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THE UNEXPECTED, THERMALLY INDUCED, CYCLIZATION OF 1,16-DIMETHYLHEXAHELICENES INTO 5H-BENZO[c,d]PYRENE-5-SPIRO-1′-INDANE DERIVATIVES

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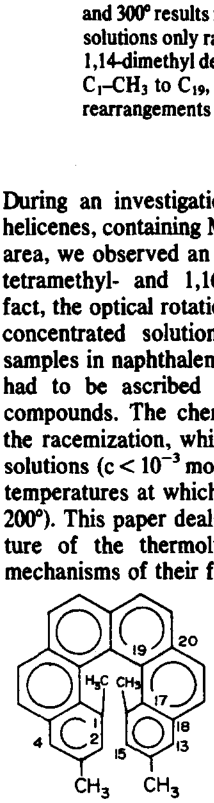
Abstract—Heating of concentrated solutions of 1,3,14,16-tetramethylhexahelicene (**1**) at temperatures between 180 and 300° results in the formation of two spiro compounds (**3** and **4**) containing a benzopyrene and an indane unit. Dilute solutions only racemize. A similar behaviour is observed with 1,16-dimethylhexahelicene (**2**) but not with the 1,3- and 1,14-dimethyl derivatives. Presumably the carbon skeleton of the pyrene moiety arises *via* a sigmatropic H-shift from C_1–CH_3 to C_{19}, followed by an electrocyclic reaction. Suggestions are given for the mechanism of the subsequent rearrangements which lead to **3** and **4**.

During an investigation[1] of the racemization of hexahelicenes, containing Me substituents in the overcrowded area, we observed an irregular behaviour with 1,3,14,16-tetramethyl- and 1,16-dimethylhexahelicene (**1**, **2**). In fact, the optical rotation sometimes increased on heating concentrated solutions (5–10%) of partially resolved samples in naphthalene. It appeared that the observation had to be ascribed to the formation of new, chiral compounds. The chemical transformation accompanied the racemization, which was the only reaction in dilute solutions ($c < 10^{-3}$ mol/l), and appeared to occur even at temperatures at which racemisation was negligible (180–200°). This paper deals with the elucidation of the structure of the thermolysis products and with possible mechanisms of their formation.



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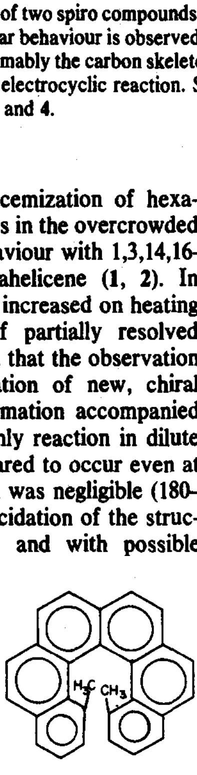

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RESULTS AND DISCUSSION

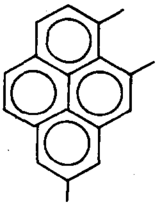
Partly resolved samples of 1,3,14,16-tetramethylhexahelicene (**1**) dissolved in naphthalene were heated in evacuated, sealed tubes at temperatures between 180 and 300°. After a suitable heating time (*ca.* 1 hr) naphthalene was removed by sublimation and the residue was subjected to column chromatography. Two main fractions were collected. One of them contained the unchanged or partly racemized starting compound. The other could be separated into two products **a** (95%) and **b** (5%), from which the latter was purified by H.P.L.C. The mass spectrum of **a** gave the molecular formula $C_{30}H_{26}$; **b** appeared to be isomeric with **1** ($C_{30}H_{24}$). Treatment of **a** with dichlorodicyanoquinone gave **b** in nearly quantitative yield.

The UV spectrum of **a** containing bands centered at 345, 282 and 247 nm pointed to a pyrene derivative. The NMR spectrum consisted of three singlets of Me groups, substituted at aromatic C atoms (δ 1.80, 2.33 and 2.67), four multiplets at δ 2.13, 2.52, 3.01 and 3.43, each corresponding to a methylene group, and five single proton singlets and two AB patterns in the aromatic region.

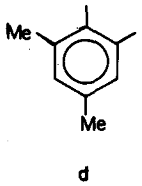
The spectral data suggest that a new bond had been formed between the Me group at C_1 and C_{19}. In this way a pyrene skeleton is formed, and only three Me groups remain. The pyrene moiety should then be trisubstituted as in **c**, and account for three singlets and two AB patterns in the aromatic region of the NMR spectrum.

The other peaks of aromatic protons may then be ascribed to a tetra-substituted benzene residue (**d**) originating from the other terminal ring of **1**. The remaining part, containing the C atoms 9, 10, 20, 11 and 12 of the starting compound should contain four methylene groups; the most reasonable structure seems to be **e**. On the basis of this analysis we propose the formula **3** for the main product of thermolysis of **1**.

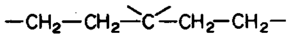
The main difference between the NMR spectra of **a** (**3**) and **b** is the absence of two methylene multiplets and the occurrence of an additional AB pattern, belonging to a disubstituted olefin, in the latter. The UV spectrum of **b** points to a conjugated pyrene derivative. Therefore, the formula **4** is proposed as the most probable structure of the minor product **b**. By heating of **4** under the same



c

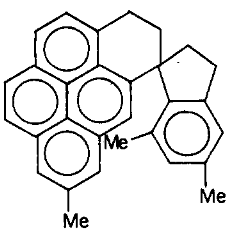


d

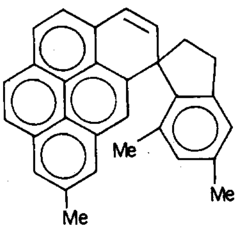


$$-CH_2-CH_2-\overset{\diagdown\,\diagup}{C}-CH_2-CH_2-$$

e



3(=a)



4(=b)

conditions as used for the thermolysis of **1** compound **3** is formed under slight carbonization. So, the sequence of the formation of the thermolysis products seems to be **1**→**4**→**3**, and the additional hydrogen atoms in **3** apparently originate from its precursor.

Heating of 1,16-dimethylhexahelicene in naphthalene led to similar thermolysis products. The UV. spectrum of the reaction mixture showed again the characteristics of pyrene derivatives; the NMR spectrum showed the same pattern in the high field region as **3**, but only one Me signal, and a more complicated pattern for aromatic protons. 1,3- and 1,14-Dimethylhexahelicene, however, were not converted into new products on heating. So, the thermolysis seems to be restricted to hexahelicenes having methyl substituents at C_1 as well as C_{16}.

In a previous paper[2] it has been shown that Me substituents at the positions 1 and 16 of hexahelicene have a relatively large influence on the conformation. The deformations of the benzene rings are more evenly spread over the helix which gets a more regular form, and the overlap of the terminal rings is increased in comparison with hexahelicene. The overlapping area is even larger than in heptahelicene. As a consequence the Me group at C_1 is just above the C_{17}–C_{19} bond, and its distance to C_{17} is very short[2] (2.6 Å). In hexahelicenes methyl-substituted at C_1 but not at C_{16} this distance will be larger.

From these data it seems that the initial step in the conversion **1**→**4** is a [1,7] suprafacial sigmatropic hydrogen shift, giving **5** as the first intermediate (Scheme). From **5** the pyrene skeleton (**6**) may arise *via* a disrotatory electrocyclic reaction. The further scheme for the formation of **4** and **3** is less clear. Radical steps leading to the intermediate **7** *via* a 1,2-phenyl radical shift deserve consideration. However, the observation that the endproducts **3** and **4** arise in optically active form provides an argument that the final steps also proceed as concerted reactions, e.g. a thermally allowed [$\pi 2s + \sigma 2a$] reaction giving **8** followed by two 1,3-hydrogen shifts.

The concentration effect in the thermolytic formation of **4** and **3** can well be understood. In solutions containing a relatively small amount of naphthalene most of the solvent will be in the vapour phase under the experimental conditions used. The hexahelicenes react then in the solid state. Indeed, heating of **1** in the solid state without solvent gave also the spiro compounds. By the closer packing of **1** in the solid state its flexibility is reduced compared to dilute solutions.

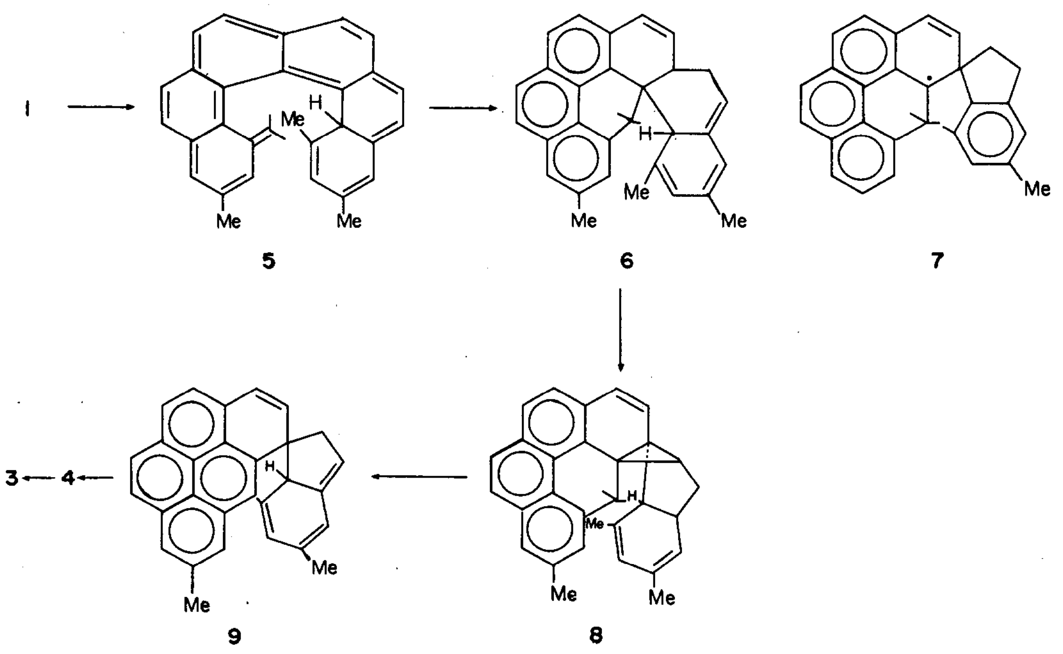
This results in a retardation of the racemization in the solid state and allows the intramolecular reaction to occur.

Recently, two other examples of intramolecular reactions in hexahelicenes containing suitable substituents in a terminal ring have been described. Martin reported the intramolecular Diels Alder reaction of β-(1-hexahelicyl)acrylic esters[3] and the formation of a spiro compound analogous to **4** from the carbonium ion formed from 1-(hydroxymethyl)hexahelicene.[4] In the latter case a substituent in only one of the terminal rings appeared to be sufficient for the formation of a bond between the substituent and C_{19}.

EXPERIMENTAL

UV spectra were recorded with a Cary-15 or Beckmann DK2A spectrophotometer. NMR spectra were measured with a Varian HA-100 or a Brucker WH90 apparatus. Mass spectra were obtained with a Varian MAT M2B spectrometer. For the measurement of optical rotations a Perkin Elmer polarimeter was used.

The syntheses of 1,3,14,16-tetramethylhexahelicene,[1] 1,14- and



1,16-dimethylhexahelicene,[2] and 1,3-dimethylhexahelicene[5] have been described previously. Partially resolved samples were obtained by elution of the compounds from a silicagel column, impregnated with 3% TAPA.[6]

The isomerizations of **1** and **2** were performed in sealed, evacuated tubes containing the helicene (*ca.* 5%) and pure naphthalene. The tubes were heated at different temps and for different times. Highest yields of thermolysis products were obtained on heating at 300° for 1 hr. Naphthalene was then removed by sublimation and the residue was separated by chromatography over silicagel. The product **3** was purified by crystallization from EtOH. The compound **4**, isolated from the mother liquor of **3**, was purified by HPLC on a silicagel column, but even then its purity was not 100%.

8,5′,7′ - *Trimethyl - 3,4 - dihydro - 5H - benzo[c,d]pyrene -5 - spiro - 1′ - indane* (**3**) had m.p. 188–190°; *m/e* 386; UV (MeOH), λ_{max} (log ϵ): 345 (4.40), 329 (4.26), 316 (3.90), 282 (4.63), 270 (4.34), 259 (4.40), 247 (4.78), 238 (4.55); NMR (CS_2), δ: 1.80 (s, 3H, $C_{7'}$–CH_3), 2.33 (s, 3H, $C_{5'}$–CH_3), 2.67 (s, 3H, C_8–CH_3), 2.13 (m, 2H), 2.52 (m, 2H), 3.01 (m, 2H), 3.43 (m, 2H), 6.74 (s, 1H, $H_{6'}$), 6.92 (s, 1H, $H_{4'}$), 7.30 (s, 1H, H_6), 7.61 (s, 1H, H_7), 7.75 (s, 1H, H_9), 7.69 and 7.92 (AB, 2H, H_1 and H_2, $J_{AB} = 8$ Hz), 7.82 and 7.88 (AB, 2H, H_{10} and H_{11}, $J_{AB} = 8$ Hz). Mass. Calc. for $C_{30}H_{26}$: 386.2034; Found: 386.2033.

8,5′,7′ - *Trimethyl - 5H - benzo[c,d]pyrene - 5 - spiro - 1′ - indane* (**4**) had m.p. 77–80°; *m/e* 384; UV (MeOH), λ_{max}: 351, 335 (sh), 293, 282, 262 (sh), 237, 206; NMR (CS_2), δ: 1.56 (s, 3H, $C_{7'}$–CH_3), 2.30 (s, 3H, $C_{5'}$–CH_3), 2.66 (s, 3H, C_8–CH_3), 2.50 (m, 2H), 3.08 (m, 2H), 6.04 and 6.73 (AB, H_3 and H_4, $J_{AB} = 10$ Hz), 7.51 and 7.82 (AB, H_1 and H_2, $J_{AB} = 8$ Hz), 7.66 and 7.72 (AB, H_{10} and H_{11}, $J_{AB} = 8$ Hz), 6.60 (s, 1H, $H_{6'}$), 6.87 (s, 1H, $H_{4'}$), 7.32 (s, 1H, H_6), 7.49 (s, 1H, H_7), 7.63 (s, 1H, H_9). Mass. Calc. for $C_{30}H_{24}$: 384.1878. Found: 384.1859.

Boiling of a soln of **3** in benzene with dichlorodicyanoquinone for 1 hr, and chromatography of the dark coloured reaction mixture over silicagel gave **4** in good yield as was established from the NMR spectrum.

Heating of a mixture of **4** and **3** in naphthalene under similar conditions as used in the thermolysis of **1** and **2** left a mixture from which only **3** could still be isolated; some carbonization had occurred.

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