CS_2}$ 5.76, 6.30, 7.50, 7.87, 7.94, 8.03, 10.50, 10.76, 11.20, 11.70, 12.60, 12.86, 13.20 μ; nmr δ 2.39 (6-*endo*, 1 H multiplet, J = 1.42, 4.29, −12.31 Hz), 2.58 (6-*exo*, 1 H multiplet, J = 0.30, 9.08, −12.31 Hz), 3.50 (5-*exo*, 1 H multiplet, J = 0.45, 4.29, 9.08 Hz), 4.05 (7-*syn*, 1 H multiplet, J = 0.30, 0.45, 1.42 Hz), 3.66 (-OCH_3, 3 H singlet).

Anal. Calcd for $C_9H_7O_2Cl_5$: C, 33.78; H, 2.26. Found: C, 33.50; H, 2.16.

1,2,3,4-*syn*-7-Pentachloro-5-*endo*-carbomethoxybicyclo[2.2.1]-2-heptene (19b) was the third compound eluted (204 min retention time, 36.6%). After crystallization from hexane it had mp 59–60°; $\lambda_{max}^{CS_2}$ 5.79, 6.30, 7.46, 7.80, 7.91, 8.04, 10.60, 11.25, 11.48, 12.16, 12.58, 13.62 μ; nmr δ 2.35 (6-*exo*, 1 H quartet, J = 9.80, −12.23 Hz), 2.55 (6-*endo*, 1 H quartet, J = 4.18, −12.23 Hz), 3.27 (5-*exo*, 1 H quartet, J = 4.18, 9.80 Hz), 4.20 (7-anti, 1 H singlet), 3.67 (-OCH_3, 3 H singlet).

Anal. Calcd for $C_9H_7O_2Cl_5$: C, 33.78; H, 2.26. Found: C, 33.50; H, 2.17.

1,2,3,4-*syn*-7-Pentachloro-5-*exo*-carbomethoxybicyclo[2.2.1]-2-heptene (19c) was the second compound eluted (156 min retention time, 10.2%). This colorless liquid had $\lambda_{max}^{CS_2}$ 5.80, 6.30, 7.47, 7.76, 7.95, 8.03, 10.25, 10.65, 11.35, 11.57, 12.06, 13.45 μ; nmr δ 2.32 (6-*endo*, 1 H quartet, J = 9.96, −12.29 Hz), 2.48 (6-*exo*, 1 H quartet, J = 3.73, −12.29 Hz), 2.95 (5-*endo*, 1 H quartet, J = 3.73, 9.96 Hz), 4.97 (7-*anti*, 1 H singlet), 3.74 (-OCH_3, 3 H singlet).

Anal. Calcd for $C_9H_7O_2Cl_5$: C, 33.78; H, 2.26. Found: C, 33.32; H, 2.18.

Epimerization of 19a, b, and c. To each of three separate solutions of 0.09 g (4.0 mg-atoms) of sodium in 4 ml of anhydrous methanol was added 0.40 g (1.3 mmoles) of the ester. The violet solution was allowed to stand for 7 days (10 days for **19c**), poured into water, acidified with hydrochloric acid, extracted with ether, the ether layer washed with water, dried over anhydrous sodium sulfate, and evaporated to dryness. The resulting acids were esterified with diazomethane in ether. Evaporation of the ether in the case of **19a** gave a 69% yield of crystals, mp 42–46°, shown by infrared spectra to be identical with starting material. Compound **19b** gave a 70% yield of a mixture of **19b** and **19c**. Glpc (QF-1 column, 210°) showed two components in the relative ratios of 63.5:36.5 which were collected and identified, by comparison of their infrared spectra with authentic samples, as **19c** and **19b**, respectively. Similarly **19c** gave a 79% yield of a mixture of esters shown to be 54% **19c** and 46% **19b**.

Reaction with Vinyl Acetate. A mixture of 3.10 g (13 mmoles) of **9** and 1.38 g (16 mmoles) of vinyl acetate in 50 ml of *p*-xylene was heated for 8 hr at 120°. Removal of the solvent gave a mixture

of adducts (73% yield) and dimer (27% yield) which was analyzed by preparative glpc (SE-30 column, 213°).

1,2,3,4-*anti*-7-Pentachloro-5-*endo*-acetoxybicyclo[2.2.1]-2-heptene (20a), white crystals, mp 88–91°, was the first compound eluted (153 min retention time, 47.7%). The compound has $\lambda_{max}^{CS_2}$ 5.74, 6.28, 7.37, 7.95, 8.49, 8.62, 9.23, 9.52, 10.47, 10.77, 11.49, 12.78 μ; nmr δ 1.82 (6-*endo*, 1 H multiplet, J = 2.22, 2.62, −13.03 Hz), 2.91 (6-*exo*, 1 H multiplet, J = 0.23, 7.77, −13.03 Hz), 4.05 (7-*syn*, 1 H multiplet, J = 0.23, 0.42, 2.22 Hz), 5.52 (5-*exo*, 1 H multiplet, J = 0.42, 2.62, 7.77 Hz), 2.01 (OAc, 3H singlet).

Anal. Calcd for $C_9H_7O_2Cl_5$: C, 33.32; H, 2.18. Found: C, 33.29; H, 2.30.

1,2,3,4-*syn*-7-Pentachloro-5-*endo*-acetoxybicyclo[2.2.1]-2-heptene (20b), white crystals, mp 83.5–84°, was the second compound eluted (165 min retention time, 45.1%). The compound has $\lambda_{max}^{CS_2}$ 5.74, 6.30, 7.37, 8.42, 8.70, 9.41, 10.00, 10.66, 11.34, 12.98 μ; nmr δ 1.95 (6-*endo*-, 1 H quartet, J = 2.83, −13.09 Hz), 2.04 (OAc, 3 H singlet), 2.69 (6-*exo*, 1 H quartet, J = 8.10, −13.09 Hz), 4.25 (7-*anti*, 1 H singlet), 5.43 (5-*exo*, 1 H quartet, J = 2.83, 8.10 Hz).

Anal. Calcd for $C_9H_7O_2Cl_5$: C, 33.32; H, 2.18. Found: C, 33.52; H, 2.24.

1,2,3,4-*syn*-7-Pentachloro-5-*exo*-acetoxybicyclo[2.2.1]-2-heptene (20c) was the third compound eluted (176 min retention time, 7.2%). The compound, a colorless liquid, has $\lambda_{max}^{CS_2}$ 5.72, 6.28, 7.35, 9.46, 9.95, 12.40, 13.40 μ; nmr δ 2.02 (6-*exo*, 1 H quartet, J = 2.61, −13.05 Hz), 2.10 (OAc, 3 H singlet), 2.68 (6-*endo*, 7.84, −13.05 Hz), 4.56 (7-*anti*, 1 H singlet), 4.96 (5-*endo*, 1 H quartet, J = 2.61, 7.84 Hz).

Anal. Calcd for $C_9H_7O_2Cl_5$: C, 33.32; H, 2.18. Found: C, 33.37; H, 2.37.

Reaction with Vinyl Bromide. A mixture of 1.55 g (6.5 mmoles) of **9**, a trace of hydroquinone, and 2.68 g (25 mmole) of vinyl bromide in 1 ml of ethyl acetate was heated in a sealed glass ampoule at 100° for 18 hr. Removal of vinyl bromide at room temperature gave a mixture shown to be a mixture of adducts (90% yield) and dimer (10%). The mixture was analyzed and separated by glpc (QF-1 column, 177°).

1,2,3,4-*anti*-7-Pentachloro-5-*endo*-bromobicyclo[2.2.1]-2-heptene (21a), a colorless liquid, was the first compound eluted (68 min retention time, 48.1%). The compound has $\lambda_{max}^{CS_2}$ 6.30, 7.88, 7.97, 10.00, 10.75, 11.72, 12.58, 12.96, 13.20, 14.09 μ; nmr δ 2.25 (6-*endo*, 1 H multiplet, J = 2.08, 3.47, −13.37 Hz), 3.04 (6-*exo*, 1 H multiplet, J = 0.38, 8.55, −13.37 Hz), 4.06 (7-*syn*, 1 H multiplet, J = 0.38, 0.42, 2.08 Hz), 4.62 (5-*exo*, 1 H multiplet, J = 0.42, 3.47, 8.55 Hz).

Anal. Calcd for $C_7H_4BrCl_5$: C, 24.35; H, 1.17. Found: C, 24.49; H, 1.29.

1,2,3,4-*syn*-7-Pentachloro-5-*endo*-bromobicyclo[2.2.1]-2-heptene (21b), a colorless liquid, was the third compound eluted (112 min retention time, 35.1%). The compound has $\lambda_{max}^{CS_2}$ 6.30, 7.77, 7.90, 10.00, 10.09, 10.41, 11.34, 11.58, 11.92, 13.21 μ; nmr δ 2.44 (6-*endo*, 1 H quartet, J = 4.07, −13.52 Hz), 2.89 (6-*exo*, 1 H quartet, J = 8.96, −13.52 Hz), 4.21 (7-*anti*, 1 H singlet), 4.34 (5-*exo*, 1 H quartet, J = 4.07, 8.96 Hz).

Anal. Calcd for $C_7H_4BrCl_5$: C, 24.35; H, 1.17. Found: C, 24.26; H, 1.16.

1,2,3,4-*syn*-7-Pentachloro-5-*exo*-bromobicyclo[2.2.1]-2-heptene (21c), a colorless liquid, was the second compound eluted (90 min retention time, 16.8%). The compound has $\lambda_{max}^{CS_2}$ 6.30, 7.80, 7.94 10.05, 10.14, 10.57, 11.30, 11.91, 13.30 μ; nmr δ 2.66 (6-*exo*, 1 H quartet, J = 3.39, −13.40 Hz), 2.92 (6-*endo*, 1 H quartet, J = 8.30, −13.40 Hz), 4.07 (5-*endo*, 1 H quartet, J = 3.39, 8.30 Hz).

Reaction with Vinyl Chloride. In a 15-ml glass ampoule 1.55 g (6.5 mmoles) of **9**, 1.63 g (26.2 mmoles) of vinyl chloride, a trace of hydroquinone, and 1 ml of ethyl acetate was heated at 100° for 26 hr. Glpc (QF-1 column, 160°) of the reaction mixture showed the presence of three adducts in 97% yield and a 3% yield of dimer.

1,2,3,4-*endo*-5-*anti*-7-Hexachlorobicyclo[2.2.1]-2-heptene (22a), a colorless liquid, was the first compound eluted (111 min retention time, 45.5%). The compound has $\lambda_{max}^{CS_2}$ 6.30, 7.86, 7.96, 10.75, 11.65, 12.34, 12.92, 13.72 μ; nmr δ 2.13 (6-*endo*, 1 H multiplet, J = 2.15, 3.20, −13.18 Hz), 3.01 (6-*exo*, 1 H multiplet, J = 0.38, 8.52, −13.18 Hz), 4.07 (7-*syn*, 1 H multiplet, J = 0.38, 0.48, 2.15 Hz), 4.66 (5-*exo*, 1 H multiplet, J = 0.48, 3.20, 8.52 Hz).

1,2,3,4-*endo*-5-*syn*-7-Hexachlorobicyclo[2.2.1]-2-heptene (22b), a colorless liquid, was the third compound eluted (185 min retention time, 40.0%). The compound has $\lambda_{max}^{CS_2}$ 6.30, 7.73, 7.87, 7.99, 8.05, 10.04, 10.31, 11.32, 12.94, 14.24 μ; nmr δ 2.30 (6-*endo*, 1 H quartet, J = 3.53, −13.37 Hz), 2.83 (6-*exo*, 1 H quartet, J = 8.60, −13.37 Hz), 4.18 (7-*anti*, 1 H singlet), 4.47 (5-*exo*, 1 H quartet, J = 3.53, 8.60 Hz).

Anal. Calcd for $C_7H_4Cl_6$: C, 27.95; H, 1.34. Found: C, 27.75; H, 1.28.

1,2,3,4,5-*exo*-7-*syn*-Hexachlorobicyclo[2.2.1]-2-heptene (22c), a colorless liquid, was the second compound eluted (141 min retention 14.5%). The compound has $\lambda_{max}^{CS_2}$ 6.30, 7.80, 7.91, 8.04, 8.16, 10.01, 10.13, 10.48, 11.30, 11.88, 13.08, 14.63 μ; nmr δ 2.48 (6-*exo*, 1 H quartet, J = 3.25, −13.39 Hz), 2.86 (6-*endo*, 1 H quartet, J = 8.37, −13.39 Hz), 4.05 (5-*endo*, 1 H quartet, J = 3.25, 8.37 Hz), 4.68 (7-*anti*, 1 H singlet).

Anal. Calcd for $C_7H_4Cl_6$: C, 27.95; H, 1.34. Found: C, 27.89; H, 1.33.

Reaction with Styrene. A solution of 2.04 g (20.0 mmoles) of styrene and 4.71 g (19.8 mmoles) of **9** in 25 ml of *p*-xylene was heated for 15 min at 142°. The xylene was removed at reduced pressure and the reaction mixture distilled at 132° (0.13 mm) to give 4.30 g (74% yield) of a yellow viscous liquid. A 1-g sample of this was chromatographed on 50 g of alumina collecting 250-ml portions. The total recovery was 0.905 g (90.5%). Another portion of the crude viscous liquid was analyzed by integrating the nmr spectrum and found to consist of two components in the ratio of 42.2:57:8.

1,2,3,4-*anti*-7-Pentachloro-5-*endo*-phenylbicyclo[2.2.1]-2-heptene (23a), present in the smaller amount, was eluted by 40–60° ligroine and after recrystallization from hexane had mp 88.5–91°, $\lambda_{max}^{CS_2}$ 6.33, 7.93, 8.55, 8.74, 9.95, 10.79, 12.95, 13.73, 14.41 μ; nmr δ 2.32 (6-*endo*, 1 H multiplet, J = 1.68, 4.42, −12.84 Hz), 2.85 (6-*exo*, 1 H multiplet, J = 0.22, 9.48, −12.84 Hz), 3.92 (5-*exo*, 1 H multiplet, J = 0.40, 4.42, 9.48 Hz), 4.06 (7-*syn*, 1 H multiplet, J = 0.22, 0.40, 1.68 Hz), 7.23 (phenyl, 5 H broad singlet).

Anal. Calcd for $C_{13}H_9Cl_5$: C, 45.58; H, 2.50. Found: C, 45.62; H, 2.67.

1,2,3,4-*syn*-7-Pentachloro-5-*endo*-phenylbicyclo[2.2.1]-2-heptene (23b), the predominant compound, a colorless liquid eluted by 5–10% benzene in ligroine was redistilled, bp 124.5–126° (0.005 mm), at which time it solidified, mp 62–66°. The compound has $\lambda_{max}^{CS_2}$ 6.32, 7.93, 9.64, 9.87, 10.06, 12.70, 13.03, 13.79, 14.44 μ; nmr δ 2.49 (6-*endo*, 1 H quartet, J = 5.61, −12.80 Hz), 2.64 (6-*exo*, 1 H quartet, J = 8.82, −12.80 Hz), 3.63 (5-*exo*, 1 H quartet, J = 5.61, 8.82 Hz), 4.35 (7-*anti*, 1 H singlet), 7.13 (phenyl, 5 H broad singlet).

Anal. Calcd for $C_{13}H_9Cl_5$: C, 45.58; H, 2.50. Found: C, 45.96; H, 2.88.

In another run 4.71 g (19.8 mmoles) of **9** and 2.04 g (20.0 mmoles) of styrene in 25 ml of *p*-xylene were heated at 100–103° for 50 min. The reaction mixture was separated by column chromatography to give a 73% yield of a mixture containing **23a** and **23b** in the ratio of 38.4:61:1.

In a third run 3.10 g (16 mmoles) of **9** and 1.67 g (13 mmoles) of styrene in 50 ml of *p*-xylene was heated for 3.5 hr at 65°. The reaction mixture (72% yield) was analyzed by glpc (QF-1 column, 220°). The first compound eluted was **23a** (88 min retention time, 38.0%) followed by **23b** (130 min retention time, 62.0%).

Attempted Thermal Isomerization of 23a and 23b. These two compounds (0.2 g) were each separately dissolved in 1 ml of *p*-xylene and heated at 115° for 1.5 hr. On glpc (QF-1 column, 220°) each compound was recovered unchanged and uncontaminated with the other isomer.

Reaction with Propene. A mixture of 1.85 g (7.8 mmoles) of **9**, 1.05 g (25 mmoles) of propene, a trace of hydroquinone, and 1 ml of ethyl acetate was heated for 6 hr at 100° in a glass ampoule. After removal of the excess propene the mixture of products (90%) and dimer (10%) was analyzed by glpc (QF-1 column, 146°).

1,2,3,4-*anti*-7-Pentachloro-5-*endo*-methylbicyclo[2.2.1]-2-heptene (24a), a colorless liquid, was the first compound eluted (102 min retention time, 31.3%). The compound has $\lambda_{max}^{CS_2}$ 6.30, 7.85, 7.92, 10.11, 10.58, 10.98, 11.30, 11.84, 12.96, 13.75 μ; nmr δ 1.00 (methyl, 3 H doublet, J = 6.73 Hz), 1.49 (quartet of doublets, smallest splitting 1.68 Hz), 2.58 (quartet of partially resolved doublets, smallest splitting 0.43 Hz), 2.85 (1 H multiplet), 3.95 (7-*syn*, 1 H doublet of partially resolved triplets, doublet splitting 1.68 Hz).

Anal. Calcd for $C_8H_7Cl_5$: C, 34.26; H, 2.52. Found: C, 34.20; H, 2.78.

1,2,3,4-*syn*-7-Pentachloro-5-*endo*-methylbicyclo[2.2.1]-2-heptene (46b), a colorless liquid, was the third compound eluted (179 min retention time, 11.7%). The compound has $\lambda_{max}^{CS_2}$ 6.30, 7.80, 7.98, 9.43, 10.57, 10.65, 11.30, 11.90, 12.11, 14.12 μ; nmr δ 1.30 (methyl, 3 H doublet, J = 6.89 Hz), 1.81 (1 H multiplet), 2.31 (2 H, broad multiplet), 4.31 (7-*anti*, 1 H sharp singlet).

Anal. Calcd for $C_8H_7Cl_5$: C, 34.26; H, 2.52. Found: C, 34.30; H, 2.78.

1,2,3,4-*syn*-7-Pentachloro-5-*exo*-methylbicyclo[2.2.1]-2-heptene (24c), a colorless liquid, was the second compound eluted (162 min retention time, 57.0%). The compound has $\lambda_{max}^{CS_2}$ 6.30, 7.80, 7.88, 9.91, 10.05, 10.51, 11.40, 12.21, 13.89 μ; nmr δ 1.04 (methyl, 3 H doublet, J = 6.59 Hz), 1.67 (1 H multiplet), 2.52 (broad, 2 H multiplet), 4.21 (*anti*-7, sharp 1 H singlet).

Anal. Calcd for $C_8H_7Cl_5$: C, 34.26; H, 2.52. Found: C, 34.25; H, 2.55.

1-Bromo-1,2,3,4,5-pentachloro-2,4-cyclopentadiene (27) was prepared according to the procedure of Mark.[36]

Phosphorus tribromide, 108 g (0.40 mole), and hexaclilorocyclopentadiene, 328 g (1.20 moles), were heated in a 500-ml three-necked flask equipped with magnetic stirrer, thermometer, and fractional distillation head. Heating was adjusted so that the pot temperature reached 160° in 4 hr and was maintained between 160 and 164°. After 7 hr at this temperature a deep red liquid (81 g) was slowly distilled from the reaction mixture between 70 and 80° over 9 hr. The contents of the reaction flask were then distilled to give unreacted hexachlorocyclopentadiene, bp 59–65° (0.25–0.30 mm), and a mixture of **27** and the hexachloro compound, bp 68–99° (0.20–0.30 mm). This was redistilled through a 10-in. Vigreux column, then twice distilled through a spinning-band distillation column, and finally through the Vigreux column again (bp 60° (0.15 mm), $n^{25}D$ 1.5870) to give 40 g (8.4% yield of **27**). Glpc (SF-96 column, 175°) indicated the purity of **27** was 99%. The reported yield is 22%, bp 43–44° (0.04 mm), $n^{25}D$ 1.5880.[36]

Reaction of 27 with Maleic Anhydride. A solution of 1.42 g (4.50 mmoles) of **27** and 0.32 g (3.25 mmoles) of maleic anhydride in 4 ml of nitrobenzene was heated for 14 hr at 136°. Completion of the reaction was indicated by the disappearance of the 12.0-μ maleic anhydride band in the infrared spectrum. Glpc (SF-96 column, 210°) showed only one peak which was collected as crystals, mp 230–250° (evacuated capillary). The nmr spectrum of this white solid was identical with that of the crude reaction mixture; it consists of two singlets at 4.19 and 4.24 ppm and four doublets at 4.07, 4.15, 4.18, and 4.26 ppm of which the first two had splittings of 2.40 Hz and the last two of 2.10 Hz. The intensity of the singlet at 4.19 ppm showed that it comprised about 50% of the isomeric mixture. The infrared spectrum of the white crystals in $CHCl_3$ was simple and had prominent peaks at 5.36, 5.60, 6.30, 9.41, 10.71, and 11.19 μ.

Anal. Calcd for $C_9H_2O_3BrCl_5$: C, 26.03; H, 0.49; Br, 19.24; Cl, 42.68. Found: C, 25.96; H, 0.44; Br, 19.06; Cl, 42.45.

Dimerization of 9. The dimerization of **9** (30% in CS_2, room temperature) was shown by the disappearance of the singlet at 4.73 ppm and the growth of two new singlets of equal intensity at 4.86 and 4.96 ppm ($W(h/2)$ = 0.2 Hz). The dimer has mp 221°; $\lambda_{max}^{CS_2}$ 6.25, 8.13, 8.31, 9.68, 10.37, 11.48, 12.60, 13.91 μ. The ultraviolet spectrum shows $\lambda_{max}^{CHCl_3}$ 249 mμ (ϵ = 760). Only one peak was detected on glpc (SE-30 column, 200°).

1,2,3,4,5,6,7,8,9,10-Decachloropentacyclo[5.2.1.$0^{2,6}$.$0^{3,9}$.$0^{4,8}$]decane (35 or 36) was prepared by irradiating a solution of 11.90 g (25 mmoles) of the dimer of **9** in 150 ml of acetone for 2 hr with a 450-W Hanovia lamp in a quartz apparatus. Completion of the reaction was indicated by disappearance of the double bond peak at 6.26 μ in the infrared spectrum. Removal of the acetone *in vacuo* gave a dark brown residue which was sublimed at 200° (1 mm) to give 9.41 g (79% yield) of white gummy crystals. A sample for analysis was further purified by elution through an alumina column with low boiling ligroine and crystallizations from a 7:1 ethanol–water mixture. The melting point taken in an evacuated capillary in an aluminum block was 372° dec. The nmr spectrum shows only a sharp singlet at 4.56 ppm ($W(h/2)$ = 0.3 Hz) for the two protons of **35** or **36**. The infrared spectrum has $\lambda_{max}^{CS_2}$ 7.93, 8.12, 8.46, 8.82, 9.04, 9.33, 9.90, 11.56, 11.88, 12.67, 13.02, 13.42 μ.

Anal. Calcd for $C_{10}H_2Cl_{10}$: C, 25.20; H, 0.42. Found: C, 25.02; H, 0.48.

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The Stereospecific Syntheses of Ferrocene Derivatives with Leaving Groups β to the Metallocene

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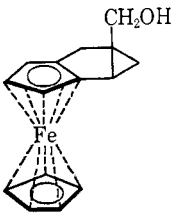
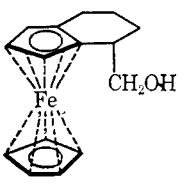
Abstract: The stereospecific syntheses of *exo*- and *endo*-α-hydroxymethyl-1,2-tetramethyleneferrocene (I and II, respectively) are discussed. The stereospecific generation of the *endo* isomer (II) results from the addition of the hydrogen of disiamylborane to α-methylene-1,2-tetramethyleneferrocene (VIII) exclusively from the *exo* direction. The exclusive neutralization of α-metallocenyl carbonium ions by *exo* attack of a nucleophile provides a stereospecific route to the *exo* isomer (I).

In connection with a continuing interest in metallocenyl carbonium ions[1-3] *exo*- and *endo*-α-tosyloxymethyl-1,2-tetramethyleneferrocene (the tosylates of I and II) were required for solvolytic studies. The stereospecific synthesis of these two isomers was therefore undertaken and forms the subject of this paper.



I



II

(1) J. H. Richards and E. A. Hill, *J. Am. Chem. Soc.*, 81, 3483 (1959).
(2) E. A. Hill and J. H. Richards, *ibid.*, 83, 3840 (1961).
(3) E. A. Hill and J. H. Richards, *ibid.*, 83, 4216 (1961).