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New Pathways to Precursors of Pentalene [1]

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Abstract. Syn-cis- (**2**) and *anti-cis-* (**3**) pentalene dimers are easily available by $CuCl_2$-induced oxidative coupling of dilithium-pentalenediide (**5**). On the other hand, NBS-bromination as well of 1,5-dihydro-pentalene (**4**) as of 1,2-dihydropentalene (**6**) gives unstable 1-bromo-1,2-dihydropentalene (**7**), while subsequent *in situ* elimination with Et_3N exclusively leads to *syn-cis*-pentalene dimer **2** in moderate yields.

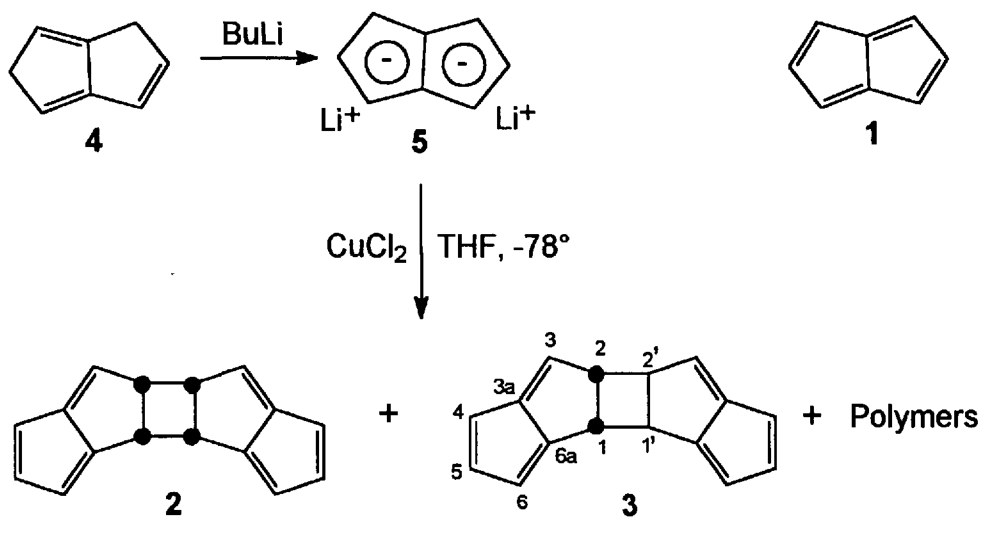
1. Introduction

Pentalene (**1**) [3] has fascinated synthetic as well as theoretical organic chemists for more than four decades. Despite all these attempts, convincing spectroscopic evidence of the parent system **1** is still missing. So far, the only pentalenes which have been isolated were either sterically shielded or electronically stabilized. Hexaphenylpentalene was the first simple pentalene to be isolated in 1962 by *Le Goff* [4], while 'push-pull-stabilized' pentalenes like 1,3-bis(dimethylamino)pentalene [5] or 1,4-diamino-3,6-dimethylpentalene-2,5-dicarbonitrile [6] did not allow any conclusions with respect to the ground-state properties of parent **1**. In the 1970's spectroscopic evidence of thermally unstable alkyl-pentalenes was increasing, starting with trapping 1-methylpentalene [7], obtaining UV evidence concerning 2-methylpentalene and 1,3-dimethylpentalene [8] and climaxing in the isolation and spectroscopic investigation of 1,3,5-tri(*tert*-butyl)pentalene [9][10]. Synthetically, thermally induced 8π-cyclizations of 8-[(dialkylamino)vinyl]fulvenes proved to be very useful [11] and finally resulted in the isolation of the pentalene dimer **2** as well as of a cycloaddition product with cyclopentadiene in cases where pentalene (**1**) was supposed to be formed as a reactive intermediate [8][10].

Similarly to the dimers of methylpentalenes [7][8], the pentalene dimers **2** and **3** are unique in so far as they would allow photochemically induced formal [2+2] cycloreversions and thermally initiated formal [8+2] cycloreversions as well. We believe that the main reason why these reactions have not been investigated in more detail [10] is that **2** and **3** are only available in a multi-step sequence in a total yield of at about 3% starting with cyclopentadienide [8]. We are reporting a much easier access of the dimers **2** and **3** by oxidative coupling of dilithium-pentalenediide (**5**).

2. Pentalene Dimers from Cyclooctatetraene

In 1987 *Meier et al.* [12] showed that the dihydropentalene **4** and its isomers [13] are available by simple gas-phase pyrolysis of cyclooctatetraene. All of a sudden, this elegant procedure allowed a straightforward access of the so far quite exotic dilithium-pentalenediide (**5**) [14]. In continuing our efforts in view of oxidative couplings of cyclopentadienides [15][16] we thought that $CuCl_2$-induced oxidative coupling of **5** could be an attractive way for preparing the pentalene dimers **2** and **3**. However, first experiments seemed to be quite discouraging since, after oxidative coupling of **5**, chromatography and evaporation, a pale-yellow solid mainly consisting of pentane-insoluble polymers was isolated in a high yield. After extraction with pentane and subse-



Scheme 1. *Synthesis of Pentalene Dimers* **2** *and* **3**

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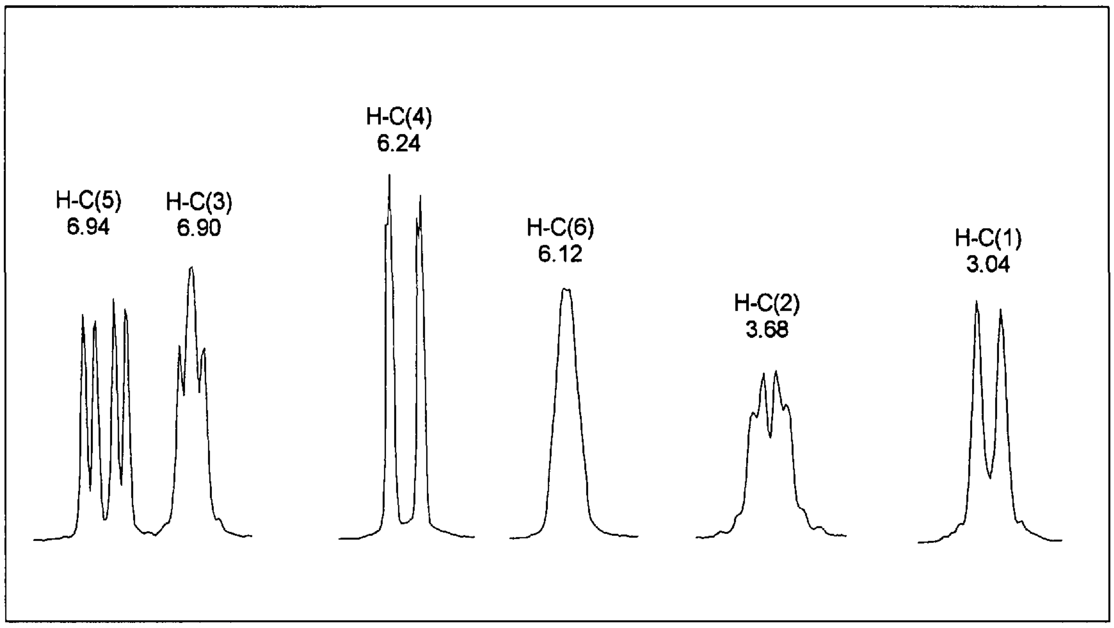
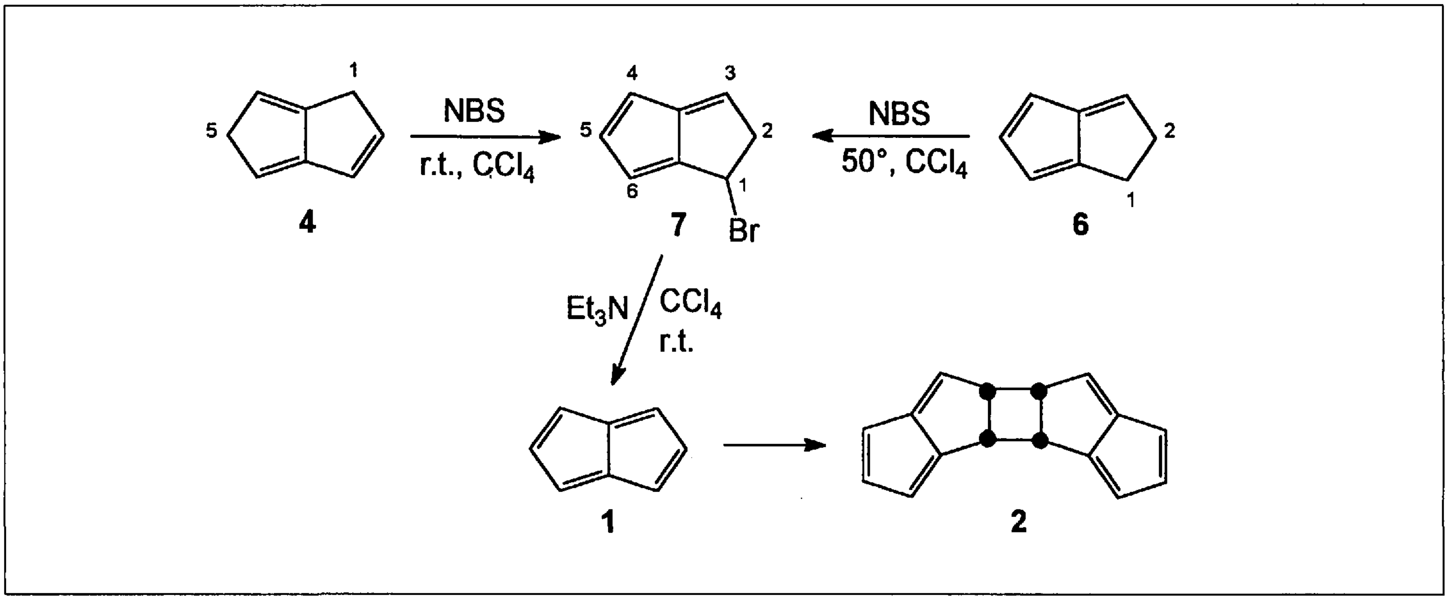


Figure. *Expansions of the* ^1H-*NMR signals of* **3** (300 MHz, $CDCl_3$)

Scheme 2. *Synthesis and Base-induced Reactions of 1-Bromo-1,2-dihydropentalene* (**7**)



quent chromatography, 12% of a solid consisting of a 1:1 mixture of **2** and **3** may be obtained. Although the total yield is moderate, the one-pot synthesis **4** → **5** → **2** + **3** provides a straightforward access to **2** and **3** [17]. They may be separated by flash chromatography with pentane/Et_2O 50:1 on Et_3N-deactivated silica gel. Their UV spectra show the typical absorptions of the pentafulvene structural units. In the mass spectra of **2** and **3**, the main fragmentation is the formation of C_8H_6 (*m/z* = 102): both the ^1H-NMR and ^{13}C-NMR spectra are compatible with the symmetry of the molecules, and the splitting of the vinylic protons of **2** and **3** is very similar.

In the ^1H-NMR spectrum of **3** (*Fig.*) the key proton for the assignment of vinylic H-atom's is H–C(5) at 6.94 ppm, a *dd* with $J(4,5)$ = 5.1 Hz and $J(5,6)$ = 1.9 Hz. The *dd* of H–C(4) absorbs at 6.24 ppm ($J(4,6)$ = 0.8 Hz), while H–C(3) corresponds to the *m* at 6.90 ppm and H–C(6) to the broad signal at 6.12 ppm. Assignments of H–C(1) and H–C(2) follow from decoupling and NOE experiments, while ^{13}C-NMR resonances are assigned by $^1H,^{13}C$-shift correlations.

Due to the similarity of splitting patterns and NMR-chemical shifts, it is not trivial to distinguish between **2** and **3**. A first tentative assignment results from the observed high-field shift of C(1) (–4.16 ppm), C(3) (–2.16 ppm) and C(6a) (–3.46 ppm) of *syn-cis*-**2** compared with *anti-cis*-**3** which has to be expected according to steric effects. The final proof results from simulations of the splitting patterns of H–C(1,1',2,2') of **2** and **3** according to *AA'XX'*, which is possible during decoupling of H–C(3,3'). It is well-known from cyclobutanes of similar structure [19] that *cis*-couplings are larger than *trans*-couplings. Spectral analysis gives $J(1,1')$ = $J(2,2')$ = 6.4 Hz and $J(1,2)$ = $J(1',2')$ = 4.7 Hz for *syn-cis* **2**, however $J(1,1')$ = $J(2,2')$ = 2.8 Hz as well as $J(1,2)$ = $J(1',2')$ = 5.2 Hz for **3**.

3. Allylic Bromination of Dihydropentalenes

Thanks to the elegant access of dihydropentalenes of type **4** [13] and **6** [20] from cyclooctatetraene [12][13], direct introduction of leaving groups may be studied as well. In principle, NBS-bromination provides a simple access to substituted dihydropentalenes, although trienes of type **4** and **6** will be prone to radical or cationic polymerizations [21]. In fact, solutions of reactive 1-bromo-1,2-dihydropentalene (**7**) are easily available both by NBS-bromination of 1,5-dihydropentalene (**4**) (at r.t.) as well as of 1,2-dihydropentalene (**6**) (at 50°). Because of the instability of **7**, base-induced HBr-elimination of **7** is applied immediately after NBS-bromination **4** → **7** (or **6** → **7**) to give, after purification by chromatography over Et_3N-deactivated silica gel, *syn-cis*-dimer **2**: 16% from **4** and 10% from **6**, respectively. In agreement with *Hafner*'s findings [10], the exclusive formation of *syn-cis* pentalene dimer **2** lets us assume that pentalene (**1**) has been formed as an intermediate.

The structure of the unstable **7** follows from the ^1H-NMR spectrum (300 MHz, $CDCl_3$) of the bromination mixture [22]. First of all, chemical shifts and ^3J coupling constants of the vinylic protons are very similar to those of the pentalene dimer **3** (*Fig.*), thus revealing the 1,2-dihydropentalene structural element of **7**. Due to additional small couplings, the fine structure of H–C(5) at 6.86 ppm is somewhat blurred. Signals of protons H–C(4)/H–C(6) are overlapping at 6.24 ppm, while H–C(3) at 6.70 ppm is split into a *dt* with $J(3,6) = 1.8$ Hz and $J(3,2a) = J(3,2b) = 2.9$ Hz which places the CH_2 unit at C(2). The allylic H-atoms produce a very typical *ABX* spectrum centered at 3.49, 3.85, and 5.19 ppm (H–C(1)) with the coupling constants $^2J_{AB} = 20.2$, $^3J_{AX} = 2.2$ and $^3J_{BX} = 5.70$ whose signals are additionally split or broadened by small couplings with vinylic protons.

Our investigations show that dihydropentalenes of type **4** [12] are attractive starting materials for the synthesis of the pentalene dimers **2** and **3** by two-step (but one-pot) syntheses, making use of dilithiumpentalenediide (**5**) (*Scheme 1*) or of unstable 1-bromo-1,2-dihydropentalene (**7**) (*Scheme 2*) as intermediates. Although the total yields of **2** and **3** are moderate in both cases, these procedures are much more simple than the so far indispensable multi-step sequences.

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[1] Coupling reactions part 16. For part 15 see [2]. The authors thank the *Swiss National Science Foundation* (projects No. 20.31217.91 and 20.37336.93) for financial support.

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[13] Gas-phase pyrolysis of cyclooctatetraene gives a total yield of dihydropentalenes varying between 49 and 57%. Between 500 and 700°, **4** is the main product, its content varying between 53 and 64% [12].

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[17] Mechanistically, pentalene dimers may either be formed by two-electron oxidation of **5** to give pentalene (**1**) (path **A**), or by one-electron abstraction from **5** to give a radical anion which would dimerize and finally give a mixture of dimers **2** and **3** after subsequent oxidation of the intermediate dianion (path **B**) [18]. Due to the fact that $CuCl_2$-induced oxidative coupling of **5** gives a mixture of **2** and **3** while base-induced elimination of 1-X-1,2-dihydropentalenes exclusively gives *syn-cis*-pentalene dimer **2** (see [10] and this work), we believe that path **B** is predominant. – The formation of 'stretched' *syn-trans*- and *anti-trans*-pentalene dimers is mechanistically unfavourable and NMR-spectroscopically excluded by analysis of the *AA'XX'* system of the cyclobutane ring protons, giving $J(1,1') = 6.4$ Hz for **2** and $J(1,1') = 2.8$ Hz for **3**, while $J(1,2')$ is around 0.5 Hz both for **2** and **3**.

[18] Cyclic voltammetry could in principle distinguish between paths **A** and **B**, but is experimentally not easy because of solubility problems and polar solvents to be used.

[19] For an example see: B. Uebersax, M. Neuenschwander, H.-P. Kellerhals, *Helv. Chim. Acta* **1982**, *65*, 74.

[20] Pentane/Et_2O 1:1 chromatography of **4** [12] over basic Al_2O_3 gives a 86:14 mixture of **6** and **4** from which fulvene **6** can be isolated. See also: D. Wilhelm, J.L. Courtneidge, T. Clark, A.G. Davies, *J. Chem. Soc., Chem. Commun.* **1984**, 810.

[21] M. Neuenschwander, P. Kronig, S. Schönholzer, M. Slongo, B. Uebersax, C. Rentsch, *Croat. Chem. Acta* **1980**, *53*, 625.

[22] Normally samples containing **4** in a purity of 75 to 80% (resulting from gas-phase pyrolysis of COT at 700° [12]) were directly subjected to NBS-bromination. Since reactive **7** did not allow purification, ^1H-NMR spectra of the bromination product still contained some benzene, styrene and COT besides small amounts of other impurities.