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# Isomerization of perchlorohexatriene in three consecutive rearrangements to perchloro-2-vinylbutadiene

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## ABSTRACT

Perchlorohexatriene isomerizes in three subsequent rearrangements to perchloro-2-vinylbutadiene. A radical-induced *Z*-*E*-equilibration of linear perchlorohexatrienes is followed by cyclization to a methylenecyclopentene. Under flash-vacuum pyrolysis conditions, a ring contraction to 1,2-dimethylenecyclobutane occurs. In the condensed phase, a radical-induced ring opening generates the branched perchloro-vinylbutadiene. All compounds are converted to hexachlorobenzene, but only at very high temperatures.

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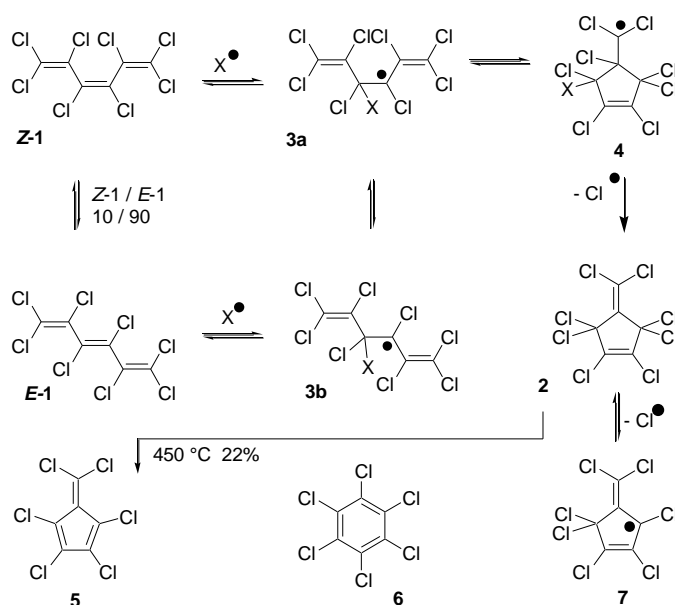
## 1. Introduction

Perchlorinated compounds were intensively investigated in the mid of the last century.<sup>1–7</sup> Recently, they regained attention due to their spectroscopic features,<sup>8,9</sup> as chemical substrates,<sup>10,11</sup> e.g. for the synthesis of fullerenes,<sup>12</sup> polycations,<sup>13</sup> and as cores for ligands used in transition-metal catalysis.<sup>14</sup> On the other hand, the appearance of highly chlorinated aromatics in the environment is a major ecological problem.<sup>15</sup> Especially the formation of persistent pollutants like hexachlorobenzene, highly chlorinated dibenzodioxines, and -furans e.g. in waste incineration is a technological challenge.<sup>16</sup> Their *de-novo* formation from dichloro acetylene in a growing mechanism is an accepted hypothesis;<sup>17</sup> the generation of a linear trimer and its cyclization to hexachlorobenzene has been proved recently.<sup>18</sup> We could show that perchlorohexatriene cyclizes in the gas phase at high temperatures, affording hexachlorobenzene.<sup>19</sup> In the condensed phase, a completely different path leads to a methylenecyclopentene, similar to a cyclization observed for 9,10-bis(trifluorovinyl)phenanthrene.<sup>20</sup> Herein, we report the successive isomerization of the linear perchlorohexatrienes in three rearrangements to a branched isomer.

## 2. *E/Z* Isomerization of 1 and 2 and Cyclization to 3

Perchlorohexatrienes **1** are prepared as *E,Z*-mixture with varying compositions;<sup>3b,19</sup> the main product **Z-1** can be converted to its *E*-isomer **E-1** at temperatures above 200 °C: At 220 °C a mixture **Z-1**:**E-1** = 89:11 changed to **Z-1**:**E-1** = 87:13 within 1 h.<sup>21</sup> The same experiment performed on pure **E-1** led to **Z-1**:**E-1** = 10:90. Addition of **2** (5 mol%) to the trienes had a strong accelerating effect on the isomerization: the composition of a mixture **Z-1**:**E-1**:**2** = 84:10:5 changed to **Z-1**:**E-1**:**2** = 73:20:7 within 1 h at 220 °C. Similarly, **E-1** (**Z-1**:**E-1**:**2** = 0:95:5) was

converted to **Z-1**:**E-1**:**2** = 22:64:14 (1 h, 220 °C) and reached **Z-1**:**E-1**:**2** = 21:53:26 after 5 h. Further heating did not change the *Z/E* ratio (1:2.5) but the amount of **2** increased to 71 %. Chlorine, like **2**, had similar accelerating effect: the *Z/E*-mixture (89:11), saturated with Cl<sub>2</sub> at ambient temperature and heated to 220 °C led to a ratio of **Z-1**:**E-1**:**2** = 27:73 within only 15 min, but 37% of the hexatrienes cyclized to **2**. Like chlorine, bromine catalyzed



**Scheme 1.** Isomerization and cyclization of perchlorohexatrienes.

the *Z/E*-isomerization: 1 h at 220 °C was sufficient to establish the *Z/E* equilibrium of 28:72 from both, the *Z/E* mixture (89:11)

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