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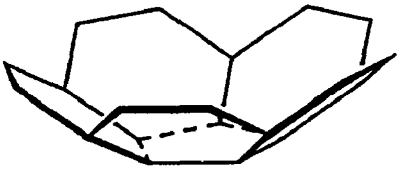
Synthesis and Hydropyrolysis of Bis-trimethylsilyl Substituted 3-(4H-Cyclopenta[def]phenanthrylidene)-1,4-pentadiyne. A New Route to Corannulene.

Gerhard Zimmermann*, Uta Nuechter+, Stefan Hagen and Matthias Nuechter

Department of High Temperature Reactions at the Institute of Chemical Technology,
University of Leipzig, Permoserstr. 15, D - 04303 Leipzig, Germany

Abstract: 3-(4H-Cyclopenta[def]phenanthrylidene)-1,5-bis-(trimethylsilyl)-1,4-pentadiyne (3) was synthesized and converted by hydropyrolysis into corannulene (1) besides others in reasonable yields. It represents a new route of the simplest bowl-shaped polycyclic aromatic hydrocarbon starting from an easily accessible precursor.

Bowl-shaped polycyclic aromatic hydrocarbons (PAH's) represent a new category of aromatic compounds consisting of five- and six-membered carbon rings and can be thought as subunits of fullerenes hydrogenated in the rim-positions.



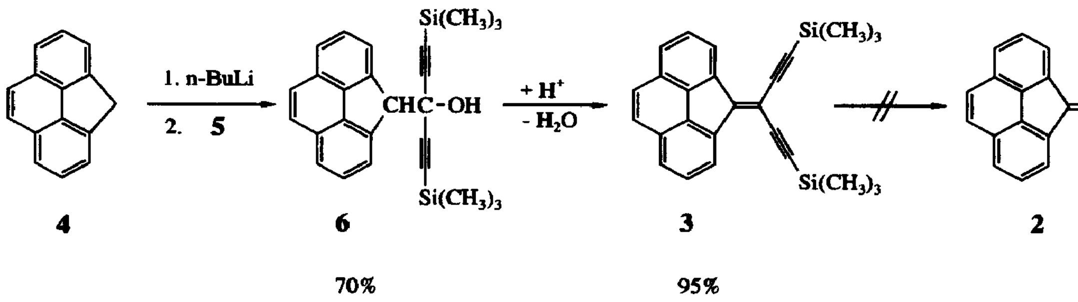
1

Corannulene (1), the smallest hydrocarbon of this category, was first prepared in an eighteen-step synthesis by Barth and Lawton.[1] Since 1991, 1 is accessible in a convenient procedure by Flash Vacuum Pyrolysis (FVP) of 7,10-diethynyl-fluoranthene or 1,6,7,10-tetra-(bromomethyl)-fluoranthene[2] (see also ref. [3]).

Within high temperature gas phase studies of highly unsaturated hydrocarbons we intended to synthesize 1 by pyrolysis of the heretofore unknown 3-(4H-cyclopenta[def]phenanthrylidene)-1,4-pentadiyne (2) in order to examine the feasibility of methylene bridged PAH as starting materials for the synthesis of bowl-shaped PAH's instead of hitherto used acenaphthylene derivatives.

Compound **2** is a cross-conjugated 1,1-diethynyl-2,2-diethenyl-ethylene derivate whereas both ethenyl groups are integrated in an aromatic structure and the two 1,3-hexadien-5-yne subunits are fitted into each other by the central CC double bond. Considering 3-(4H-cyclopenta[def]phenanthrylidene)-1,5-bis(trimethylsilyl)-1,4-pentadiyne (**3**) as a stable precursor for the synthesis of **2**, we succeeded the preparation of **3** in 66% yield in a two-step procedure from commercially available 4H-cyclopenta[def]phenanthrene (**4**).

The lithium salt of **4** obtained by reaction of **4** with n-butyllithium, was converted first with 1,5-bis(trimethylsilyl)-1,4-pentadiyn-3-one (**5**)[4] to 1,5-bis(trimethylsilyl)-3-(4H-cyclopenta[def]-phenanthryl)-1,4-pentadiyn-3-ol (**6**)[5] (70% after chromatographic purification), which is conveniently dehydrated with a catalytic amount of p-toluenesulfonic acid to **3** (95% after vacuum sublimation).[6]



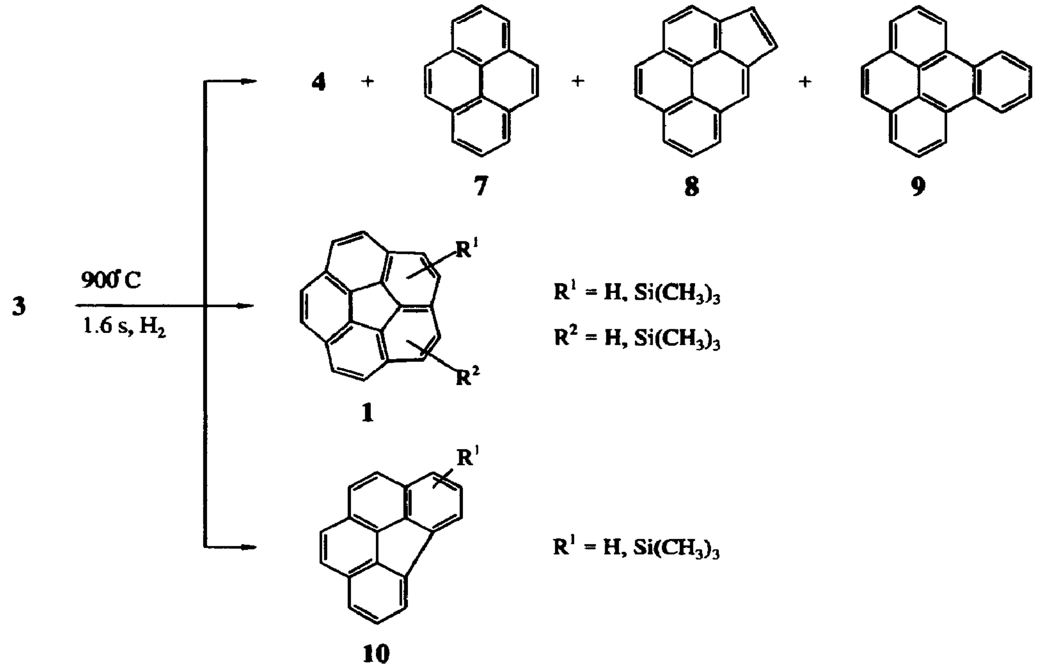
Scheme 1

After desilylation of **3** we failed, however, to isolate the compound **2** because of its instability and strong tendency to polymerize (compare also ref.[7]). So we pyrolyzed **3** instead of **2** in a tubular flow system in hydrogen as carrier gas at a temperature of 900°C.[8] The separation of **1** out of the pyrolyzates by column chromatography (Al_2O_3, cyclohexane/toluene = 90:10) results in slightly yellow-coloured crystals (m.p. 264°C, lit. 268 - 269°C[1]) of corannulene[9] in a yield of 15% of theory on a 20 to 40 mg scale as being about 1.5 to 3.0 mg per run.

Although this yield is comparable with those reported by Scott[2] and Siegel[3], in addition to **1** the further PAH's like **4**, pyrene (**7**), cyclopenta[cd]pyrene (**8**), benzo[e]pyrene (**9**) and benzo[ghi]fluoranthene (**10**) could be identified by GC-MS, GC-FTIR and HPLC-DAD techniques in the hydropyrolysis products of **3**.[10]

If **3** is pyrolyzed under FVP conditions or in nitrogen instead of hydrogen as carrier gas, solid deposits and some PAH's < C_{20} are only formed but no **1** could be detected at temperatures between 800°C and 1000°C and residence times of about 1.6 s.

In contrast to Scott[2] and in agreement with very recently obtained results[11] it is supposed that under our conditions **1** is formed preferably by repeated cycloaddition of vinyl-type radicals (generated by addition of H-atoms to the triple bonds of **3**), while **10** is formed by cleavage of an trimethylsilylethynyl group after the first cyclization step. Radicals resulting from H-addition to the double bond of **3** are considered to be the initial species for the formation of **4** (destructive hydrogenation) as well as **7** - **9** by well-known homoallyl-cyclopropyl rearrangement.



Scheme 2

Acknowledgements

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References and Notes

\+ Part of the planned Ph. D. Thesis, Leipzig, 1995

1. (a) Barth, W.E.; Lawton, R.G. *J.Am.Chem.Soc.* **1966**, *88*, 380.
   (b) Barth, W.E.; Lawton, R.G. *J.Am.Chem.Soc.* **1971**, *93*, 1730.
2. Scott, L.T.; Hashemi, M.; Meyer, D.T.; Warren, H.B. *J.Am.Chem.Soc.* **1991**, *113*, 7082.

3. Borchardt, A.; Fuchicello, A.; Kilway, K.V.; Baldridge, K.K.; Siegel, J.S. *J.Am.Chem.Soc.* **1992**, *114*, 1921.
4. The synthesis of **5** was patterned after ref.[12] and [13].
   5: yellow crystals, mp = 51°C, 50%.
5. **6**: yellow crystals, mp = 106°C; ^{1}H-NMR (250 MHz, $CDCl_3$) δ(ppm) = -0.01 (s, 18H), 2.85 (s, 1H), 4.93 (s, 1H), 7.6 - 8.47 (m, 8H); GC-MS (m/e) 412 (M^+); UV (nm, acetonitrile) λ_{max} (lg ε) = 257 (4.7), 288 (4.1), 300 (4.1).
6. **3**: yellow crystals, mp = 146°C; ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ(ppm) = -0.24, 61.50, 102.5, 103.8, 123.5, 124.9, 125.8, 127.6, 128.7, 130.6, 136.1, 148.2; GC-MS (m/e) 394 (M^+); UV (nm, acetonitrile) λ_{max} (lg ε) = 235 (4.5), 245 (4.5), 281 (4.0), 293 (4.1), 312 (4.1), 329 (4.3), 341 (4.4), 411 (3.9).
7. About the properties of similar compounds see also: Van Loon, J.-D.; Seiler, P.; Diederich, F. *Angew.Chem.* **1993**, *105*, 1235.
8. The electrically heated vertical laboratory tubular furnace (quartz, l = 350 mm, i.d. = 15 mm) was connected at the inlet of the furnace with a special contained receiver from which the starting material was vaporized by means of carrier gas and discharged directly into the furnace and at the outlet with a cooling and condensation section (liquid nitrogen) where the solid pyrolyzate was precipitated.
9. **1**: GC-MS (m/e) 250 (100%) M^+, 125 (20%) $M^+/2$, 83 (1%) $M^+/3$; FT-IR (cm^{-1}) 3090, 3050, 1514, 1458, 1378, 1299, 1225, 1162, 1072, 913, 837; DAD-UV (nm, acetonitrile : water = 80 : 20) λ_{max} = 242, 245, 250, 286, 317 (shoulder).
   The GC-MS-, UV-, IR- and ^{1}H-NMR-data are in agreement with that presented in ref.[1].
10. The mono- and bis-trimethylsilyl derivates of **1** (M^+ = 322 and M^+ = 394) and the mono-trimethylsilyl derivate of **10** (M^+ = 298) as well as products with M^+ = 240, 264 and 276 are identified by GC-MS and formed in traces only.
11. Zimmermann, G.; Hofmann, J.; Nuechter, U.; Homann, K.H. unpublished results of the thermal cyclization of hydrocarbons with en-yne structure fragments, Leipzig 1992.
12. Jones, E.R.H.; Skattebol, L.; Whiting, M.C. *J.Chem.Soc.* **1956**, 4765.
13. Hauptmann, H. *Tetrahedron Lett.* **1974**, *40*, 3587.

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