



Experimental and theoretical studies of Diels–Alder dimerization of 1,2,3,4,5-pentachlorocyclopentadiene and of Diels–Alder cycloaddition of polychlorinated cyclopentadienes to norbornadiene

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Abstract—Diels–Alder cyclodimerization of 1,2,3,4,5-pentachlorocyclopentadiene (**1**) affords **2a** as the exclusive reaction product. Diels–Alder cycloaddition of **1** to norbornadiene also proceeds stereoselectively to produce a single [4+2] cycloadduct, **4c**. The structures of **2a** and **4c** were established unequivocally via application of single crystal X-ray crystallographic techniques. The origins of the observed diastereofacial selectivity in each of these cycloaddition processes have been investigated by application of semiempirical (AM1 Hamiltonian) and ab initio (Hartree–Fock 3-21G*) calculations. The computational results thereby obtained, which are based upon consideration of the kinetically favored transition state for each of the two cycloaddition reactions studied, are consistent with experiment. These semiempirical and ab initio methods also have been used to investigate the mechanisms of the Diels–Alder reactions that have been used to prepare aldrin and isodrin (**7** and **8**, respectively). The results thereby obtained suggest that isodrin formation via Diels–Alder cycloaddition of cyclopentadiene to 1,2,3,4,7,7-hexachloronorbornadiene proceeds with kinetic control of product stereochemistry. © 2003 Published by Elsevier Science Ltd.

1. Introduction

Thermal [4+2] cycloadditions between dienes and dienophiles have provided a mainstay of organic synthesis ever since this important reaction was first discovered by Diels and Alder in 1928.¹ Reactions of this type have been employed extensively for regio-, stereo-, and enantioselective synthesis of carbocyclic² and heterocyclic³ six-membered rings.

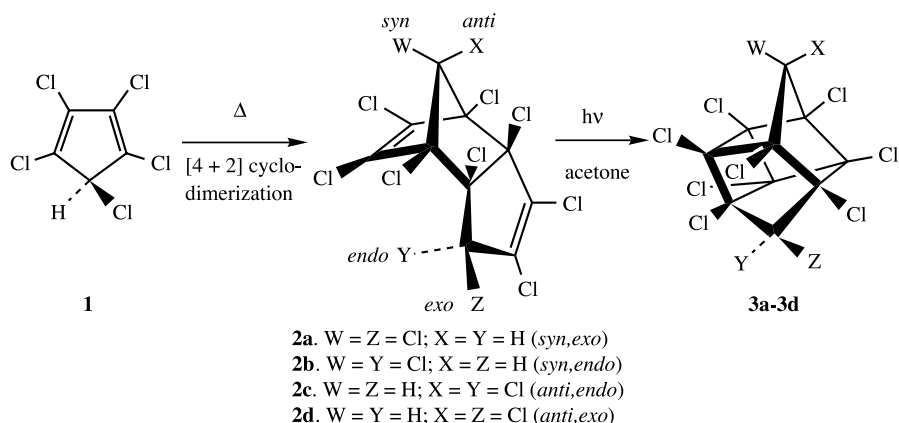
Diastereofacial selectivity that accompanies product formation has been reported for thermal [4+2] cycloadditions between cage-annulated dienes and dienophiles in which one or both of the reactants contains stereoelectronically non-equivalent π -faces.^{4,5} In an effort to gain additional insight into the origin of this phenomenon, we now report the results of an investigation of Diels–Alder cycloaddition reactions that involve 1,2,3,4,5-pentachlorocyclopentadiene (**1**) as substrate.

Compound **1** was considered to be an excellent candidate substrate for a study of diastereofacial selectivity in Diels–Alder reactions. Indeed, **1** functions as both diene and dienophile during thermal [4+2] cyclodimerization. Thus, investigation of the course of its kinetically controlled cyclodimerization is expected to provide important information concerning the characteristics of the transition state for a Diels–Alder reaction in which both the diene and dienophile components possess diastereotopically non-equivalent π -faces. In addition, it was of interest to determine the influence of extensive substitution of C–H by C–Cl in the diene and dienophile upon the course of this reaction. Importantly, the presence of five Cl substituents in **1** assures that this molecule will be configurationally stable by excluding the possibility of [1,5]-sigmatropic shifts. If operative, thermal, suprafacial sigmatropic shifts would result in effective scrambling of a 5-substituent throughout the cyclopentadiene ring.⁶

In 1955, McBee and Smith⁷ reported that thermal [4+2] cyclodimerization of **1** occurs spontaneously at ambient temperature to afford a cycloadduct, **2**, that displays mp 220–221°C. Subsequently, Williamson and co-workers⁸ confirmed that only one product was formed via thermal cyclodimerization of **1**. However, these investigators

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Scheme 1.

recognized that as many as four [4+2] cycloadducts, i.e. **2a–2d** (Scheme 1), might be formed, if it is assumed that the reaction proceeds in accordance with the Alder–Stein rule of ‘maximum accumulation of unsaturation’.⁹

Williamson and co-workers⁸ attempted to assign the configuration of the cyclodimerization product, **2**. They found that irradiation of an acetone solution of this material affords the corresponding decachloropentacyclic cage compound, **3**, thereby confirming the fact that **2** possess the *endo* configuration. The ¹H NMR spectrum of **3** was found to consist of a sharp singlet at δ 4.56; this result is consistent only with structures **3a** (W=Z=Cl, X=Y=H) and **3c** (W=Z=H, X=Y=Cl), each of which possesses the required molecular symmetry. This result, in turn, requires that the cyclodimerization product, **2**, from which **3** is derived must possess either structure **2a** or **2c**. However, Williamson and co-workers were not able to distinguish between these two alternative structures for **2**, either by chemical means or via analysis of the ¹H NMR spectrum of the product formed via cyclodimerization of **1**.⁸

We now report the results of single crystal X-ray structural analysis of **2**, which provides unequivocal confirmation of structure **2a** for this cyclodimerization product. Corresponding semiempirical and ab initio transition state calculations also have been performed in an effort to provide additional insight into the kinetically controlled cyclodimerization reaction.

In addition, Diels–Alder cycloaddition of **1** to norbornadiene, another dienophile that contains diastereotopically non-equivalent π -faces, has been studied, and the structure of the cycloadduct has been established unequivocally via application of X-ray crystallographic techniques. Semiempirical and ab initio transition state calculations also have been performed for this reaction.

2. Results and discussion

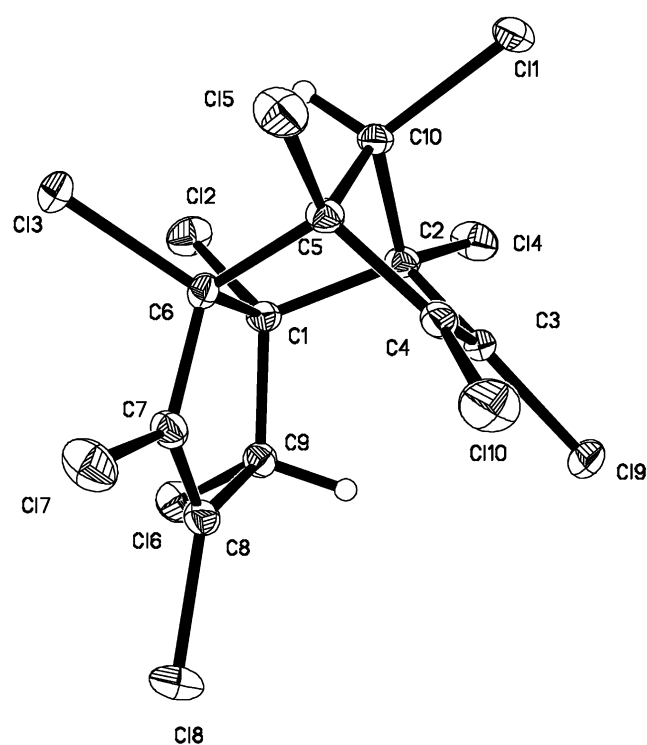
2.1. Synthesis and X-ray structure of the product formed via thermal [4+2] cycloaddition of **1**

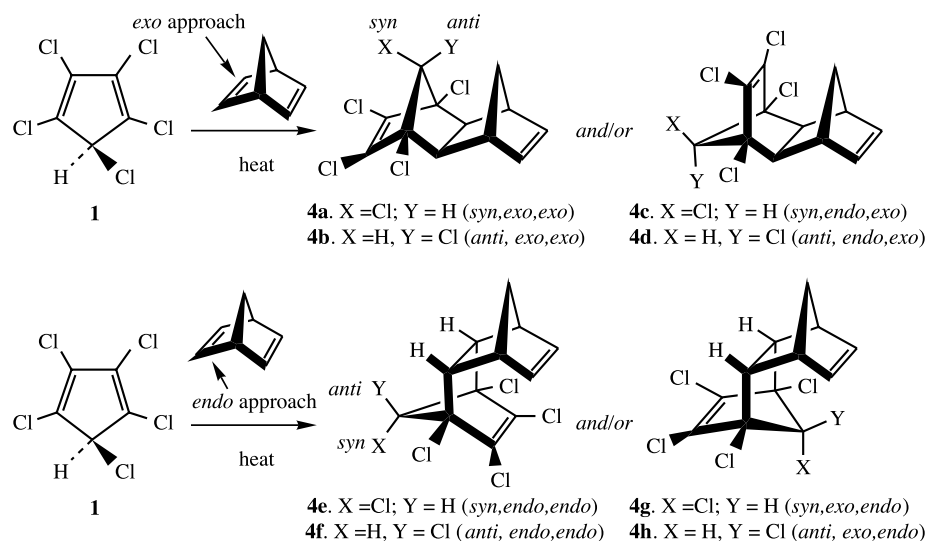
Compound **1** was prepared via SnCl₂ promoted hydrogenolysis of one of the C(5)–Cl bonds in hexachlorocyclo-

pentadiene by following a previously reported procedure.¹⁰ After purification of **1** had been completed, the pure material was allowed to stand at ambient temperature, whereupon spontaneous [4+2] cyclodimerization ensued to afford a single product.^{7,8} A suitable single crystal of this material, mp 210–211°C, was obtained by fractional recrystallization from hexane. The structure of this compound was shown to be **2a** via single crystal X-ray structural analysis (see Section 5). An X-ray structure drawing of **2a** appears in Figure 1.

2.2. Synthesis and X-ray structure of the product formed via thermal [4+2] reaction of **1** with norbornadiene

In general, cycloadditions of dienes to norbornadiene (dienophile) occur via approach of the diene toward the *exo* face of the dienophile.¹¹ However, by allowing for the possibility that *endo* approach of the diene upon a

Figure 1. X-Ray structure drawing of **2a**.



Scheme 2.

norbornadiene C=C double bond might occur, it is conceivable that any or all of eight cycloadducts, **4a–4h** (Scheme 2) could arise via this cycloaddition reaction.

In our hands, this reaction afforded a single [4+2] cycloadduct. A suitable single crystal of this material, mp 82–83°C, was obtained via fractional recrystallization from hexane. The structure of this compound was shown to be **4c** via single crystal X-ray structural analysis (see Section 5). An X-ray structure drawing of **4c** appears in Figure 2.

3. Theoretical results and discussion

3.1. Computational investigation of the thermal [4+2] cycloaddimerization of **1**

Fully optimized semiempirical calculations (AM1 Hamiltonian)¹² and ab initio transition state calculations performed at the Hartree–Fock HF/3-21G* level of theory¹³ have been carried out in an effort to obtain additional insight into the kinetically controlled cycloaddimerization reaction. The results of these calculations appear in Table 1. Therein, it can be seen that **2a** is favored on the basis of

thermodynamic (i.e. product stability) considerations. In addition, the transition state that leads to the formation of **2a** is the least energetic of the four possible *endo* transition states for thermal [4+2] cycloaddimerization of **1**. Hence, **2a**, whether formed under conditions of kinetic or thermodynamic control of the cycloaddition reaction, is expected to be the major (if not exclusive) reaction product, a result that is consistent with experiment.

The AM1-calculated transition state geometries for **2a–2d**

Table 1. Calculated transition state and ground state energy differences (kcal mol⁻¹) for thermal [4+2] cycloaddimerization of **1**

Isomer	AM1		HF/3-21G*	
	Transition state	Ground state	Transition state	Ground state
2a (<i>syn,exo</i>)	0.0	0.0	0.0	0.0
2b (<i>syn,endo</i>)	4.0	1.7	7.3	3.3
2c (<i>anti,endo</i>)	9.0	3.8	8.8	5.4
2d (<i>anti,exo</i>)	4.8	2.15	15.8	8.5

Table 2. Lengths of forming σ -bonds (a) and (b) [i.e. $r_{(a)}$ and $r_{(b)}$, in Å] in the four transition states for thermal [4+2] cycloaddimerization of **1**

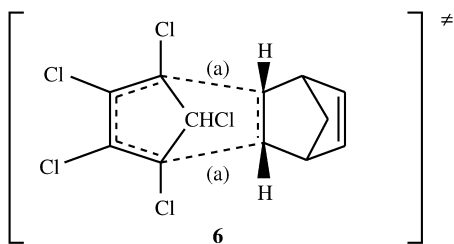
Isomer	AM1 transition state	
	$r_{(a)}$ (Å)	$r_{(b)}$ (Å)
2a (<i>syn,exo</i>)	2.120	2.249
2b (<i>syn,endo</i>)	2.153	2.229
2c (<i>anti,endo</i>)	2.162	2.245
2d (<i>anti,exo</i>)	2.135	2.258

Figure 2. X-Ray structure drawing of **4c**.

Table 3. Calculated transition state and ground state energy differences (kcal mol⁻¹) for thermal [4+2] cycloaddition of **1** to norbornadiene

Isomer	AM1		RHF/3-21G*// RHF/AM1 ^a	
	Transition state	Ground state	Transition state	Ground state
4a (<i>syn, exo, exo</i>)	3.1	0.8	5.3	1.5
4b (<i>anti, exo, exo</i>)	11.2	7.5	19.2	14.4
4c (<i>syn, endo, exo</i>)	0.0	0.4	0.0	1.0
4d (<i>anti, endo, exo</i>)	2.3	0.3	2.1	0.0
4e (<i>syn, endo, endo</i>)	3.0	0.0	6.9	1.5
4f (<i>anti, endo, endo</i>)	13.9	9.8	25.0	16.4
4g (<i>syn, exo, endo</i>)	6.0	3.0	4.5	4.7
4h (<i>anti, exo, endo</i>)	6.3	2.4	6.8	3.2

^a Single point calculations performed at the HF/3-21G* level of theory by using AM1 geometries.

Table 4. Lengths of forming σ -bonds (a) [i.e. $r_{(a)}$, in Å] in the eight AM1 calculated transition states for thermal [4+2] cycloaddition of **1** to norbornadiene

Isomer	AM1 transition state $r_{(a)}$ (Å)
4a (<i>syn, exo, exo</i>)	2.170
4b (<i>anti, exo, exo</i>)	2.186
4c (<i>syn, endo, exo</i>)	2.162
4d (<i>anti, endo, exo</i>)	2.172
4e (<i>syn, endo, endo</i>)	2.168
4f (<i>anti, endo, endo</i>)	2.184
4g (<i>syn, exo, endo</i>)	2.162
4h (<i>anti, exo, endo</i>)	2.172

are consistent with a concerted [4+2] cycloaddition process and are slightly asynchronous in nature. Two new σ -bonds are formed in the transition state during the cyclodimerization process. The bonds of interest in this connection are identified as 'a' and 'b' in transition state structure **5** (Table 2); the relevant calculated bond lengths are presented in Table 2.

The data in Table 2 indicate that bonds (a) and (b) are similar in length but not equal; the calculated length of bond (b) is consistently greater than that of bond (a). The fact that these two bonds are formed to differing extents in each

transition state is not unexpected, given the unsymmetrical nature of the transition states.

3.2. Computational investigation of the thermal [4+2] cycloaddition of **1** to norbornadiene

In the case of this [4+2] cycloaddition process, both the diene (**1**) and the dienophile (norbornadiene) possess diastereotopically non-equivalent π -faces. Thus, as can be seen in Scheme 2, a total of eight transition states must be considered explicitly. Semiempirical calculations (AM1 Hamiltonian)¹² and single point ab initio transition state calculations performed at the Hartree–Fock HF/3-21G* level of theory¹³ have been carried out for the eight transition states of interest, i.e. **6a–6h**, that lead to the formation of **4a–4h**, respectively (Scheme 2).

The computational results obtained at the AM1 and HF/3-21G* levels of theory both predict that the transition state which leads to *syn,endo,exo* cycloadduct **4c** is preferred energetically (Table 3), i.e. **4c** is predicted to be the product of kinetic control of Diels–Alder cycloaddition of **1** to norbornadiene, in agreement with experiment (Fig. 2). By way of contrast, the results of AM1 calculations suggest that **4c–4e** all possess comparable (thermodynamic) stabilities, whereas the corresponding results obtained at the HF/3-21G* level of theory suggest that there may be a somewhat greater preference for formation of **4d** if the cycloaddition were to be performed under conditions of thermodynamic control.

The AM1 calculated transition state geometries suggest that all eight possible transition states are concerted and synchronous in nature. The newly forming C··C σ -bond lengths in transition states of the type **6** range between 2.16 and 2.19 Å, as shown in Table 4.

3.3. Computational investigation of the thermal [4+2] cycloadditions halogenated cyclopentadienes and norbornadienes: aldrin and isodrin

Thermal reaction of 1,2,3,4,5,5-hexachlorocyclopentadiene with norbornadiene leads to the formation of an *exo,endo* [4+2] cycloadduct (i.e. 'aldrin', **7**, Scheme 3) as the exclusive reaction product. By way of contrast, the corresponding cycloaddition of cyclopentadiene to 1,2,3,4,7,7-hexachloronorbornadiene affords a single [4+2] cycloadduct, which possesses the *endo,endo* configuration (i.e. 'isodrin', **8**, Scheme 3).¹⁴

At the time when both aldrin and isodrin were used extensively as insecticides, these Diels–Alder reactions were important commercially.¹⁵ In the context of the

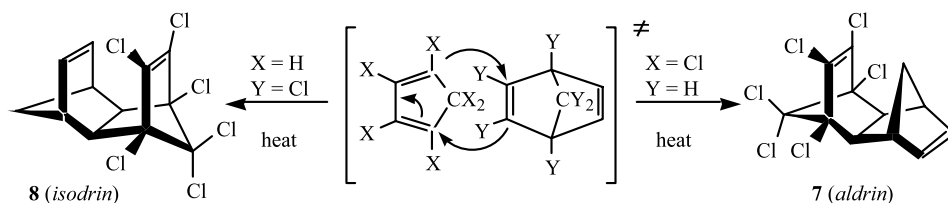
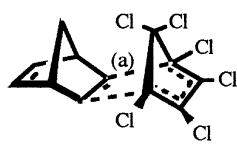
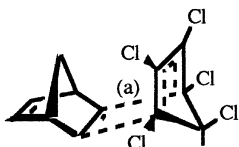
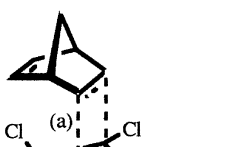
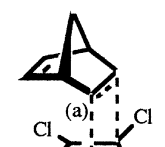
**Scheme 3.**

Table 5. Calculated transition state and ground state energy differences (kcal mol⁻¹) and lengths of forming σ -bonds (a) [i.e. $r_{(a)}$, in Å] in the four transition states for thermal [4+2] cycloaddition of **1** to norbornadiene

				
	7a (<i>exo,exo</i>)	7b (<i>exo,endo</i>)	7c (<i>endo,exo</i>)	7d (<i>endo,endo</i>)
Bond length, σ -bond (a) (Å)	2.189	2.179	2.187	2.180
Transition state energies (kcal mol ⁻¹)				
AM1	10.5	0.0	12.9	4.0
RHF/3-21G*/RHF/AM1	19.0	0.0	25.3	5.0
Ground state energies (kcal mol ⁻¹)				
AM1	10.8	0.0	12.2	2.4
RHF/3-21G*/RHF/AM1	19.3	0.0	21.3	3.6

present study, their significance lies in the fact that the stereochemical outcome of these two closely related reactions is so clearly disparate. This observation suggests that at least one, if not both, of these cycloadditions is subject to kinetic control. In the present study, we have investigated these cycloadditions by using only low-level semiempirical (AM1 Hamiltonian) and ab initio (HF/3-21G*) theoretical approaches in an attempt to rationalize the course of each reaction.

First, Diels–Alder cyclization of 1,2,3,4,5,5-hexachlorocyclopentadiene and norbornadiene, which leads to the formation of aldrin (**7**) via one of four possible transition states, i.e. **7a–7d**, was examined computationally. The results thereby obtained are shown in Table 5.

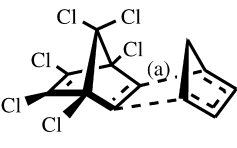
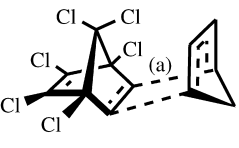
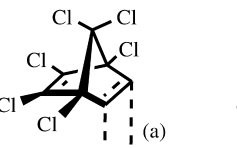
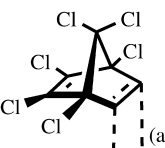
The results of AM1-optimized geometry calculations suggest that all four possible transition states are concerted and synchronous in nature. The newly forming C–C σ -bond lengths range between 2.18 and 2.19 Å (Table 5).

The AM1 calculated transition and ground state results clearly predict that the *exo,endo* cycloadduct, i.e. that which results via transition state **7b**, should be the preferred product formed via Diels–Alder cycloaddition of 1,2,3,4,5,5-hexachlorocyclopentadiene to norbornadiene. The results of single point calculations performed at HF/3-21G* level of theory predict an even greater preference for formation of **7b**. Importantly, the prediction that emerges from the computational results obtained for both the transition state and ground state calculations agree with experiment, i.e. that aldrin is expected to be the preferred product, whether formed via kinetic or via thermodynamic control of the cycloaddition reaction.

Next, Diels–Alder cyclization of cyclopentadiene to 1,2,3,4,7,7-hexachloronorbornadiene, which leads to the formation of isodrin (**8**), via one of four possible transition states, i.e. **8a–8d**, was examined computationally. The results thereby obtained are shown in Table 6.

The AM1 calculated transition state geometries suggest that

Table 6. Calculated transition state and ground state energy differences (kcal mol⁻¹) and lengths of forming σ -bonds (a) [i.e. $r_{(a)}$, in Å] in the four transition states for thermal [4+2] cycloaddition of cyclopentadiene to 1,2,3,4,7,7-hexachloronorbornadiene

				
	8a (<i>exo,exo</i>)	8b (<i>exo,endo</i>)	8c (<i>endo,exo</i>)	8d (<i>endo,endo</i>)
Bond length, σ -bond (a) (Å)	2.156	2.132	2.158	2.137
Transition state energies (kcal mol ⁻¹)				
AM1	11.4	8.2	1.1	0.0
RHF/3-21G*/RHF/AM1	22.0	14.5	4.7	0.0
Ground state energies (kcal mol ⁻¹)				
AM1	10.8	12.2	0.0	2.4
RHF/3-21G*/RHF/AM1	19.3	21.3	0.0	3.6

all four possible transition states are concerted and synchronous in nature. The newly forming C···C σ -bond lengths range between 2.13 and 2.16 Å (Table 6).

The results obtained via AM1 calculation of transition state energetics suggest that the *endo,endo* cycloadduct, i.e. that which results via transition state **8d**, should be the preferred product formed via kinetic control of Diels–Alder cycloaddition of cyclopentadiene to 1,2,3,4,7,7-hexachloronorbomadiene, in accord with experimental observations. Interestingly, the computational results predict aldrin (formed via transition state **8c**) to be the preferred product of thermodynamic control of this cycloaddition.

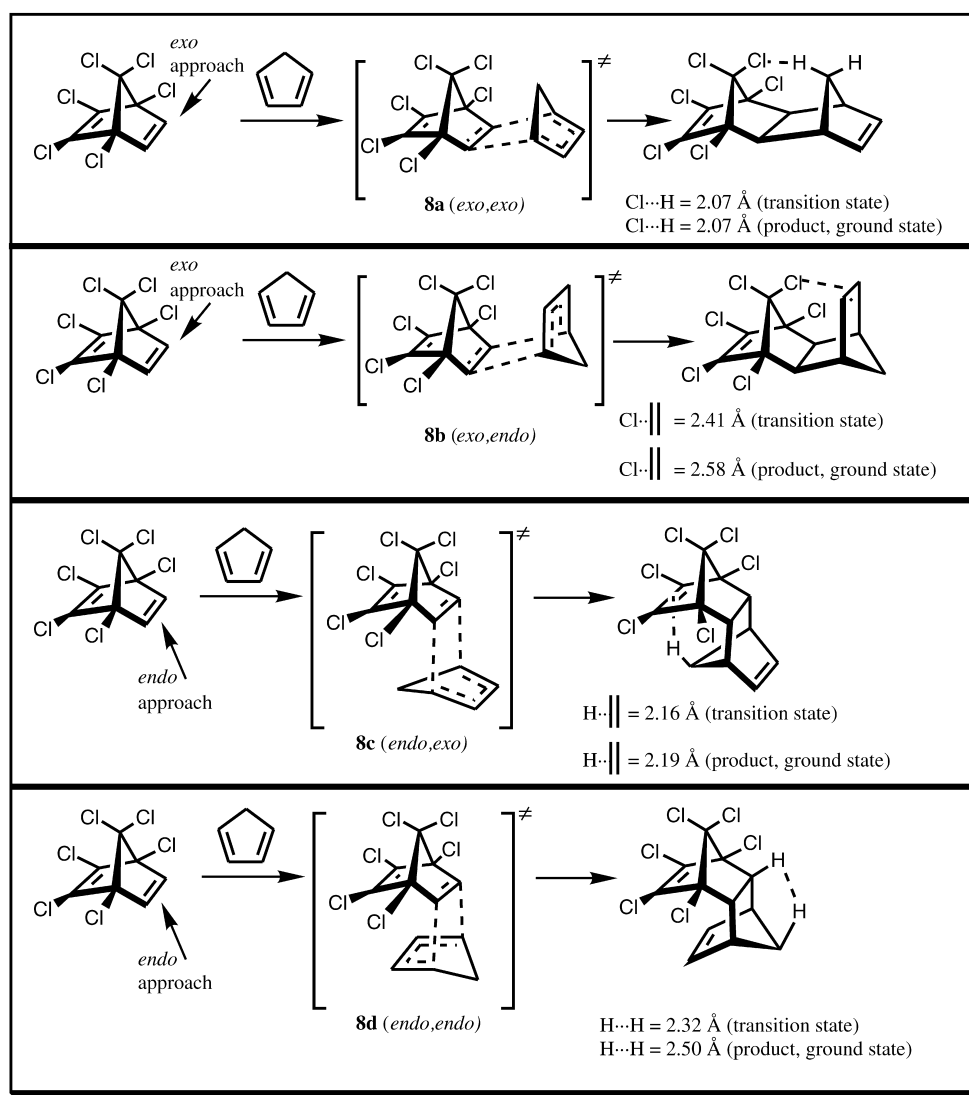
As was observed for the corresponding calculations performed for Diels–Alder cycloaddition of 1,2,3,4,5,5-hexachlorocyclopentadiene to norbornadiene (vide supra), the results of single point calculations performed at HF/3-21G* level of theory agree with the corresponding AM1 calculated results. In addition, the HF/3-21G* results show larger energy differences among **8a**–**8d** transition states and also among the corresponding ground states than are

predicted via application of semiempirical (AM1) computational methodology (see Table 6).

3.4. Aldrin vs isodrin: comparison of relevant transition states

Formation of aldrin and isodrin (i.e. **7** and **8**, respectively) via the kinetically controlled Diels–Alder reactions described herein is governed in each case by a subtle interplay among often conflicting stereoelectronic effects. Aldrin is formed via approach of 1,2,3,4,5,5-hexachlorocyclopentadiene toward the *exo* face of one of the 2 equiv. norbornadiene C=C double bonds. This same mode of approach is followed in the corresponding Diels–Alder cycloaddition of cyclopentadiene to norbornadiene.¹⁶ Thus, the presence of the six C–Cl groups in the dienophile does not appear to have a dramatic effect upon the stereo- and regiochemical course of the former process.

However, the situation is quite different in the case of the kinetically controlled cycloaddition of cyclopentadiene to 1,2,3,4,7,7-hexachloronorbomadiene, which leads



Scheme 4.

exclusively to the formation of isodrin (**8**). Buildup of intramolecular Cl \cdots H non-bonded interactions is likely to occur in **8a** as the cycloaddition reaction proceeds to afford the corresponding *exo,exo* cycloadduct (Scheme 4). Electrostatic repulsions between the negative end of a C–Cl bond dipole and a neighboring C=C double bond are likely to be significant as **8b** proceeds to form the corresponding *exo,endo* cycloadduct (Scheme 4). Kinetically favored transition state **8d** proceeds in accordance with the Alder–Stein rule⁹ and develops only minimal intramolecular H \cdots H non-bonded interactions as it proceeds to afford the observed *endo,endo* [4+2] cycloadduct, **8** (Scheme 4).

4. Summary and conclusions

Thermal [4+2] cyclodimerization of 1,2,3,4,5-pentachlorocyclopentadiene (**1**) and the corresponding Diels–Alder cycloaddition of **1** to norbornadiene have been carried out. In each case, only one cycloadduct was isolated. The reaction products thereby prepared were shown to be **2a** and **4c**, respectively. The structure of each cycloadduct was established unequivocally via application of single crystal X-ray crystallographic techniques.

The mechanisms of the Diels–Alder cycloadditions that have been used historically to prepare aldrin and isodrin (**7** and **8**, respectively) have been examined computationally. The results of semempirical (AM1 Hamiltonian) and ab initio (Hartree–Fock HF/3-21G*) calculations both suggest that the formation of isodrin via Diels–Alder cycloaddition of cyclopentadiene to 1,2,3,4,7,7-hexachloronorbornadiene is a kinetically controlled process. It seems likely that the same is true for the analogous formation of aldrin via Diels–Alder cycloaddition of 1,2,3,4,5,5-hexachlorocyclopentadiene to norbornadiene.

In the cycloaddition that leads to the formation of aldrin, the kinetically preferred transition state involves approach of the diene upon the *exo* face of one of the two equiv. C=C double bonds in the dienophile (norbornadiene). Of the two pathways by which *exo* approach of the diene upon the dienophile might occur, that which leads to the formation of aldrin minimizes non-bonded steric interactions between a C(5)–Cl bond in the diene and the *anti* C–H(7) bond in the dienophile.

In the cycloaddition that leads to the formation of isodrin, the kinetically preferred transition state involves approach of the diene upon the *endo* face of the non-chlorinated C=C double bond in the dienophile (1,2,3,4,7,7-hexachloronorbornadiene). Of the four possible pathways by which the diene might approach the dienophile might occur, that which leads to the formation of isodrin minimizes non-bonded steric interactions between a C(5)–H bond in the diene and the dienophile (see transition states **8a–8d**, as depicted in Table 6 and Scheme 4).

The course of each of the Diels–Alder reactions that leads to the formation of aldrin and isodrin appears to be governed by a subtle interplay among frequently conflicting stereo-electronic effects. In the case of isodrin formation via [4+2] cycloaddition of cyclopentadiene to 1,2,3,4,7,7-hexa-

chloronorbornadiene to norbornadiene, the resultant of these effects can override the normal preference for *exo* approach of the diene upon a norbornadiene C=C double bond.¹¹ Similarly, the normal regiochemical course of [4+2] thermal cycloadditions that typically adhere to the familiar Alder–Stein rule⁹ is not followed in the case of aldrin formation via [4+2] cycloaddition of 1,2,3,4,5,5-hexachlorocyclopentadiene to norbornadiene.

Recently, we noted the fact that application of relatively low levels of theory (i.e. semiempirical and Hartree–Fock molecular orbital calculations with small basis sets) can be used to provide chemically meaningful predictions with regard to the regio- and stereochemical course of Diels–Alder reactions.⁵ The corresponding results obtained in the present study are consistent with this observation and serve to further demonstrate the utility of low-level, inexpensive theoretical methods for this purpose.

5. Experimental

High-resolution mass spectral data reported herein were obtained by Professor Jennifer S. Brodbelt at the Mass spectrometry Facility at the Department of Chemistry and Biochemistry, University of Texas at Austin by using a ZAB-E double sector high resolution mass spectrometer (Micromass, Manchester, England) that was operated in the chemical ionization mode. Elemental microanalytical data was obtained by personnel at M-H-W Laboratories, Inc., Phoenix, AZ.

5.1. Computational methodology

Semiempirical (AM1) calculations have been performed for all the possible transition state and ground state geometries.¹³ The transition states and ground states have been characterized via complete vibrational frequency analyses. Single point calculations have been performed at the HF/3-21G* level of theory by using AM1 calculated geometries.

5.1.1. Pentachlorocyclopentadiene. A solution of hexachlorocyclopentadiene **14** (20.4 g, 74.9 mmol) in acetone (10 mL) was cooled via application of an external ice-water bath. To this cooled solution was added dropwise with stirring a solution of SnCl₂·H₂O (17.2 g, 76.7 mmol) in acetone (50 mL) in such a manner that a reaction temperature of 30–35°C was maintained throughout the addition process. After the addition of the reducing agent had been complexed (ca. 10 min), the external ice-water bath was removed, and the brown reaction mixture was allowed to warm gradually to ambient temperature while stirring during 1 h. The reaction mixture was concentrated in vacuo without external heating, and CH₂Cl₂ (50 mL) was added to the residue. The aqueous (upper) layer was removed via pipette, and the remaining organic layer was dried (CaCl₂), and filtered, and the filtrate was concentrated in vacuo without external heating. The residue was distilled in vacuo via application of an external oil bath that was heated rapidly to 100°C. Pure 1,2,3,4,5-pentachlorocyclopentadiene (6.0 g, 34%) was thereby obtained as a yellow oil: bp 105–107°C (5 torr.) [lit.¹⁰ bp 73–76°C (4 torr.)]; IR

(film) 2938 (m), 1603 cm^{-1} (s); ^1H NMR (CDCl_3) δ 4.75 (s); ^{13}C NMR (CDCl_3) δ 60.2 (d), 129.0 (s), 129.6 (s).

5.1.2. Diels–Alder dimerization of 1,2,3,4,5-pentachlorocyclopentadiene. Upon standing at ambient temperature, a sample of 1,2,3,4,5-pentachlorocyclopentadiene (3.0 g, 6.3 mmol) slowly was converted into a single Diels–Alder dimer, $\text{C}_{10}\text{H}_2\text{Cl}_{10}$.⁸ This material was purified via fractional recrystallization from hexane. Pure **2a** (2.4 g, 80%) was thereby obtained as a colorless microcrystalline solid: mp 210–211°C (lit^{7,8} mp 220–221°C); IR (KBr) 2996 (w), 1607 (s), 1313 (m), 1232 (s), 1156 (m), 870 cm^{-1} (m); ^1H NMR (CDCl_3) δ 4.92 (s, 1 H), 5.01 (s, 1 H); ^{13}C NMR (CDCl_3) δ 64.7 (d), 78.7 (d), 81.7 (s), 82.1 (s), 82.3 (s), 86.2 (s), 129.5 (s), 131.6 (s), 134.4 (s), 134.7 (s). Anal. Calcd for $\text{C}_{10}\text{H}_2\text{Cl}_{10}$: Cl, 74.38. Found: Cl, 73.85.

5.1.3. Diels–Alder cycloaddition of 1,2,3,4,5-pentachlorocyclopentadiene to norbornadiene. A solution of 1,2,3,4,5-pentachlorocyclopentadiene (2.38 g, 1.0 mmol) and norbornadiene (920 mg, 1.0 mmol) in toluene (200 mL) was refluxed during 24 h. The reaction mixture then was concentrated in vacuo, and the residue was purified via column chromatography on silica gel by eluting with hexane. Pure **4c** (1.4 g, 50%) was thereby obtained as a colorless microcrystalline solid: mp 82–83°C; IR (KBr) 3072 (w), 3035 (w), 1591 (s), 1470 (s), 1315 (s), 1250 (s), 1015 cm^{-1} (s); ^1H NMR (CDCl_3) δ 1.31 (AB, $J_{\text{AB}}=10.7$ Hz, 1 H), 1.50 (AB, $J_{\text{AB}}=10.7$ Hz, 1 H), 2.47 (s, 2H), 2.90–2.92 (m, 2H), 4.34 (s, 1H); 6.28 (s, 2H); ^{13}C NMR (CDCl_3) δ 40.2 (t), 41.2 (d), 55.2 (d), 75.9 (s), 82.4 (d), 129.8 (s), 140.9 (d). Exact mass (CI-HRMS) Calcd for $\text{C}_{12}\text{H}_9\text{Cl}_5$ [$M_r^+ + \text{H}$]⁺ m/z 328.9225. Found: M_r^+ 328.9216. Anal. Calcd for $\text{C}_{12}\text{H}_9\text{Cl}_5$: C, 43.61; H, 2.75. Found: C, 43.35; H, 3.00.

5.2. X-Ray structure determination of **2a** and **4c**

All X-ray data were collected on a Bruker SMART[™] 1000 CCD based diffractometer. The frames were integrated with the SAINT program package¹⁷ by using a narrow-frame algorithm, and the structures were solved and were refined by using the SHELXTL program package.¹⁸ The structures were checked by using PLATON.¹⁹ The molecules are well packed with no solvent voids. Thermal ellipsoid plots are drawn at the 30% probability level. The five and six-membered rings exhibit envelope and boat conformations, respectively. Packing interactions lead to several $\text{Cl}\cdots\text{H}$ and $\text{Cl}\cdots\text{Cl}$ interactions that are slightly shorter than the sum of the van der Waals radii. X-Ray data for **2a** and **4c** are listed in Table 7. Complete crystallographic details are available as supplementary material and have been deposited at the Cambridge Crystallographic Data Centre [CCDC 196805 (**4c**) and 196806 (**2a**)].

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Table 7. X-Ray data collection and processing parameters for **2a** and **4c**

Compound	2a	4c
Formula	$\text{C}_{10}\text{H}_2\text{Cl}_{10}$	$\text{C}_{12}\text{H}_9\text{Cl}_5$
Size (mm)	0.51×0.48×0.21	0.61×0.25×0.16
Space group	<i>Pca</i> 2(1)	<i>Pbca</i>
<i>a</i> (Å)	15.239(1)	8.0602(6)
<i>b</i> (Å)	7.4327(6)	14.367(1)
<i>c</i> (Å)	13.708(1)	23.144(2)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
<i>V</i> (Å ³)	1552.6(2)	2680.6(4)
<i>Z</i> -value	4	8
<i>D</i> _{calc} (g cm ⁻³)	2.039	1.638
μ (mm ⁻¹)	1.777	1.055
<i>T</i> (K)	213(2)	298
θ range for data collection (deg.)	2.67–28.24	1.76–28.31
Total reflections	9201	15,810
Independent reflections	3310	3217
<i>R</i> _{int}	0.0393	0.0643
$I \geq 2\sigma(I)$	3310	3217
Parameters	188	155
Goodness of fit	1.030	1.027
<i>R</i> , <i>R</i> _w	0.0278; 0.0728	0.0421; 0.1086
ρ_{max} , ρ_{min} (e Å ⁻³)	0.594; -0.288	0.368; -0.394

kindly obtained the high-resolution chemical ionization mass spectral data reported herein.

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