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High Temperature Synthesis towards Bowl-Shaped Subunits of Fullerenes - III. [1,2]
From 4,4'-Bi-4*H*-cyclopenta[def]phenanthrenylidene towards [5.5]Circulene

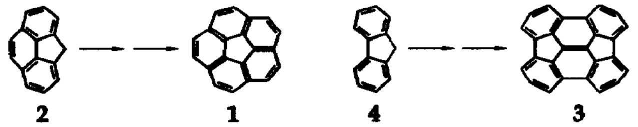
Stefan Hagen, Uta Nuechter, Matthias Nuechter and Gerhard Zimmermann *

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

Abstract: Diindeno[4,3,2,1-opqr;4',3',2',1'-avut]picene (**8**) and dibenzo[mn,qr]fluoreno-[2,1,9,8,7-defghi]naphthacene (**9**) have been synthesized by thermal and catalytic dehydrocyclization, respectively.

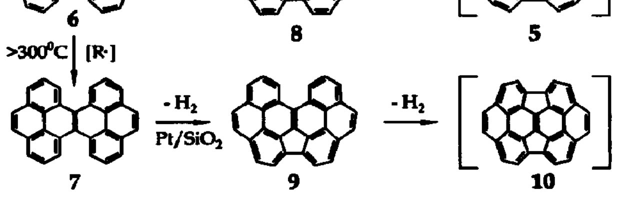
The synthesis of corannulene (**1**) from 4H-cyclopenta[def]phenanthrene (**2**)[1] as well as that of diindeno[1,2,3,4-defg;1',2',3',4'-mnop]chrysene (**3**) from 9,9'-bi-9*H*-fluorenylidene (**4**)[2] show clearly that methylene bridged polycyclic aromatic compounds are to be considered as useful parent compounds for the generation of aromatics with highly curved structures (Scheme 1). We have therefore tried to synthesize [5.5]-circulene (**5**),[3] a bowl-shaped C_{30} subunit of C_{60} fullerene hydrogenated in the marginal positions, by double thermal dehydrocyclization of 4,4'-bi-4*H*-cyclopenta[def]phenanthrenylidene (**6**)[4] (Scheme 2).

Scheme 1



Because of the strong tendency of **6** to isomerize to tetrabenzo[de,hi,mn,qr]naphthacene (**7**) via a homo-allyl-cyclopropyl carbinyl rearrangement on heating, which is initiated by thermally generated radicals,[5] we pyrolyzed **6** at 840°C and 700 Pa by running a solution of 800 mg of **6** in benzene/toluene (10:1) through a capillary into the pyrolysis reactor.[6] The purification of the accumulated pyrolyzate by repeated column chromatography on silica gel and aluminium oxide with cyclohexane/toluene = 1:1 results in 120 mg of **7** (15 %, m.p. 306°C, lit. 306-308°C [7]) and 35 mg (4.4 %) of diindeno[4,3,2,1-opqr;4',3',2',1'-avut]picene (**8**) (canary-yellow needles, m.p. 350.5-354.5°C after recrystallization in toluene/n-hexane = 1:3 [8]).

Scheme 2



At temperatures above 850°C, the pyrolysis of **6** results, additionally, in traces of dibenzo[mn,qr]fluoreno-[2,1,9,8,7-defghi]naphthacene (**9**), a dehydrocyclization product of **7** and a structural isomer of **8**. A more convenient route to **9** turned out to be the catalytic dehydrocyclization of **7** on a 0.7 wt.% Pt/SiO_2 catalyst at temperatures of about 750°C, which facilitates the synthesis of **9** in a 25 % yield (m.p. 374.5-376.5 °C after purification by two-stage column chromatography and recrystallization in toluene/n-hexane = 1:1 [9,10]).

However, at temperatures below 980°C, we have not hitherto succeeded to dehydrocyclize **8** into **5**, and **9** into difluoreno-[2,1,9,8,7-defghi;2′,1′,9′,8′,7′-mnopqr]naphthacene (**10**) which is also bowl-shaped. That is obviously caused by the large distance between those carbon atoms which are thought to participate in the formation of the supplementary CC-bond and, of course, by the rigid carbon frameworks of **8** and **9**.

Acknowledgements

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References and Notes

1. Part I: Zimmermann, G.; Nuechter, U.; Hagen, S.; Nuechter, M. accepted for publication in *Tetrahedron Lett.*.
2. Part II: Hagen, S.; Nuechter, U.; Nuechter, M.; Zimmermann, G. submitted to *Polycyclic Aromatic Compounds*.
3. The term of this compound follows on the recommendation of Dopper, J.H. and Wynberg, H. *Tetrahedron Lett.* **1972**, *9*, 763-766.
4. Wittig, G.; Pieper, G. *Liebigs Ann. Chem.* **1947**, *558*, 218-230; the dehydration of the carbinol followed by means of p-toluenesulfonic acid, 62 %.
5. Alder, R. W.; Whittaker, G. J. *Chem. Soc. Perkin Trans. 2*, **1975**, 712-713.
6. Silica capillary (l = 200 mm, i.d. = 0.1 mm); the sectional heated pyrolysis reactor (quartz, i.d. = 15 mm) is subdivided into an evaporation zone (100 mm, 520°C) filled with quartz wool and a reaction zone (l = 350 mm, 840°C).
7. GC-MS (70eV): m/z = 376 $[M^+]$, ^1H-NMR and UV spectral data are in agreement with that presented by
   a) Harvey, R. G.; Abu-Shaqara, E.; Yang, C. X. *J. Org. Chem.* **1993**, *58*, 5866 and
   b) Clar, E.; Guye-Vuilleme, J. F.; Stephen, J. F. *Tetrahedron* **1964**, *20*, 2107.
8. (**8**): UV (CH_2Cl_2): λ_{max} (lg ε) = 243 nm (4.748), 282 (4.631), 288 (4.630), 301 (4.443), 327 (4.447), 334 (sh, 4.343), 373 (4.126), 395 (4.220), 440 (3.090). - ^1H-NMR (CS_2/[D_6]acetone = 6 : 1): σ = 8.54 (d, J = 8.5 Hz, 2 H), 8.44 (d, J = 7.0 Hz, 2 H), 8.09 (d, J = 8.5 Hz, 2 H), 7.99 (d, J = 8.9 Hz, 2H), 7.97 (s, 4 H), 7.80 (dd, J = 7.0 Hz and J = 8.0 Hz, 2 H). - GC-MS (70 eV), m/z (%): 374 (100) $[M^+]$, 372 (14) $[M^+-2]$, 187 (56) $[M^{++}]$, 186 (38) $[M^{++}-2]$.
9. (**9**): UV (CH_2Cl_2): λ_{max} (lg ε) = 238 (4.806), 269 (4.534), 286 (4.529), 303 (4.662), 315 (4.832), 374 (3.898), 392 (4.286), 415 (4.556), 455 (3.352), 485 (3.273), 520 (3.029). - ^1H-NMR (CS_2/[D_6]acetone = 6 : 1): σ = 9.79 (d, J = 8.0 Hz, 2 H), 8.55 (d, J = 7.9 Hz, 2 H), 8.35 (d, J = 7.7 Hz, 2 H), 8.28-8.21 (m, 4 H), 8.03 (s, 2 H), 8.02 (s, 2H). - GC-MS (70 eV), m/z (%): 374 (100) $[M^+]$, 372 (19) $[M^+-2]$, 187 (22) $[M^{++}]$, 186 (23) $[M^{++}-2]$.
10. Clar, E.; Robertson, J.M.; Schloegl, R.; Schmidt, W. *J. Am. Chem. Soc.* **1981**, *103*, 1320-1328. It is suggested by Clar et al. that **9** is a minor product in the Elbs pyrolysis of an o-toloylacetyl derivate of **3** without its isolation. Therefore, analytical data of **9** were hitherto not available.

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