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-dihydorpentalene (6) gives unstable 1-bromo-1,2-dihydorpentalene (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 methyl-pentalenes [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-
sequent 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$_2$O 50:1 on Et$_3$N-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$_8$H$_6$ (m/z = 102): both the $^1$H-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 $^1$H-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 $^1$H,$^{13}$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

Figure. Expansions of the $^1$H-NMR signals of 3 (300 MHz, CDCl$_3$)
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) as easily available both by NBS-bromination of 1,5-dihydropentalene (4) (at r.t.) as well as of 1,2-dihydropentalene (6) (at 50°C). 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 Et3N-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, CDCl3) of the bromination mixture [22]. First of all, chemical shifts and 1J 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 CH2 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 2JAB = 20.2, 3JAX = 2.2 and 4JXY = 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 divinyl-umpentalene diide (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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[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 intermediately dianion (path B) [18]. Due to the fact that CuCl2-induced oxidative coupling of 5 gives a mixture of 2 and 3 while base-induced elimination of 1-X-1,2-dihydropentalene exclusively gives syn-cis-