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Thermal Rearrangements of Perchlorohexatrienes–Structures and Experimental and Theoretical Evaluation of Pathways to Isomerization and Cyclization

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Dedicated to Barry Dellinger

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We have prepared *trans*- (**1**) and *cis*-octachloro-1,3,5-hexatriene (**2**) by known routes and studied their thermal behavior experimentally and theoretically by ab initio calculations. The three double bonds in **1** and **2** are completely decoupled due to steric hindrance by the eight Cls, as indicated by calculations as well as the single-crystal X-ray structure of **1**. The *cis* isomer **2** can be isomerized to the *trans* isomer **1** by heating it to 220–250 °C either neat or dissolved in high-boiling solvents, leading to a roughly 2:1 mixture of *trans* and *cis* isomers. Calculations at several different levels of theory predict **1** and **2** to be isoenergetic within 2 kJ mol^{-1}. Unimolecular *cis*/*trans* isomerization is predicted to occur through an unusual vinylcyclobutene intermediate **7**, whose formation faces a barrier of more than 150 kJ mol^{-1}, but whose stability is comparable to that of **1** and **2**. The isomerization rate is strongly enhanced by the addition of small amounts of Br_2 or Cl_2 or by **3** and can be explained by a radical-induced isomerization mechanism. The heating of trienes **1** and **2** to 250 °C leads to cyclization, yielding 71 % of the cyclopentene isomer **3**. Compound **3** can be dechlorinated by treatment with copper powder to give fulvene derivative **4**. Using flash vacuum pyrolysis, the thermal conversion of trienes **1** and **2** to hexachlorobenzene (**5**) occurs at higher temperatures between 600–1000 °C, likely via perchlorinated 1,3-cyclohexadiene (**6**) as an intermediate. The elimination of molecular Cl_2 from **3** and **6** requires very high activitation energies in agreement with calculations.

Introduction

The thermal formation of various classes of chloroaromatic compounds like chlorobenzenes, chlorophenols, and chlorinated dibenzodioxins and furans (PCDD/F) has been observed in technical incineration processes like municipal waste incineration and other thermal processes.[1] These micropollutants enter the environment by the emitted gases, and some of the products are toxic, like PCDD/F.[2] Therefore, the thermal formation pathways of PCDD/F have been intensively investigated in the last two decades, and it was shown that these compounds are mainly formed in the postcombustion zone of the incinerators at temperatures of 300–450 °C on the surface of fly ash particles.[3,4] Two main pathways have been postulated for the formation of these chloroaromatic compounds: (1) by so-called de novo synthesis from particulate C and (2) by inorganic Cl and/or the formation from chlorinated precursors ("precursor theory").[4] A variety of chloroaliphatic, four-C and six-C compounds has been identified by this method, and relevant mechanisms have been suggested.[5] These growing reactions can start with simple chloromethanes and involve perchlorinated alkenes like ethylene, propene, butadiene, and the coupling products thereof. Though the formation of several of these perchloroalkenes has been observed, the mechanisms for their formation and transformation to hexachlorobenzene are not clear. Whereas the chemistry of the corresponding hydrocarbons is well-understood, one must expect that the steric and electronic effects of the Cl substituents strongly affect the stability of reactants, products, and transient intermediates. The interpretation of the reaction mechanisms of perchlorinated alkenes in analogy to simple hydrocarbon analogs may thus be misleading. Our particular focus here is on the cyclization reactions of perchloro-1,3,5-hexatriene (**1**), whose cyclization leads to a methylenecyclopentene product instead of the expected cyclohexadiene.[6] Triene **1** represents a key intermediate in the

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growing process, and its cyclization may thus be part of the main reaction pathway leading to hexachlorobenzene.[5,7] Pattern analysis has also been used to elucidate the mechanism.[8a] In order to obtain a detailed picture of the cyclization/elimination reactions leading from **1** to hexachlorobenzene, we have now studied the thermal reactivity of **1** in the condensed phase and in the gas phase using a combination of experimental and theoretical techniques.

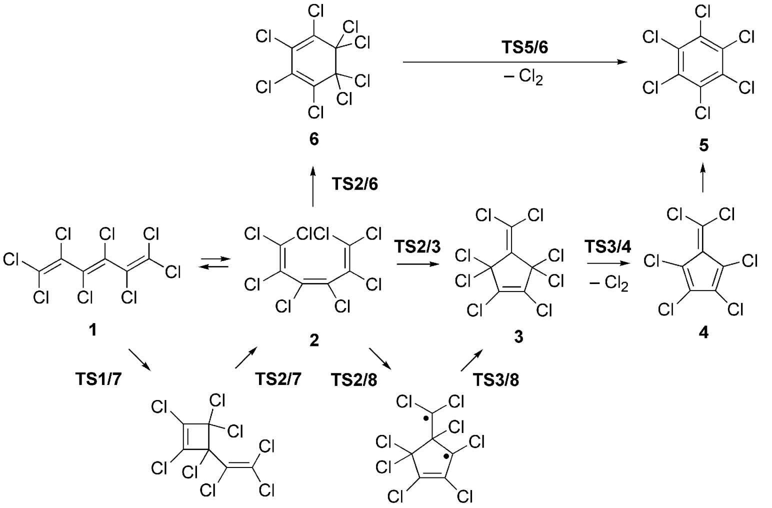
Results and Discussion

Experimental Cyclization of Perchlorohexatrienes 1 and 2

There are 12 structural isomers with the formula C_6Cl_8, but most isomers with three- or four-membered rings are too strained to exist as stable species in higher temperature regimes. Until now, only five C_6Cl_8 isomers have been prepared and characterized.[8] Some of these isomers are most likely precursors for hexachlorobenzene as the thermodynamically most stable product under the high-temperature conditions of incineration processes. They can be formed by so-called "growing reactions" from dichloroacetylene as the starting compound, which was shown experimentally using a tubular furnace reactor.[5] Scheme 1 describes several pathways for the formation of hexachlorobenzene (**5**) starting from *trans*-octachloro-1,3,5-hexatriene (**1**). These involve the C_6Cl_8 isomers **2**, **3**, **6**, and **7** as potential intermediates, as well as perchlorofulvene (**4**)[8f] as the product of Cl elimination from **3**.

The syntheses of *trans*- and *cis*-octachloro-1,3,5-hexatriene (**1** and **2**, respectively), octachloromethylenecyclopentene (**3**), and the fulvene derivative **4** have been described by the groups of Prins[9] and of Roedig[8c–8f] previously. Further studies by Simonov et al. concerned the electrochemical properties of these compounds.[10] We followed the procedure given by Prins[9b] for the synthesis of decachloro-1,5-hexadiene, which was dechlorinated according to Roedig et al.[8e] with KOH in acetone to yield *trans*- and *cis*-octachloro-1,3,5-hexatriene in a 4:1 ratio. The dechlorination with triphenylphosphane in diethyl ether at 0 °C resulted in a 8:1 mixture of **2/1** (see Exp. Sect.). The thermal isomerization of **2** to *trans* isomer **1** had been performed by Roedig et al. either by heating it to 250 °C[8d] or by boiling it in fuming nitric acid and adding concentrated HCl.[8e] We observed several by-products when following the latter procedure. Therefore, we heated the mixture of the *trans* and *cis* trienes (1:4) to 220 °C until the ratio reached 1:1. We detected only traces of other products **3**–**5** by GC. The isolation and purification of **1** was possible by crystallization from methanol. All the products were characterized by IR, MS, and ^{13}C NMR spectroscopy. Additionally, we obtained single-crystal X-ray structures from the solid *trans* triene **1**, perchloromethylenecyclopentene **3**, and the fulvene derivative **4** (see Figures 1, 2, and 3).

The X-ray diffraction of crystals of triene **1** shows a unique disordered packing of the molecules (Figure 1). We found two superimposed molecules to occupy identical positions for the eight Cl atoms and the two central C atoms, but the peripheral vinyl groups are disordered. For both molecular units, the positions of Cl-1B/Cl-1B′ are identical, but the positions of Cl-2/Cl-2′ and Cl-1A/Cl-1A′of the first unit are adopted by Cl-1A/Cl-1A′ and Cl-2/Cl-2′ of the second unit. We found two independent sets of positions for the C atoms C-1,C-2/C-1′,C-2′ with crossed double bonds. The length of the central double bond (1.330 Å) is similar to that found for tetrachloroethylene (1.372 Å),[11] while the peripheral double bonds are slightly shorter (1.318 Å). Also the lengths of the C–Cl bonds (1.715–1.731 Å) are in good agreement with the value found for tetrachloroethylene (1.724 Å). The three vinylidene groups are connected by single bonds, each with a length of 1.480 Å. A bond angle of 115.5° at the terminal Cl–C–Cl group reflects the reduced degree of steric compression compared with that of C_2Cl_4 (113.3°). The structural data obtained from the X-



Scheme 1. Isomerization and cyclization reactions of hexatrienes **1** and **2**.

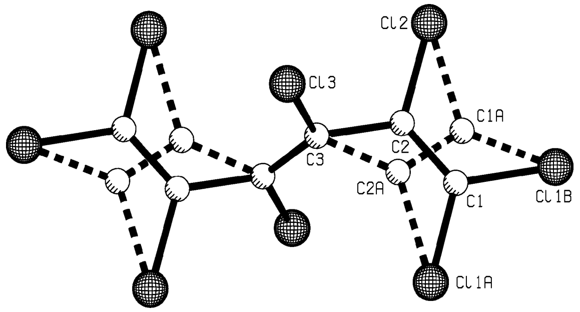


Figure 1. X-ray structure of **1**. Selected bond lengths and bond angles [values calculated at the B3LYP/6-31G(2d) level are given in square brackets]: C(1)–C(2): 1.318 Å [1.342], C(1)–Cl(1B): 1.723 Å [1.724], C(1)–Cl(1A): 1.715 Å [1.732], C(2)–C(3): 1.480 Å [1.471], C(2)–Cl(2): 1.727 Å [1.745], C(3)–C(3′): 1.330 Å [1.341], C(3)–Cl(3): 1.731 Å [1.752], C(2)–C(1)–Cl(1B): 122.7°, C(2)–C(1)–Cl(1A): 121.8°, Cl(1A)–C(1)–Cl(1B): 115.5°, C(1)–C(2)–C(3): 123.0°, C(1)–C(2)–Cl(2): 120.9°, C(3)–C(2)–Cl(2): 116.1°, C(3′)–C(3)–C(2): 126.8°, C(3′)–C(3)–Cl(3): 119.8°, C(2)–C(3)–Cl(3): 113.2°, Cl(1B)–C(1)–C(2)–C(3): –178.6°, Cl(1A)–C(1)–C(2)–C(3): 1.4°, Cl(1B)–C(1)–C(2)–Cl(2): –1.2°, Cl(1A)–C(1)–C(2)–Cl(2): 178.8°, C(1)–C(2)–C(3)–C(3′): –74.1° [–84.0], Cl(2)–C(2)–C(3)–C(3′): 108.3°, C(1)–C(2)–C(3)–Cl(3): 111.1°, Cl(2)–C(2)–C(3)–Cl(3): –66.5°.

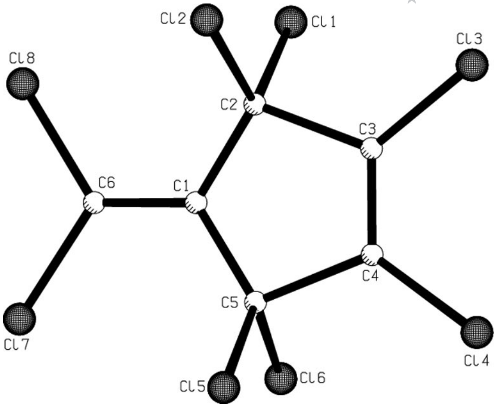


Figure 2. X-ray structure of **3**. Selected bond lengths and bond angles [values calculated at the B3LYP/6-31G(2d) level are given in square brackets]: Cl(1)–C(2): 1.818 Å [1.819], Cl(2)–C(2): 1.796 Å, Cl(3)–C(3): 1.667 Å, Cl(4)–C(4): 1.706 Å [1.709], Cl(5)–C(5): 1.724 Å, Cl(6)–C(5): 1.766 Å, Cl(7)–C(6): 1.728 Å [1.724], Cl(8)–C(6): 1.719 Å, C(1)–C(6): 1.320 Å [1.342], C(1)–C(2): 1.448 Å, C(1)–C(5): 1.461 Å [1.518], C(2)–C(3): 1.587 Å [1.501], C(3)–C(4): 1.309 Å [1.338], C(6)–C(1)–C(2): 122.7°, C(6)–C(1)–C(5): 122.7°, C(2)–C(1)–C(5): 114.3°, C(1)–C(2)–C(3): 102.4°, C(1)–C(2)–Cl(2): 118.2°, C(3)–C(2)–Cl(2): 108.5°, C(1)–C(2)–Cl(1): 115.2°, C(3)–C(2)–Cl(1): 99.5°, Cl(2)–C(2)–Cl(1): 110.7°, C(4)–C(3)–C(2): 104.7°, C(4)–C(3)–Cl(3): 127.7°, C(2)–C(3)–Cl(3): 121.5°, C(3)–C(4)–Cl(4): 124.7°, C(1)–C(5)–Cl(5): 123.4°, C(1)–C(5)–Cl(5): 111.8°, Cl(5)–C(5)–Cl(6): 110.0°, C(1)–C(6)–Cl(8): 121.8°, C(1)–C(6)–Cl(7): 123.8°, Cl(8)–C(6)–Cl(7): 114.9°, C(6)–C(1)–C(2)–C(3): –178.3°, C(5)–C(1)–C(2)–C(3): 6.6°, C(6)–C(1)–C(2)–Cl(2): 62.6°, C(5)–C(1)–C(2)–Cl(2): –112.5°, C(6)–C(1)–C(2)–Cl(1): –71.5°, C(5)–C(1)–C(2)–Cl(1): 113.4°, C(1)–C(2)–C(3)–C(4): –4.4°, Cl(2)–C(2)–C(3)–C(4): 121.4°, Cl(1)–C(2)–C(3)–C(4): –123.0°, C(1)–C(2)–C(3)–Cl(3): 179.1°, Cl(2)–C(2)–C(3)–Cl(3): –55.1°, Cl(1)–C(2)–C(3)–Cl(3): 60.5°, C(2)–C(3)–C(4)–Cl(4): –171.6°, Cl(3)–C(3)–C(4)–Cl(4): 4.6°, C(6)–C(1)–C(5)–Cl(5): –66.4°, C(2)–C(1)–C(5)–Cl(5): 108.7°, C(6)–C(1)–C(5)–Cl(6): 68.4°, C(2)–C(1)–C(5)–Cl(6): –116.5°, C(2)–C(1)–C(6)–Cl(8): –1.5°, C(5)–C(1)–C(6)–Cl(8): 173.2°, C(2)–C(1)–C(6)–Cl(7): –176.1°, C(5)–C(1)–C(6)–Cl(7): –1.4°.

ray analysis of *trans* triene **1** and calculations at the B3LYP/6-31G(2d) level are in good agreement. The measured C–Cl bond lengths of 1.723/1.715/1.727 Å are slightly shorter (≤1%) than the calculated values of 1.723/1.732/1.745 Å. The same holds for the C–C distances of 1.318/1.480/1.330 Å compared to the theoretical values of 1.342/1.471/1.341 Å. We found the three vinyl units to be nearly planar in the X-ray structure and completely planar in the calculated structure. We found slightly larger deviations for the dihedral angles between the central and lateral vinyl units with 74.1° (X-ray) and 84.0° (calculation). Still, both approaches indicate the complete decoupling of the triene system. Calculations indicate this also to be true for the *cis* isomer **2**. This is in strong contrast to the fully planar nonchlorinated parent system C_6H_8.[23a]

The X-ray analysis of crystalline perchloromethylenecyclopentene (**3**) shows unsymmetrical molecules. The reduced symmetry can result from disordered packing of the molecules in the crystal, a well-known problem in the determination of crystal structures of highly chlorinated compounds.[12] The deviations from planarity are in the range of 0.9 to 8.4°. We found the length of the exocyclic double bond to be 1.320 Å, and the C–Cl bonds of 1.719/1.728 Å length are close to the values found for the terminal double bonds of **1**. We found strongly reduced bond lengths for the endocyclic double bond (1.309 Å) and the corresponding C–Cl bonds (1.667/1.706 Å). C–C single bonds connecting the endocyclic double bond and the adjacent dichloromethylene C are significantly longer (1.587 Å) than bonds connecting the latter with the exocyclic vinylidene group (1.448/1.461 Å). These deviations most likely result from disordered packing as the calculated gas-phase structure is fully C_{2v} symmetric. A comparison of the measured and calculated structural data gives good agreements for the C–Cl bond lengths. We obtained larger diversions for the C framework. The values calculated for the exocyclic double bond (1.343 Å), the adjacent single bonds (1.518 Å), and the endocyclic double bond (1.338 Å) are significantly larger than those from the X-ray analysis (1.320/1.448/1.309 Å).

The crystals of fulvene **4** are built from completely planar molecules with dihedral angles of 4° or less. The molecular structure of **4** is well-described by the Lewis formula in Scheme 1, featuring short exocyclic and endocyclic C–C double bonds of 1.354/1.346 Å and longer lengths of 1.483/1.487 Å for the formal C–C single bonds. Similar values have been found in the X-ray crystal structure of perchloroheptafulvalene,[13] indicative of the highly localized double bonds in **4**. The structural data from the X-ray analysis are in excellent agreement with the calculated data; the calculated values of the C–Cl bonds are slightly higher (≈ 1%) than these obtained from X-ray diffraction.

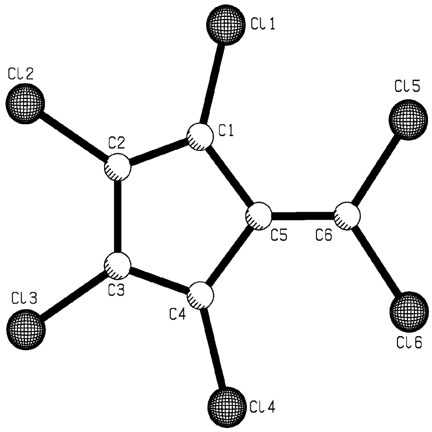


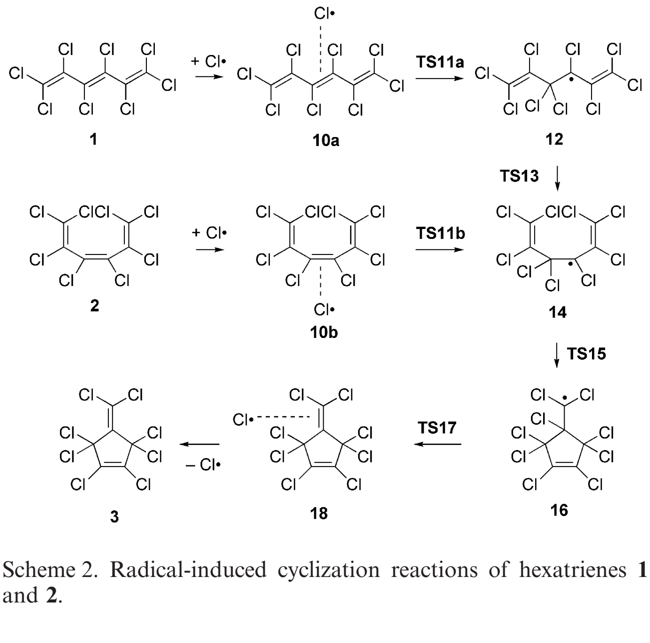
Figure 3. X-ray structure of **4**. Selected bond lengths and bond angles [values calculated at the B3LYP/6-31G(2d) level are given in square brackets]: Cl(1)–C(1): 1.701 Å [1.722], Cl(2)–C(2): 1.704 Å [1.713], Cl(3)–C(3): 1.700 Å, Cl(4)–C(4): 1.704 Å, Cl(5)–C(6): 1.704 Å [1.726], Cl(6)–C(6): 1.712 Å, C(1)–C(2): 1.345 Å [1.357], C(1)–C(5): 1.483 Å [1.485], C(2)–C(3): 1.456 Å [1.460], C(3)–C(4): 1.346 Å, C(4)–C(5): 1.481 Å, C(5)–C(6): 1.354 Å [1.357], C(2)–C(1)–C(5): 108.2°, C(2)–C(1)–Cl(1): 123.1°, C(5)–C(1)–Cl(1): 128.6°, C(1)–C(2)–C(3): 109.5°, C(1)–C(2)–Cl(2): 127.1°, C(3)–C(2)–Cl(2): 123.4°, C(4)–C(3)–C(2): 109.1°, C(4)–C(3)–Cl(3): 127.1°, C(2)–C(3)–Cl(3): 123.8°, C(3)–C(4)–C(5): 108.5°, C(3)–C(4)–Cl(4): 123.1°, C(5)–C(4)–Cl(4): 128.4°, C(6)–C(4)–C(4): 127.8°, C(6)–C(5)–C(1): 127.6°, C(4)–C(5)–C(1): 104.7°, C(5)–C(6)–Cl(6): 123.9°, Cl(5)–C(6)-Cl(6): 112.3°; all torsion angles are smaller than |3.6°|.

Thermal Isomerization in Condensed Phase and in Solution

The thermal rearrangements of **1** and **2** have been studied by Roedig et al. before.[8f] It was reported that **2** isomerized to **1** within 40 min at 250 °C; an isomerization of **1** to the *cis* isomer **2** was not mentioned. Both isomers were irreversibly converted to **3** within 5 min by heating to 290 °C or, in the presence of an excess of Cl_2, within 10 min at 150 °C.

In our hands, heating the mixture of **1** and **2** neat, in 1,2,4-trichlorobenzene, or in n-octadecane led to the isomerization of **2** to **1**. At 220 °C, the ratio of **1**:**2** rose from 1:8 to 1:3 in the neat compounds within 7 h, in trichlorobenzene within 5 h, and in n-octadecane within 13 h. Contrary to the solutions, small amounts (<3%) of **3**–**5** formed by the heating of the neat mixture for 7 h at 220 °C. The composition of this mixture changed completely upon prolonged heating (9 h), whereas the relative amount of **3** increased to 71%, accompanied by 10% of **4** and 6% of **5**, only 9% of **1** and 5% of **2** remained. The formation of **3** was retarded in trichlorobenzene and suppressed in octadecane. The addition of **3** (5 mol-%) to a solution of **1** and **2** in trichlorobenzene had a strong accelerating effect on the *cis*/*trans* isomerization; within 2 h at 220 °C, the *trans*/*cis* ratio reached 1:2. Starting with pure **1**, heating to 220 °C for 1 h was sufficient to produce a 3:1 ratio of **1**/**2** together with **3** (14%). After 5 h, the composition had changed to a ratio of 53% of **1**, 21% of **2**, and 26% of **3**. At this point, the cyclization to **3** became fast. Within 1 h, the amount of **3** rose to 71%, and the ratio of the hexatrienes remained constant at 2.5:1. The addition of azobisisobutyronitrile as a radical-chain initiator or CuCl to the mixture of the pure compounds did not have a significant effect on reaction rates or the composition of the reaction mixture. The question of the thermodynamic equilibrium of the isomers **1** and **2** will be further discussed below.

The origin of the catalytic effect of **3** on the *cis*/*trans* isomerization and the autocatalysis of the cyclization to **3** is probably the fission of one of the allylic C–Cl bonds in **3**, generating a $Cl^{\cdot}$ and a planar pentadienyl radical. The weakness of these C–Cl–bonds in **3** results in the formation of traces of fulvene **4** (≈ 3%) if **3** is heated for 3 h to 220 °C. In solution, **3** is quantitatively dechlorinated to **4** with copper powder. The reduced rate of the *cis*/*trans* isomerization and the suppression of the ring closure to **3** in n-octadecane, together with the formation of high-boiling hydrocarbons as by-products, indicate a trapping of intermediate radicals. We further illustrated the pivotal role of Cl in these reactions by saturating a *trans*/*cis* mixture (1:8) with Cl_2 at ambient temperature and heating the mixture to 220 °C in an open tube. Within 15 min, the *trans*/*cis* ratio increased to a value of 2.7:1, and 37% of the hexatrienes underwent ring closure to **3**. Like Cl_2, the presence of Br_2 strongly accelerated the *cis*/*trans* isomerization. Within 1 h at 220 °C, catalytic amounts of Br_2 in the *trans*/*cis* mixture or in pure *trans*-perchlorohexatriene (**1**) were sufficient to establish the *trans*/*cis* equilibrium of 2.55:1. Contrary to Cl_2, Br_2 did not initiate the cyclization. In Scheme 2 we propose a mechanism for the thermal behavior of these compounds, which is derived from calculations (see below).



Scheme 2. Radical-induced cyclization reactions of hexatrienes **1** and **2**.

A halogen radical attack on C(3) of perchlorohexatriene **1** generates an allylic radical and enables the molecule to rotate around the C(3)–C(4) bond. The elimination of a $Cl^{\cdot}$ results in *trans*/*cis* equilibration. If the terminal C-6 atom of the allylic radical attacks the π-orbital of the C(1)–C(2) bond in an *exo-trig* process, ring closure can occur. Splitting off the Cl$^\cdot$ from C(2) completes the formation of **3** and allows for the propagation of the isomerization/cyclization process. Cl attack is equally possible at the C(1) or C(2) positions of hexatriene **1**, but the conversion of the primary adducts to product **3** will then require additional intramolecular Cl migration steps. For the sake of simplicity we will thus concentrate on the mechanism shown in Scheme 2.

In addition to the thermal isomerization of the trienes **1** and **2** neat and in solution, we performed flash vacuum pyrolysis experiments. The relative composition of the pyrolysis products is strongly dependent on the temperature (Figure 4).

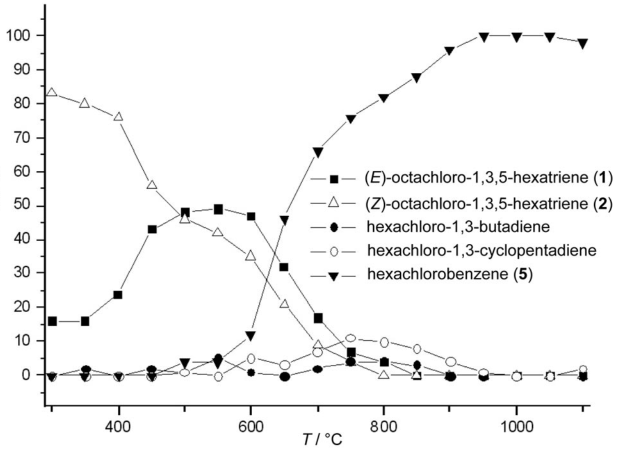


Figure 4. Flash vacuum pyrolysis of mixture of **1** and **2**.

In the temperature regime below 650 °C, mainly *cis*/*trans* isomerization occurs. The *trans* isomer **1** appears to be the preferred product in the 500–600 °C range. At 500 °C, the formation of hexachlorobenzene **5** becomes significant and strongly increases in the 650–700 °C range reaching a plateau of about 96% between 900 and 1100 °C. Traces of hexachlorocyclopentadiene and hexachlorobutadiene have been identified by GC as by-products in varying ratios mainly between 750 and 900 °C. Analogously, starting with pure **1**, we observed mainly isomerization to a mixture of **1** and **2** at temperatures below 600 °C, whereas fragmentation and the formation of **5** dominated above 700 °C.

The results show that while the isomerization of C_6Cl_8 **1** and **2**, other thermal reactions like the formation of hexachlorobutadiene and hexachlorocyclopentadiene only occur at more elevated temperatures between 600 and 900 °C. The formation of the latter two products presumably results from retro-reactions.[1b]

trans-Octachlorohexatriene (**1**) appears to be thermodynamically more stable than its *cis* isomer at higher temperatures. The calculated enthalpy difference between **1** and **2** is very small at room temperature, but this difference may change in favor of *trans* **1** at higher temperature. The equilibrium distribution [$K(\mathbf{1/2})$] of isomers **1** and **2** has been calculated over the temperature range 278.15–900 K from the free energy difference between these two species [$\Delta G(\mathbf{1/2}) = G(\mathbf{1}) - G(\mathbf{2})$] according to Equation (1). The free energies can be dissected further into enthalpy and entropy contributions according to Equation (2).

$$K(\mathbf{1/2}) = \exp[-\Delta G(\mathbf{1/2})/\text{r.t.}] \tag{1}$$

$$\Delta G(\mathbf{1/2}) = \Delta H(\mathbf{1/2}) - T\Delta S(\mathbf{1/2}) \tag{2}$$

We obtained the free energies of **1** and **2** at different temperatures by combining gas-phase total energies obtained at the G3(MP2)B3 level with thermal corrections obtained at the B3LYP/6-31G(2d) level. The latter are based on the rigid-rotor/harmonic oscillator model and standard thermodynamic formulae for enthalpies and entropies. As can be seen in Figure 5, the **1**:**2** ratio varies between 5.5 and 6.5 over the temperature range considered here, always favoring the *trans* isomer **1** by a small margin. The very small influence of the temperature observed here is due to the very small enthalpy difference between **1** and **2**, which amounts to 0.42–0.46 kJ mol^{-1} over the respective temperature range. From the vacuum pyrolysis experiments on mixtures of **1** and **2** described above, it can be seen that the rate of isomerization accelerates in the temperature region between 400 and 500 K. The almost 1:1 mixture of **1** and **2** obtained at 500 °C may thus correspond to the equilibrium mixture at this particular temperature. A comparison of the experimentally and theoretically predicted isomer ratio at 500 °C thus allows us to estimate the accuracy of the theoretical approach taken here to ± 7 kJ mol^{-1}. The thermodynamically most stable C_6Cl_8 isomer, **3**, which appears to be the final product in the condensed phase (below 250 °C) is only formed in trace amounts. Contrary to the condensed phase, an intramolecular reaction has to be assumed in the vacuum pyrolysis experiments. The activation barrier for the monomolecular cyclization of **1** and **2** must be much higher than for their *cis*/*trans* isomerization. Only at very high temperatures (800–1100 °C) we observed nearly exclusive formation of hexachlorobenzene (**5**).

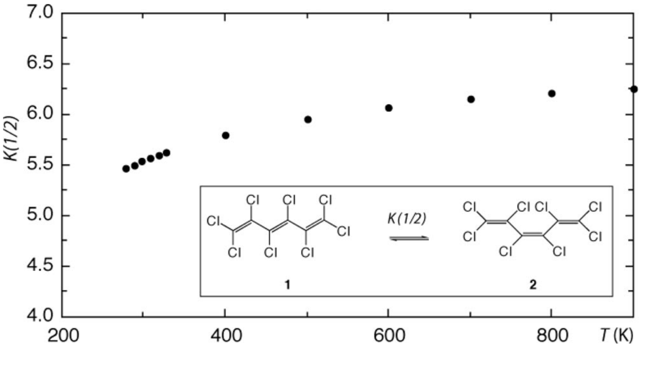


Figure 5. Temperature dependence of the **1/2** ratio, as calculated at the G3(MP2)B3 level of theory.

If this transformation proceeds by cyclization of **1/2** to **3** as the initial step, only relatively low activation barriers would separate **3** from **5**, since **3** is detected only in minor amounts. Considering that we detected Cl_2 and fulvene **4** as by-products, it is possible that fulvene **4** can be another intermediate which rearranges to **5** at high temperatures. According to the results reported by Roedig et al.,[8f] the photochemical activation of **4** in benzene results in quantitative transformation into **5**.

An alternative pathway for the formation of hexachlorobenzene is the disrotatory, pericyclic, ring closure of the 6π-electron system to perchloro-1,3-cyclohexadiene **6** followed by aromatization through the elimination of Cl. This compound had been observed as part of a mass spectrum of a mixture.[14a] Attempts to prepare intermediate **6** as a pure compound by the reaction of *o*-chloranil and PCl_5 failed, yielding an inseparable mixture of **6** and hexachlorobenzene (**5**) instead.[14b] The chlorination of *p*-chloranil resulted in a mixture of **5** and octachloro-1,4-cyclohexadiene.[14c] Heating the 1,4-diene to 150 °C resulted in a fast and quantitative formation of **5** by dechlorination and aromatization.[14b]

Table 1. Relative energies and enthalpies at 298.15 K of stationary points on the C_6Cl_8 potential energy surface (units: $kJ\,mol^{-1}$).

Entry	Structure	ΔH_{298} (B3LYP)[a]	ΔH_{298} (MP2)[b]	ΔH_{298} (G3MP2B3)[c]
1	**1**	0.0	0.0	0.0
2	**2**	+2.9	+1.9	–0.5
3	**3**	–47.5	–92.3	–78.4
4	**4** + Cl_2	+51.2	+84.9	+83.3
5	**5** + Cl_2	–73.9	–59.0	–44.8
6	**6**	–23.4	–86.1	–69.6
7	**7**	+41.8	–0.2	+11.6
8	TS**1/7**	+182.3	+153.6	+171.0
9	**TS2/3**	+216.7	+124.9	+159.6
10	**TS2/6**	+180.1	+130.7	+167.7
11	**TS2/7**	+133.9	+94.7	+119.9
12	**TS5/6**	+163.5	+224.2	+272.2
13	**TS2/8**	+190.1	+119.4	+155.0
14	**8**	+222.6	+105.2	+130.0
15	**TS3/8**	+227.7	+116.21	+149.3

[a] RB3LYP/6-311+G(3df)//RB3LYP/6-31G(2d). [b] MP2(FC)/G3MP2large//RB3LYP/6-31G(2d). [c] G3MP2B3 level based on RB3LYP/6-31G(2d) geometries.

Cyclization Reactions of Hexatrienes 1 and 2 – Theoretical Aspects

In order to understand the experimental results described above in more detail, we investigated several conceivable pathways for the conversion of perchlorohexatrienes **1** and **2**. We performed geometry optimizations at the B3LYP/6-31G(2d) level of theory and subsequently calculated improved relative energies following three different approaches: (1) the calculation of B3LYP/6-311+G(3df) single-point energies and their combination with thermal corrections from B3LYP/6-31G(2d) calculations to derive relative enthalpies at 298 K, (2) the calculation of MP2(FC)/G3MP2large single-point energies and their combination with thermal corrections from B3LYP/6-31G(2d) calculations to derive relative enthalpies at 298 K; the G3MP2large basis set is closely related to the 6-311+G(2df) basis set and has been optimized for use in the compound G3MP2 method, and (c) the calculation of G3MP2B3 enthalpies using a series of single-point calculations as suggested by Curtiss et al.[15] (Table 1). Of these three levels, the latter one can be expected to be the most accurate but also the most demanding. A survey of the results obtained at all three levels in Table 1 shows that the MP2 results are somewhat closer to those obtained at the G3MP2B3 level than they are to the B3LYP results. Since G3MP2B3 calculations were not feasible for the larger open-shell systems discussed below, the subsequent discussion will focus on the MP2 results exclusively.

A first point concerns the relative stability of *trans*-perchlorohexatriene **1** and its *cis* isomer **2**. These isomers are found to be almost isoenergetic at all levels of theory considered here (Table 1). One pathway for the interconversion of **1** and **2** leads through octachloro-3-vinylcyclobutene (**7**), which is predicted to be isoenergetic with **1**. Conrotatory, electrocyclic, ring opening[16,17] of **7** can occur with the trichlorovinyl substituent rotating outward with a barrier of +153.8 $kJ\,mol^{-1}$ through transition state **TS1/7**, forming *trans*-hexatriene **1** as the product. Alternatively, ring opening can occur with the trichlorovinyl substituent rotating inward with a barrier of +94.9 $kJ\,mol^{-1}$ through transition state **TS2/7**, now forming *cis*-hexatriene **2**. This "torquoselectivity"[16] is reminiscent of the reaction outcome in perfluorinated cyclobutenes, in which strongly electronegative substituents such as CF_3 are found to prefer inward rotation.

All attempts to locate a transition state for direct *trans*/*cis* isomerizations of trienes **1** and **2** through rotation around the central C(3)–C(4) bond failed, leading to either **TS1/7** or **TS2/7** instead.[23b] This is in marked contrast to the *trans*/*cis* isomerization reactions of unsubstituted alkenes, in which this process represents the main reaction pathway under thermal reaction conditions.

A second electrocyclic process relevant to the fate of perchlorohexatriene **2** is the disrotatory 6π-electrocyclization to octachlorocyclohexadiene **6**. This reaction is exothermic by 88.0 $kJ\,mol^{-1}$ but faces a reaction barrier of +128.8 $kJ\,mol^{-1}$. The structure of the corresponding transition state **TS2/6** is quite in line with expectations for this process.[17] The elimination of Cl_2 from **6** can potentially yield hexachlorobenzene **5**, but this step is thermochemically endothermic by 27.1 $kJ\,mol^{-1}$ and features a very high reaction barrier of over 310.3 $kJ\,mol^{-1}$. Aside from the 6π- and 4π-electrocyclization reactions (forming **6** and **7**, respectively) hexatriene **2** can also cyclize in a hitherto unknown fashion to the five-membered-ring product **3**. The formation of this latter compound is exothermic by 94.2 $kJ\,mol^{-1}$, making **3** the thermochemical sink of the potential energy surface shown in Scheme 1. The transition state **TS2/3** for the interconversion of **2** and **3** is a true transition state at the RB3LYP/6-31G(2d) level of theory, featuring only one imaginary frequency corresponding to 151 cm^{-1} in its vibrational frequency spectrum. Intrinsic reaction path calculations show that **TS2/3** connects the minima **2** and **3** without the intermediacy of any further species. The structure of **TS2/3** has substantial structural similarity to what may be expected for a biradical intermediate such as **8**, and smoothly combines two bond-making/bond-breaking processes: (i) the formation of a new C–C bond between C(2) and C(6) and (ii) Cl migration from C(2) to

C(3) (all with respect to atom numbering in reactant **2**). The animation of the imaginary frequency as well as the inspection of the structure of **TS2/3** shows that the C–C bond formation is well-advanced while Cl migration has hardly begun. In order to probe the involvement of biradical intermediates, we reinvestigated the potential energy surface between **2** and **3** at the unrestricted UB3LYP/6-31G(2d) level of theory. Biradical **8** now represents a true intermediate located 103.3 kJ mol^{-1} above reactant **2**. The transition state **TS2/8** for the formation of **8** from hexatriene **2** is energetically and structurally very similar to transition state **TS2/3** located at the RB3LYP level and located only 14.2 kJ mol^{-1} above biradical **8**. Subsequent Cl migration through transition state **TS3/8** is slightly more facile with a barrier of +11.0 kJ mol^{-1}. A comparison of the sequence obtained from RB3LYP geometry optimizations (**2**–**TS2/3**–**3**) with that obtained at the UB3LYP level (**2**–**TS2/8**–**8**–**TS3/8**–**3**) shows that the predicted reaction barriers are rather similar in both cases and that the intermediacy of biradical intermediates such as **8** can neither be strictly excluded nor confirmed at this stage. The elimination of Cl_2 from **3** to yield perchlorofulvene **4** is strongly endothermic by 177.2 kJ mol^{-1}, and the subsequent rearrangement to perchlorobenzene **5** is exothermic by 143.9 kJ mol^{-1}. This implies that the conversion of **3** to benzene **5** + Cl_2 is endothermic by 33.3 kJ mol^{-1} at 298.15 K, highlighting the high thermochemical stability of **3**. The exothermic rearrangement of **4** to **5** has been observed by Roedig et al.[8d] upon the photolytic activation of fulvene **4**.

In addition to the unimolecular isomerization pathways shown in Scheme 1, it is also conceivable that the cyclization reactions of hexatrienes **1** and **2** are induced by external species. One option involves the addition of $Cl^{\cdot}$ atoms as described in Scheme 2. Starting from weakly bound complexes between $Cl^{\cdot}$ and trienes **1** and **2**, the actual barriers for the addition step are rather low at +1.5 and +5.3 kJ mol^{-1}, respectively. The adduct radicals **12** and **14** can only formally be classified as allyl radicals. A closer analysis of the structures shows that the bond lengths along the C–C backbone as well as the corresponding dihedral angles are more in line with localized C–C double bonds with little interaction with the adjacent radical center. Rotation around the C(3)–C(4) bond in adduct radical **12** is quite facile with a barrier of +9.2 kJ mol^{-1}. The radical-induced *cis*/*trans* isomerization involving the sequence **1**–**10a**–**TS11a**–**12**–**TS13**–**14**–**TS11b**–**10b**–**2** thus provides an attractive, low-barrier alternative to the unimolecular isomerization described in Scheme 1. The highest barrier along the former sequence amounts to +45.3 kJ mol^{-1}, which compares favorably to the barrier for the latter sequence of +153.6 kJ mol^{-1} (both at the MP2 level of theory). The cyclization of radical **14** to provide the five-membered-ring cyclopentenylmethyl radical **16** is equally facile, facing a barrier of only +6.9 kJ mol^{-1}. Radical **16** is exceedingly stable from a thermochemical perspective and represents the lowest energy point of the potential energy surface shown in Scheme 2. The structure of **16** is fully in line with the Lewis structure shown in Scheme 2 and sports an impressively long C–Cl bond adjacent to the radical center (1.86 Å). The cleavage of this C–Cl bond through transition state **TS17** is endothermic by 60.8 kJ mol^{-1} and faces an equally large barrier. The reaction passes through the weakly bound complex **18**, located 12.9 kJ mol^{-1} below **3** + $Cl^{\cdot}$ (Table 2). Taken together, the radical-induced conversion of hexatriene **1** through intermediates **14** and **16** to cyclopentene **3** faces a barrier of not more than +60.8 kJ mol^{-1}, and thus, provides a worthwhile alternative to the unimolecular pathways described in Scheme 1. The highest barrier in this latter case amounts to +171.0 kJ mol^{-1} if we include the *cis*/*trans* isomerization process between **1** and **2** or +155.5 kJ mol^{-1} for the reaction starting from **2**.

Table 2. Relative energies and enthalpies at 298.15 K of stationary points on the $Cl^{\cdot}$ + C_6Cl_8 potential energy surface (units: kJ mol^{-1}).

Entry	Structure	ΔH_{298} (B3LYP)[a]	ΔH_{298} (ROMP2)[b]
1	**1** + $Cl^{\cdot}$	0.0	0.0
2	**10a**	–17.07	–22.51
3	**TS11a**	+4.87	–21.01
4	**12**	–17.89	–48.32
5	**TS13**	+1.12	–39.14
6	**2** + $Cl^{\cdot}$	+2.87	–2.07
7	**10b**	–10.46	–24.61
8	**TS11b**	+9.08	–19.30
9	**14**	–27.86	–64.56
10	**TS15**	+4.29	–57.68
11	**16**	–68.58	–153.11
12	**TS17**	–45.95	–112.81
13	**18**	–47.22	–105.19
14	**3** + $Cl^{\cdot}$	–47.46	–92.27

[a] UB3LYP/6-311+G(3df,2p)//UB3LYP/6-31G(2d). [b] ROMP2-(FC)/G3MP2large//UB3LYP/6-31G(2d).

The absolute barriers cited here depend, of course, substantially on the chosen level of theory. However, the dramatically lower reaction barriers for the radical-induced isomerization mechanisms outlined in Scheme 2 as compared to the unimolecular isomerization pathways shown in Scheme 1 persist at any level of theory studied here.

Conclusions

The thermal behavior of C_6Cl_8 isomers **1**–**3** as well as the C_6Cl_6 isomers **4** and **5** were studied by heating the compounds in neat form and in *n*-octadecane or trichlorobenzene solutions. The *trans*- and *cis*-octachloro-1,3,5-hexatrienes **1** and **2** show thermal equilibration from both sides at 220 °C, and the rate is enhanced by catalytic amounts of Br_2, Cl_2, or **3**; *cis*-triene **2** can be regarded as the key compound en route to the cyclized **3** and **4** at 250 °C; at higher temperatures, between 600–1000 °C, the formation of hexachlorobenzene (**5**) is observed, likely via octachloro-1,3-cyclohexadiene (**6**) as an intermediate. The calculations of all compounds and the corresponding transition states can explain and accommodate the experimental findings and highlight the catalytic effects of open-shell intermediates. These reactions are fundamental for understanding the formation of chlorinated micropollutants such as **5**, which are observed in technical incineration processes and are an important indicator and precursor for PCDD/F.

Experimental Section

General: Meltings points are uncorrected. All NMR spectra were recorded with a Bruker AC 300 spectrometer, and TMS was used as an internal standard. MS was performed with a Finnigan MAT 95 instrument. IR spectra were recorded with a Perkin–Elmer Paragon 500 FT-IR spectrometer. UV/Vis spectra were recorded with a Perkin–Elmer Lambda 16 spectrometer. GLC conditions: Perkin–Elmer DB 35MS (30 m) column, temperature program: start at 150 °C, then 2 °C/min to 180 °C, then 10 °C/min to 240 °C, then 240 °C for 5 min, FID detector, N_2 carrier gas, Merck–Hitachi D 2500 Chromato-Integrator.

1,5-Decachlorohexadiene: The diene was prepared from hexachloropropene with cuprous chloride as the coupling agent according the procedure given by Prins.[9b] IR (KBr): ṽ = 1518, 1060, 938, 892, 858, 808, 780, 732, 644, 627 cm^{-1}. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 94.5 (C-3,4), 128.1 (C-1,6), 131.2 (C-2,5) ppm. MS (FD): 426 (100%, Cl_{10} pattern) $[M]^+$. C_6Cl_{10} (426.596): calcd. C 16.89%; found C 17.06%.

***cis*-1,3,5-Octachlorohexatriene (2):** The compound was prepared according to the procedure given by Roedig et al.,[8e] resulting in a 1:4 mixture of the *trans* and the *cis* isomers as a colorless oil. Alternatively, K_2CO_3 (2.1 g, 0.015 mol) was added to 1,5-decachlorohexadiene (6.4 g, 0.015 mol) in anhydrous diethyl ether (30 mL) and 2-propanol (1 mL). The mixture was cooled in a water/ice bath, and triphenylphosphane (3.9 g, 0.015 mol) was added with stirring. The mixture was stirred for 90 min at 0 °C, at which time the phosphane had been consumed (TLC), and water (30 mL) was added. The organic layer was separated, and the aqueous phase was extracted with cyclohexane (50 mL). The pooled organic solutions were washed with brine (20 mL), dried with Na_2SO_4, and concentrated. After chromatography on silica gel with cyclohexane as an eluent, a 1:8 mixture of **1** and **2** was obtained as a colorless oil in 84% yield (4.5 g). IR (neat): ṽ = 1575, 1540, 1197, 1161, 1131, 970, 951, 898, 860, 831, 808, 683, 628 cm^{-1}. *cis*-**2**: ^{13}C NMR (75 MHz, $CDCl_3$): δ = 130.51 (C-2), 127.24 (C-1), 123.00 (C-3) ppm. UV (ethanol): λ ($\log\varepsilon$) = 216 (4.36), 255 (sh, 3.76) nm. C_6Cl_8 (355.690): calcd. C 20.26%; found C 20.23%.

***trans*-1,3,5-Octachlorohexatriene (1):** The compound was prepared from the *cis*/*trans* mixture (1.2 g) by heating it for 1 h to 220 °C and adding Br_2 (3 × 100 mg) until the composition of the mixture reached a **1**:**2** ratio of 2.5:1. Purification was performed by repeated crystallization from dichloromethane and methanol to yield 24% (0.3 g) of colorless crystals; m.p. 74 °C, ref.[8e] m.p. 72 °C. IR (KBr): ṽ = 1592, 1168, 955, 849, 790, 611 cm^{-1}. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 127.9 (C-3), 126.4 (C-1), 123.2 (C-3) ppm. MS (FD): 356 (100%, Cl_8-pattern) $[M]^+$. UV (ethanol): λ ($\log\varepsilon$) = 212 (4.39), 257 (sh, 3.92) nm. C_6Cl_8 (355.690): calcd. C 20.26%; found C 20.08%. For an X-ray structure, the product was crystallized from the same solvent mixture.

Octachloro-4-methylenecyclopent-1-ene (3): The compound was prepared by heating **1** or a mixture of **1** and **2** for 5 h to 250 °C and subsequent recrystallization of the product from chloroform/methanol to yield colorless crystals; m.p. 183 °C, ref.[8e] m.p. 183 °C. IR (KBr): ṽ = 1638, 1599, 1551, 1168, 916, 840, 801, 630 cm^{-1}. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 81.8 (C-3, 5), 135.5, 16.5, 137.5 ppm. UV (ethanol): λ ($\log\varepsilon$) = 216 (4.97) nm. C_6Cl_8 (355.690): calcd. C 20.26%; found C 20.26%.

Hexachlorofulvene (4): Methanol (20 mL) was added to a warm solution of **3** (3.56 g, 0.01 mol) in toluene (6 mL) while stirring. Copper powder (1.42 g, 0.022 mol) was added, and the suspension was stirred for 4 h at ambient temperature. After adding dichloromethane (30 mL), the mixture was filtered into water (40 mL), the organic layer was separated, the aqueous phase was extracted with dichloromethane, and the pooled organic solutions were washed with water and dried with $MgSO_4$. Purification by chromatography on silica gel with cyclohexane as an eluent (R_f = 0.95) yielded 3.31 g (93%) of product; m.p. 153–154, ref.[8d] m.p. 152–153 °C IR (KBr): ṽ = 1552, 1567, 1279, 1257, 1223, 931, 709, 637 cm^{-1}. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.9, 131.0, 130.5, 117.5 ppm. UV (ethanol): λ ($\log\varepsilon$) = 206 (3.94), 298 (4.07), 309 (4.07), 423 (2.49) nm. C_6Cl_6 (284.784): calcd. C 25.31%; found C 24.90%.

Flash Vacuum Pyrolysis Experiments: The sample (100 mg) was placed in a flask (100 mL) directly connected to a quartz tube (25 mm inner diameter and 60 cm length) placed in a horizontal tubular furnace (heated zone: 35 cm) and connected to a cold trap (–196 °C). Pyrolysis was performed at 10^{-2} Torr and temperatures between 300 and 1100 °C. After the experiment, the cold trap was flushed with N_2, warmed to ambient temperature, and the products were dissolved in chloroform and analyzed by GLC. The response factors of the GC detector (FID) of the isomeric trienes **1** and **2** were identical and defined as 1. The relative sensitivity for hexachlorobenzene **5** was 1.14, whereas the sensitivity for **3** was only 0.94.

Thermolysis of *trans*- and *cis*-Octachlorohexatrienes: A mixture of *cis*- and *trans*-1,3,5-octachlorhexatriene (85:15) was used. The trienes (neat or as a 10% solution in 1,2,4-trichlorobenzene or octadecane) were heated in a sand bath, and samples were taken and analyzed by GLC. For the Br_2-catalyzed isomerisation, small amounts of pure Br_2 (ca. 30 µL) were added to the sample (1.2 g), which was placed in an open flask at 220 °C. Within 20 min, the color faded due to the evaporation of Br_2, and the mixture was analyzed. Three subsequent additions of Br_2 were sufficient to establish an equilibrium of **1**:**2** = 2.6:1. Catalysis of the isomerization was performed by bubbling Cl_2 through the liquid at ambient temperature and heating the Cl_2-saturated mixture in an open flask. Heating **3** to 220 °C for 3 h in a test tube led to the formation of small amounts of **4** (<5%). For the study of the isomerization in the condensed phase, a mixture of **1** and **2** [neat or as a 0.2 M solution in 1,2,4-trichlorobenzene or *n*-octadecane] was heated to 220 °C, and samples, taken at 1 h intervals, were analyzed by GLC.

X-ray Structure Determination of 1: Performed with a SMART CCD Bruker Nonius instrument using a transparent, colorless plate. Crystal data: C_6Cl_8 M = 355.7 $g\,mol^{-1}$, $0.12 \times 0.24 \times 0.36\ mm^3$, monoclinic, space group $P2_1/c$, Mo-K_α, graphite monochromation: 0.71069 Å, T = 193 K, unit cell dimensions: a = 6.3235(4), b = 13.0794(7), c = 7.5282(4) Å, β = 109.557(4)°, V = 586.7(7) $Å^3$, Z = 2, d_{calc} = 2.013 $g\,cm^{-3}$, absorption μ = 1.87 mm^{-1}, the Θ range for data collection was 2° to 28.3°, and the index ranges were $-8 \le h \le 8$, $-17 \le k \le 17$, and $-10 \le l \le 10$. Number of reflections collected: 5956; independent reflections: 1456 [R_{int} = 0.0871]. The structure was solved by direct methods (program SIR 92, refinement by SHELXL-97).[18]

Structure refinement was performed by full-matrix least-squares on 71 parameters, weighted refinement: $w = 1/[\sigma^2(F_o^2) + (0.0552 \times P)^2]$ with $P = [\max(F_o^2,0) + 2 \times F_o^2]/3$, and non-hydrogen atoms were improved with anisotropic refinement. Goodness-of-fit on S = 0.957, maximum change of parameters 0.001 × e.s.d, final R indices: R_1 = 0.0410, wR_2 = 0.1029, the final difference Fourier map showed minimum and maximum values of –0.62 and 0.62 e Å^{-3}, respectively.

X-ray Structure Determination of 3: Performed with a SMART CCD Bruker Nonius instrument using a colorless block. Crystal data: C_6Cl_8, M = 355.66 g mol^{-1}, 0.25 × 0.35 × 0.45 mm^3, monoclinic, space group $P2_1/n$, Mo-K_α, graphite monochromation: 0.71069 Å, T = 295 K, unit cell dimensions: a = 5.914(6), b = 13,8758(7), c = 7.0237(13) Å, β = 90.088(2)°, V = 592.9(1) Å^3, Z = 2, d_{calc} = 1.992 g cm^{-3}, absorption μ = 1.853 mm^{-1}, the Θ range for data collection was 2° to 28.3°, and the index ranges were $-7 \leq h \leq 7$, $-18 \leq k \leq 18$, and $-9 \leq l \leq 9$. Number of reflections collected: 7152; independent reflections: 1464 [R_{int} = 0.0638]. The structure was solved by direct methods (program SIR 92, refinement by SHELXL-97).[18]

Structure refinement was performed by full-matrix least-squares on 127 parameters, weighted refinement: $w = 1/[\sigma^2(F_o^2) + (0.0456 \times P)^2 + 0.07 \times P]$ with $P = [\max(F_o^2,0) + 2 \times F_c^2]/3$, and all non-hydrogen atoms improved with anisotropic refinement. Goodness-of-fit on S = 0.992, maximum change of parameters 0.001 × e.s.d, final R indices: R_1 = 0.0278, wR_2 = 0.0763, the final difference Fourier map showed minimum and maximum values of –0.27 and 0.26 e Å^{-3}, respectively.

X-ray Structure Determination of 4: Performed with an Enraf–Nonius Turbo-Cad4 instrument equipped with a rotating anode using a red needle. Crystal data: C_6Cl_6, M = 284.75 g mol^{-1}, 0.16 × 0.16 × 1.392 mm^3, monoclinic, space group $P2_1/c$, Cu-K_α, graphite monochromation: 1.54180 Å, T = 143 K, unit cell dimensions: a = 16.318(2), b = 3,7721(9), c = 16.702(2) Å, β = 118.954(5)°, V = 899.6(3) Å^3, Z = 14, d_{calc} = 2.103 g cm^{-3}, absorption μ = 16.89 mm^{-1}, corrected with 6 surfaces, the Θ range for data collection was 2° to 73°, and the index ranges were $0 \leq h \leq 20$, $-4 \leq k \leq 0$, and $-20 \leq l \leq 18$. Number of reflections collected: 2170; independent reflections: 1806 [R_{int} = 0.0407]. The structure was solved by direct methods (program SIR 92, refinement by SHELXL-97).[18] Structure refinement was performed by full-matrix least-squares on 109 parameters, weighted refinement: $w = 1/[\sigma^2(F_o^2) + (0.1084 \times P)^2 + 2.10 \times P]$ with $P = [\max(F_o^2,0) + 2 \times F_c^2]/3$, and all non-hydrogen atoms improved with anisotropic refinement. Goodness-of-fit on S = 1.120, maximum change of parameters 0.001 × e.s.d, final R indices: R_1 = 0.0511, wR_2 = 0.1553, the final difference Fourier map showed minimum and maximum values of –1.01 and 0.97 e Å^{-3}, respectively.

CCDC-684678 (**1**), -177377 (**3**), -684679 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/datarequest/cif.

Theoretical Methods: Geometry optimizations of all stationary points shown in Scheme 1 were performed at the Becke3LYP/6-31(2d) level of theory. The same level of theory was used to calculate analytic second derivatives in order to verify the nature of all stationary points and calculate thermochemical corrections to enthalpies at 298.15 K. Structures of open-shell character were optimized at the unrestricted UB3LYP/6-31G(2d) level. Improved relative energies for all stationary points were then obtained through single-point calculations at the (U)B3LYP/6-311+G(3df) level of theory. A combination of these energies with thermal corrections calculated at the (U)B3LYP/6-31G(2d) level yielded the ΔH_{298}(B3LYP) values listed in Tables 1 and 2. Alternatively, single-point energies were also calculated at the MP2(FC)/G3MP2large level, with a restricted reference for both closed- and open-shell systems. A combination of the (RO)MP2(FC)/G3MP2large energies with the thermal corrections calculated at the (U)B3LYP/6-31G(2d) level yielded the ΔH_{298}(MP2) values listed in Tables 1 and 2. Finally, improved energies for the system described in Scheme 1 were also obtained with a slight modification of the G3(MP2)B3 compound method.[15] One deviation from the original recipe concerns the use of B3LYP/6-31G(2d) [instead of B3LYP/6-31G(d)] geometries as well as the use of the same thermochemical corrections as before. Given the possibility of intermediates with some open-shell character, the QCISD(T)/6-31G(d) single-point calculations in the original recipe were replaced by CCSD(T)/6-31G(d) calculations. The use of CCSD(T) [instead of QCISD(T)] calculations has previously been found by several authors to yield significant improvements in the calculations of open-shell systems.[19–21] The final enthalpies obtained from this procedure are nevertheless termed "H_{298}(G3MP2B3)" in order to reflect the spirit of the original recipe. All calculations have been performed with GAUSSIAN 03.[22]

Supporting Information (see also the footnote on the first page of this article): Theoretical data, structures and energies of minima and transition states.

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