

Solid-State Photoisomerization of Perchloro-*p*-xylene to Perchloro-1-methyl-1,3,6-cycloheptatriene: A Serendipitous Synthesis of Perchloroheptafulvene

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Perchloroheptafulvene (**4**) is prepared by photoisomerization of perchloro-*p*-xylene (**1**) in a surprising and key-step solid-state ring-expansion reaction yielding perchloro-1-methyl-1,3,6-cycloheptatriene (**3**), followed by dechlorination of **3** with $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$. X-ray analyses of **3** and **4** are reported and discussed in relation to the already known crystal structure of xylene **1** suggesting that in the first step the strained molecular geometry of **1** assists its ring expansion.

Introduction

Although the influence of the molecular crystalline environments on solid-state reactions are well-known,¹ very few papers document the influence of molecular geometry of sterically crowded compounds in solid-state unimolecular rearrangements. In this paper we present an example of ring-expansion, the valence-isomerization of perchloro-*p*-xylene (**1**), a highly strained molecule,² which presents a distorted structure with a "boat" conformation.³ While usually the aromatic chlorocarbons are very stable, inert substances,⁴ when steric strain is present such as in perchlorotoluene² and xylene **1** they are thermally,⁵ chemically² and photochemically⁶ reactive. It is also known that the reduction of xylene **1** with iodide ion yields perchloro-*p*-xylylene (**2**)⁷ (isomer of perchloro-7-methylene-1,3,5-cycloheptatriene (perchloroheptafulvene) (**4**)) and that the reductocondensation of **1** with $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ gives perchloropoly-*p*-xylenediylidene along with xylylene **2** as byproduct.^{4a,b} However, in the course of some of our recent experiments on copolymerization of other trichloromethyl aromatic compounds with xylene **1** using $\text{Cl}_2\text{Sn} \cdot 2\text{H}_2\text{O}$, surprisingly minor amounts of heptafulvene **4** were isolated as a byproduct.⁸ A six-step synthesis of **4**, starting from perchlorocyclopentadiene, has been previously reported by Roedig,⁹ consequently, our interest was focused in the puzzling synthesis of **4** from **1** or **2**, this being the aim of the present work.

Results and Discussion

Synthesis of Perchloroheptafulvene (4). The isomerization of perchloro-*p*-xylylene (**2**) to heptafulvene **4** was attempted by heating (340 °C), by illumination with UV or white light, by treatment with $\text{Fe}(\text{CO})_5$ in refluxing benzene, and by treatment with SnCl_2 in refluxing ethyl ether. In all cases xylylene **2** was recovered almost quantitatively. The fortuitous observation that the perchloro-*p*-xylylene of a small Pyrex container left on a laboratory shelf near a window had lost its characteristic yellowish color prompted us to study that sample. Surprisingly, its IR spectrum showed the presence of strong new peaks in the C=C stretching region ($\sim 1600 \text{ cm}^{-1}$), and the HPLC chromatogram presented the peak corresponding to **1** along with another one of comparable intensity. In view of these results the study of the photoreactivity of **1** was undertaken. While the UV irradiation of **1** in cyclohexane yielded mainly carbonyl compounds (IR, HPLC), the irradiation of finely powdered solid **1** with UV light through a Pyrex filter gave 35% (57% conversion) of perchloro-1-methyl-1,3,6-cycloheptatriene (**3**) characterized by IR and UV spectra and X ray diffraction and elemental analyses. The reaction of **3** with $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in ethyl ether at room temperature gave heptafulvene **4** almost quantitatively (96%, HPLC), also identified by IR and UV spectra and X-ray diffraction and elemental analyses (Scheme 1).

Proposed Mechanism. The mechanism of this surprising reaction can be accounted for as a photochemical ($8e^-$) [1,2] chlorine sigmatropic rearrangement of xylene **1** to perchloro-3-methyl-2,4-norcaradiene (**5**) followed by an electrocyclic rearrangement¹⁰ to the cycloheptatriene system (**3**) (Scheme 2). It must be pointed out that this is not a usual reaction since the normal behavior is the opposite process, cycloheptatrienes yield benzene derivatives; i.e., perchlorocycloheptatriene undergoes a thermal (185–190 °C) isomerization to perchlorotoluene,¹¹ and heptafulvene **4** at 340 °C gives a mixture of perchlo-

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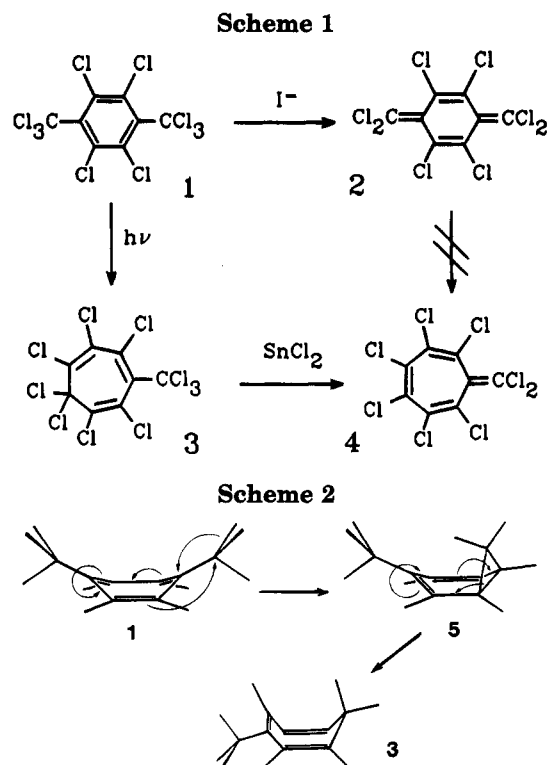
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robenzocyclobutene and perchlorostyrene.⁹ The preceding mechanism can be justified taking into account that xylene **1** is a highly strained molecule with a boatlike conformation.³ Its strain energy has been estimated to be about 48 kcal/mol,² a value that roughly exceeds that of the resonance energy of benzene (36 kcal/mol)¹² and consequently its relief, along with the suitable boatlike conformation of **1**, can be the driving forces allowing the isomerization. This justification agrees with the experimental fact that perchlorotoluene does not undergo photochemical isomerization to perchlorocycloheptatriene under the same conditions. In this case the estimated strain energy of perchlorotoluene is only 24 kcal/mol,² not enough to overcome the loss of the resonance energy of benzene (36 kcal/mol),¹² and consequently, the reverse reaction (isomerization of perchlorocycloheptatriene to strained perchlorotoluene) takes place.¹¹

Crystal Structures of 3 and 4. Methylcycloheptatriene **3** and heptafulvene **4** crystallize as colorless prismatic crystals in the triclinic *P*1 and monoclinic *P*2₁/*c* space groups, respectively (Figure 1 shows ORTEP drawings with atom numbering). Theoretical studies on the cycloheptatriene system indicate a nonplanar boatlike geometry with strongly alternating bond lengths.^{13,18} This is confirmed in the case of compounds **3** and **4**, where the X-ray diffraction analyses show this bond alternance along with high dihedral angles between the three planes defined by the boat conformation. Table 1 presents the bond distances and dihedral angles of **3** and **4** along with those of xylene **2**¹⁴ and xylene **1**³ for comparison. It must be pointed out that while the boatlike conformation of xylene **1**³ is the result of the steric interactions between the α and *o*-chlorines and consequently highly strained

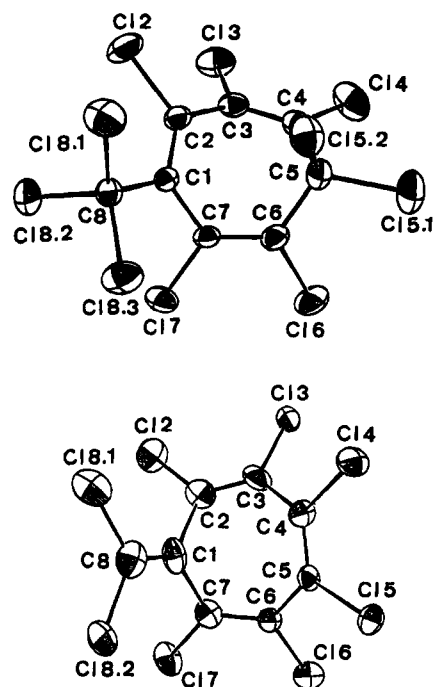


Figure 1. ORTEP diagram of cycloheptatriene **3** (top) and heptafulvene **4** (bottom), with atom numbering.

Table 1. Mean Values of Bond Distances and Dihedral Angles for Compounds 1-4

C no.	C=C (Å)		C-C (Å)		C-Cl (Å)		dihedral angle (deg)
	cycl.	exo. arom.	cycl.	exo.	C _{sp3}	C _{sp2}	
1 ³		1.404	1.533	1.722	1.718		~17
2 ¹⁴	1.323	1.329	1.468		1.731		36.9 38.7
3	1.343		1.496	1.533	1.773	1.718	50.0 38.3
4	1.305	1.286	1.487		1.729		51.8 37.2

(it must be a *planar* aromatic system), the boatlike conformations of cycloheptatriene **3** and heptafulvene **4** are normal for cycloheptatriene compounds and, consequently, strain free.¹⁵

The crystal structure of perchloroheptafulvene (**4**) deserves a special comment since its asymmetric cell unit contains four molecules (a-d) with the same molecular structure. One of them (d) presents the chlorine atoms in definite positions while the carbon atoms C1d, C2d, C3d, C8d (and the corresponding C1d', C6d', C7d', C8d') (Figure 2) show a high degree of disorder with fractional occupation factors of 0.57 and 0.43, respectively. A similar phenomenon has already been observed by Mano in the crystal structure of perchlorofulvene at room temperature.¹⁶

Experimental Section

Perchloro-1-methyl-1,3,6-cycloheptatriene (3). Powdered crystalline perchloro-*p*-xylene² (**1**) (0.600 g) was irradiated at room temperature through a Pyrex filter with a 150-W Heraeus high-pressure Hg lamp. IR and HPLC monitoring of the reaction indicated roughly a 50% conversion (about 7 h). The solid mixture was recrystallized (hexane), giving (a)

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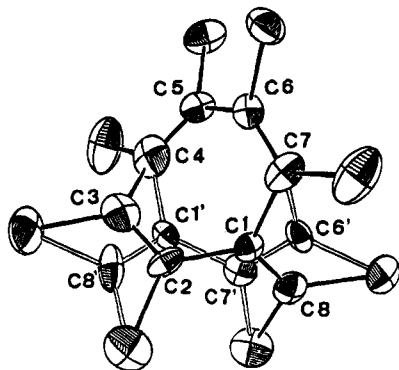


Figure 2. ORTEP diagram of the disordered molecule of heptafulvene 4, with carbon atom numbering.

xylene **1** (0.234 g, 39%) identified by mp and IR spectrum and (b) cycloheptatriene **3** (0.212 g, 35%) as colorless prisms: mp 120–2 °C; IR (KBr) 1575 (m), 1540 (m), 1512 (m), 1220 (s), 1140 (s), 1093 (s), 1043 (s), 1003 (s), 960 (m), 875 (m), 765 (s), 703 (s), 653 (s), 605 (s), 580 (s) cm^{-1} ; UV (cyclohexane) λ 253, 280 (sh), 353 (sh) nm (ϵ 14 500, 13 200, 5300). Anal. Calcd for C_8Cl_{10} : C, 21.3; Cl, 78.7. Found: C, 21.2; Cl, 78.6. The yield in **3** was 57% when the recovered **1** is considered.

Evaporation of the mother liquors yielded a viscous oil containing the two above compounds; no carbonyl compounds were detected (IR).

Attempted Synthesis of Perchlorocycloheptatriene. The above reaction was repeated with perchlorotoluene (0.5

g). Starting product was recovered quantitatively (IR spectrum and HPLC).

Perchloroheptafulvene (4). $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (0.350 g) was added to a solution of perchloro-1-methyl-1,3,6-cycloheptatriene (**3**) (0.077 g) in ethyl ether (50 mL) at room temperature. The reaction was monitored by HPLC (30 min; 96.1% of **4**). The resulting mixture was washed with aqueous HCl and with water, dried, and evaporated. The oily solid was purified through silica gel (hexane) and recrystallized in acetonitrile to give **4** (0.058 g, 90%), mp 91–93 °C (lit.^{9,17,18} mp 77 °C)^{9,17} identified by X-ray analyses: IR (KBr) 1615 (m), 1450 (s), 1190 (s), 1149 (s), 949 (s), 725 (s), 680 (s), 605 (s) cm^{-1} ; UV (cyclohexane) λ 213, 241, 253 (sh) nm (ϵ 31 800, 24 260, 19 520). Anal. Calcd for C_8Cl_8 : C, 25.4; H, 0.0; Cl, 75.0. Found: C, 25.3; H, 0.1; Cl, 74.8.

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(17) In view of the mp discrepancy (91–93 °C versus 77 °C) the possibility of polymorphism was envisaged. However, recrystallization of **4** in methanol (the solvent used by Roedig)⁹ gave crystals with unchanged (93–5 °C) mp. The difference is probably due to purity standards.

(18) The authors have deposited the atomic coordinates, bond distances, and bond angles for the X-ray structures of compounds **3** and **4** at the Cambridge Crystallographic Data Center. These data can be obtained, on request, from the Director, Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1E2, U.K.