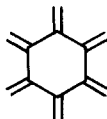


74. Hexakis (methylidene)-cyclohexane (“[6]Radialene”)



Chemical and Spectral Properties

Preliminary communication

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Summary

Upon flash pyrolysis between 580 to 660°, 2,4,6-tris(chloromethyl)mesitylene (**2**) leads to products formed through the loss of one, two and three molecules of HCl. The highly reactive chlorine free product is shown to be [6]radialene (**1**) both by its chemical reactions and by its spectral properties.

Radialenes are a class of cyclic unsaturated hydrocarbons of composition $C_{2n}H_{2n}$ possessing n ring atoms and n exocyclic double bonds which have attracted considerable interest in recent years both from the theoretical [1] and from the experimental [2] side. While the lower members of this series have been known for some time ([3]radialene [3]; [4]radialene [4]) the formation of [6]radialene (**1**) has been claimed only recently [5]. This latter communication prompts us to report results of our own efforts in this field.

We have obtained the title compound **1** in one single operation from commercially available 2,4,6-tris(chloromethyl)mesitylene **2** through triple HCl-elimination upon flash thermolysis¹⁾. For this purpose a sample of **2** is distilled at reduced pressure through a hot quartz tube. The gaseous products are either condensed on a cold finger (-78°) at the exit of the pyrolysis tube or transferred through an electrically heated vacuum adapter into a receiver containing the appropriate solvent precooled to -78° . From the rate of distillation (1 g in 15 min), pressure (10 Pa)²⁾ and dimension of the hot tube (25×1 cm) a contact time of

¹⁾ The synthetic usefulness of pyrolytic methods for the preparation of strained and reactive compounds has recently been reviewed [6]. Pertinent examples are the formation of benzocyclobutenones from *o*-methylaroylchlorides [7] and of benzocyclobutenes from *o*-methylaryl-methylchlorides [8] upon flash pyrolysis.

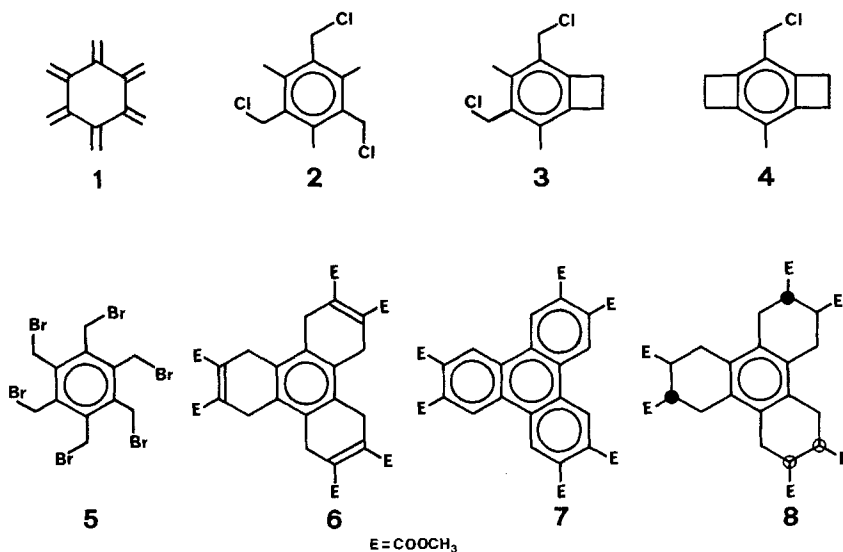
²⁾ 1 Pa = $7,5 \cdot 10^{-3}$ Torr.

0.01 s is estimated. Base titration of the content of the dry ice cooled receiver and of a second, liquid nitrogen cooled trap indicates that one mol of HCl is eliminated at 580° and that elimination is almost complete (2.85 mol) above 660°. In the pyrolysis mixture obtained at 615°, starting material **2** (25%) and two new compounds **3**³⁾ (m.p. 90-92°, 25%) and **4**³⁾ (m.p. 71-74°, 11%) are found which can be isolated by silicagel chromatography. The linear 1,2,4,5-arrangement of the two annealed cyclobutene rings in the bis-dehydrochlorination product follows from its ¹³C-NMR. spectrum. This shows only 8 signals for the 12 carbon atoms in accord with the symmetric structure **4**.

At 660° there are only traces of **2**, **3** and **4** left in the pyrolysate. Upon conventional work-up a cream coloured oxygen containing polymeric material is obtained, which is completely insoluble in the usual organic solvents. After standing suspended in methanol for several hours at room temperature it analyses for C₁₂H₁₂O_{2,9}, indicating that oxygen has been taken up from the air.

The following chemical evidence points to the [6]radialene structure **1** for the monomeric precursor of this polymeric material. Upon addition of excess bromine to a cold chloroform solution of the pyrolysate hexakis(bromomethyl)benzene (**5**) m.p. 295-296° [9] is precipitated in 38% yield. With excess dicarbomethoxyacetylene the tris-adduct **6**³⁾ of m.p. 241-243° is isolated in 4% yield [¹H-NMR. (δ-values in CDCl₃): 3,57 (s, 2n H) and 3,85 (s, 3n H); MS. (70 eV, m/e): 582 (M⁺), 580, 576, 545, 403]. Treatment of this adduct with 10% Pd/C under reflux in *o*-dichlorobenzene leads to the aromatisation product **7** of m.p. 341-348^{o3)} [¹H-NMR. (δ-values in CDCl₃): 4,10 (s, 3n H) and 8,90 (s, 1n H)].

Scheme



³⁾ All stable new compounds gave spectroscopic data and combustion analyses in accord with their proposed structures.

The low yield of tris-cycloadduct obtained from **1** may be due to the preferential formation of a linear bis-adduct with *p*-xylylene structure leading to polymer upon work-up as suggested previously [5]. Accordingly the yield of cycloadduct from **1** was not greatly improved by the use of more reactive dienophiles. Addition of fumaroylchloride, reported to be at least 10^4 times more reactive towards dienes than dicarbomethoxyacetylene [10], to a solution of the 660° pyrolysate of **2** in chloroform, removal of solvent and excess reagent and treatment with methanol leads to the expected cycloadduct **8** of m.p. $261-263^{(3)}$ as a mixture of stereoisomers in a yield of only 5%. We conclude that contrary to previous observations [5] **1** readily undergoes triple cycloaddition reactions, albeit in low yield.

The [6]radialene structure **1** for the primary product formed upon triple HCl elimination from **2** can be fully corroborated by the spectral properties of the (660°)-pyrolysate trapped at $-78^{(4)}$. In CDCl_3 solution it shows a single sharp $^1\text{H-NMR}$. signal at $\delta=5,30$ ppm corresponding to the 12 identical olefinic hydrogen atoms of **1**. This signal persists for an extended period of time if the solution is kept below -40° . It slowly decreases in intensity however at -20° and rapidly disappears at 0° without giving rise to any new signal.

The yield of **1** as determined by a comparison of its $^1\text{H-NMR}$. signal intensity with that of a known amount of cyclohexane added as an internal standard to the solution varies between 35 and 48%⁵). In the $^{13}\text{C-NMR}$. spectrum (CDCl_3 , -40°) two signals appear at 143,8 and 109,7 ppm, the latter being split into a triplet upon off-resonance decoupling. The IR. spectrum in CS_2 resembles closely that of [3]- and [4]radialenes (s. [3] [4]) showing a strong $=\text{CH}_2$ out of plane bending vibration at 897 cm^{-1} . Additional sharp but weaker absorptions appear at 764, 1061, 2920 and 3090 cm^{-1} . A very weak inflection at 1790 cm^{-1} may be due to an overtone of the 897 cm^{-1} band. A sample purified by short path sublimation at 1 mPa/ -10° gives a M^+ -signal of moderate intensity at 156 and additional peaks at 141, 129, 128, 127, 115 and 77 *m/e* in the mass spectrum. The UV. spectrum in hexane solution shows a strong maximum at 220 nm with absorption extending far into the long wave length range but showing no additional structure⁶).

The above results place the existence of [6]radialene **1** beyond doubt and make this compound easily available for additional studies on which we will report in this journal in due course. Furthermore this work demonstrates the usefulness of pyrolytic methods for the preparation of strained and reactive compounds of

4) These properties are clearly different from the known spectral data of butatriene [$^1\text{H-NMR}$.: s. [11]; $^{13}\text{C-NMR}$.: s. [12]; IR.: s. [13]; UV.: s. [14]], a possible pyrolysis product of **1** or **2** and also differ from those which would be expected from tris(cyclobuteno)benzene, a valence isomer of **1**.

5) Solutions of [6]radialene (**1**) are stable even in the presence of air if kept below -40° . Solid **1**, a white microcrystalline product, behaves capriciously upon warm-up to room temperature. It could be purified by short path sublimation at 1 mPa in small quantities only and has decomposed violently several times upon attempted high vacuum transfer of larger samples. A solid sample rinsed with CS_2 from a cold finger without inert gas protection has ignited spontaneously!

6) The extinction at 275 nm amounts to 10% and at 315 nm to 1% of the extinction value at 220 nm. Upon exposure to daylight, faster upon UV.-irradiation, three additional maxima attributed to a photoproduct of unknown structure appear at 269, 280 and 291 nm. Hexamethyl[6] radialene [1] [15], which shows a distinct shoulder at 280 nm, behaves similarly upon UV.-irradiation [16].

synthetic or theoretical interest. We are actively pursuing new applications of this technique.

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