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1-HYDROXYMETHYL [6] HELICENE : ACID CATALYSED INTRAMOLECULAR REARRANGEMENT INVOLVING THE HELICENE SKELETON.

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Abstract. On acid treatment, 1-hydroxymethyl [6] helicene (1) gives 5-H-benzo [c,d] pyrene-5-spiro-1'-indene (2). The structure of the rearranged hydrocarbon was provisionally assigned by catalytic hydrogenation, ^{2}H labelling, U.V., ^{1}H- and ^{13}C-NMR spectroscopy and confirmed by an X-ray diffraction study (M. Van Meerssche and coll., personal communication).

In the carbo-helicene series, no chemical reaction involving the skeleton frame has yet been described1). We now wish to report such a reaction (1 → 2)2).

A solution of 1-hydroxymethyl [6] helicene (1) (0.16 g) and p.toluene sulfonic acid (0.08 g) in C_6H_6 (30 ml) is refluxed for 15 min and the reaction product purified by prep. TLC (Merck silica-gel, p. ether 60-70°/C_6H_6 3:1). Yield 63%. Yellow needles, m.p. 157-159° (acetonitrile). M^+ for m/e 340 (80%), M-1 339 (100%); calc. for $C_{27}H_{16}$: C, 95.3; H, 4.7. Found: C, 95.0; H, 4.9%.

The ^{1}H-NMR spectrum (Bruker HX 90 MHz, CS_2, TMS=0) of this new hydrocarbon shows the following spin systems: 1. Four AB systems: a. δ_{ppm} 5.480 and 7.010 (calc.) J 9.7 Hz; b. δ_{ppm} 6.488 and 6.818 (calc.) J 5.3 Hz; c. δ_{ppm} 7.656 and 7.961 (calc.) J 7.9 Hz; d. δ_{ppm} 7.828 two protons quasi-singlet ($\nu_{\frac{1}{2}}$ 0.8 Hz). 2. A complex aromatic ABCD system (center of the multiplet at 7.13 ppm; width 48 Hz). 3. An aromatic ABC system: a one proton multiplet at 7.87 ppm (width 15 Hz) and a two protons multiplet at 7.70 ppm (width 17 Hz). 4. A one proton quasi-singlet at 7.202 ppm ($\nu_{\frac{1}{2}}$ 1.1 Hz).

By the use of the INDOR technique, the molecule can be divided in two parts, unconnected by (detectable) long range couplings: the aromatic ABCD system and the AB system b. (J 5.3 Hz) on the one hand, and the remaining protons on the other hand (Fig. 1).

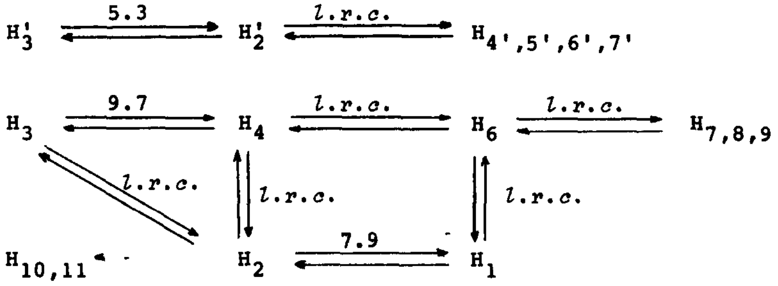
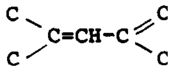
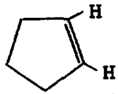
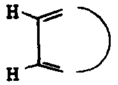
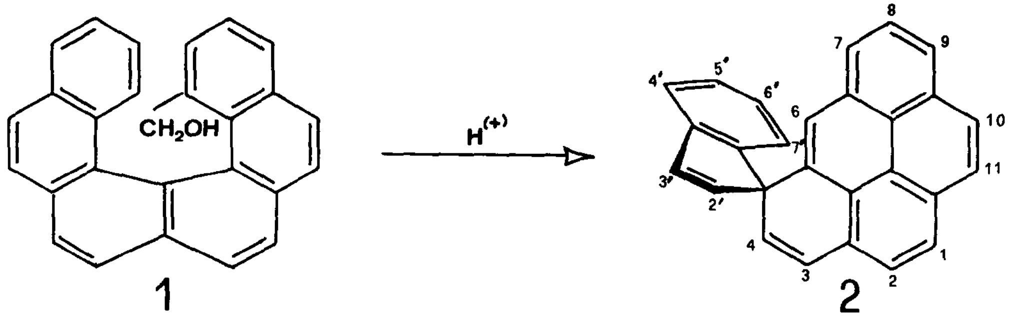


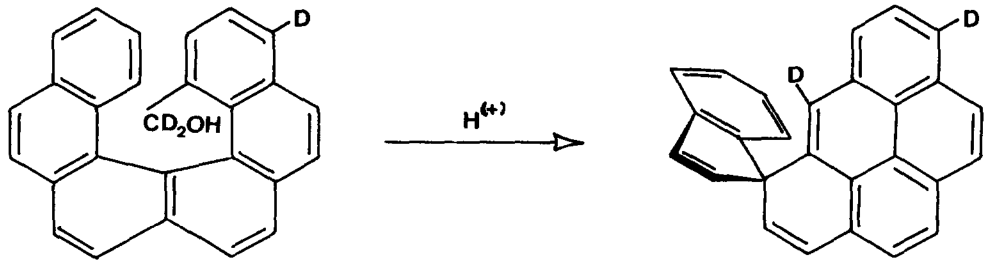
Fig. 1. ^{1}H-NMR; INDOR experiments on compound 2.

The ^{13}C-NMR spectrum (Bruker HX 90, 22.63 MHz, CS_2, TMS=0) showed that the only sp^3 carbon atom (δ_{ppm} 59.72) is quaternary. The other signals are located between 121.34 and 155.36 ppm.

Pertinent results are as follows: 1. The $C_{27}H_{16}$ hydrocarbon contains seven rings (26 Csp^2 + 1 Csp^3). 2. The quaternary sp^3 carbon atom does not derive from the $-CH_2OH$ of 1 (loss of the quasi-singlet in the ^{1}H-NMR spectrum of 4). Thus, if there is no deuterium migration during the rearrangement, the $-CH_2OH$ must be incorporated in a system such as  $\begin{matrix}C\\C\end{matrix}{>}C{=}CH{-}C{<}\begin{matrix}C\\C\end{matrix}$ 3. The sp^3 carbon atom is probably the central atom of a spirane structure (the arguments leading to this conclusion are too elaborate to be developed here). 4. The AB system b. (J 5.3 Hz) belongs to a structure such as  (for a 6 or 7 membered ring J ≃ 9.5 Hz) or  . Based essentially on the above considerations, structure 2 was provisionally assigned to the hydrocarbon. This structure is compatible with the ^{1}H-NMR assignments shown in Fig. 2. According to these assignments, H_6 is shifted to high fields (0.63 ppm) relative to the chemical shift of the corresponding proton in pyrene.



1 2



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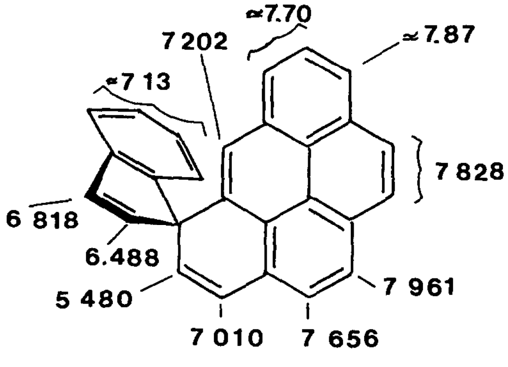


Fig. 2. ^{1}H-NMR assignments (2) (δ_{ppm} from TMS).

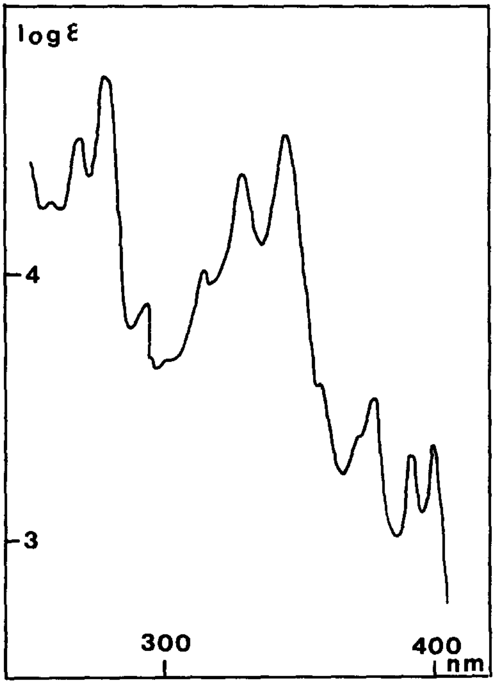
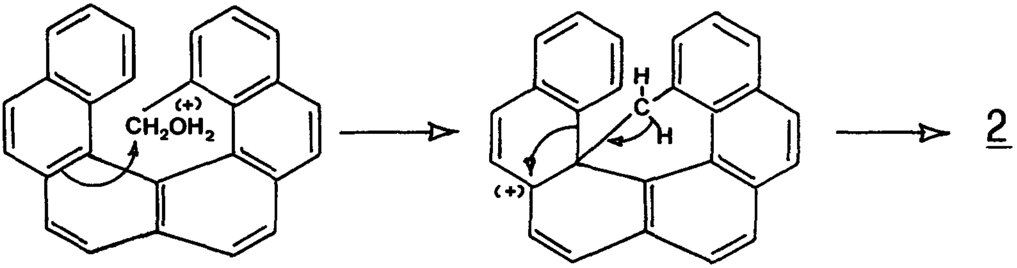


Fig. 3. UV spectrum (dioxan) of the 3,4,2',3'-tetrahydro

Catalytic hydrogenation. The rearranged hydrocarbon (2) gives a tetrahydro derivative (M^+ for *m/e* 344), the U.V. spectrum (Fig. 3) of which is akin to the spectrum of pyrene. The ^{1}H-NMR spectrum shows the loss of the two AB systems assigned to H_3/H_4 and H_2'/H_3' in 2 (Fig. 2).

The structure of the $C_{27}H_{16}$ hydrocarbon was definitely proved to be 2 by an X-ray diffraction study, kindly carried out by M. Van Meerssche and coll. (personal communication).

The acid catalysed skeleton rearrangement (1 → 2)$^{3)}$ can easily be visualised as shown in Scheme 1.



Scheme 1

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Footnotes.

1. It should however be recalled that R.C. Dougherty [J. Amer. Chem. Soc., 90, 5788 (1968)] has observed the formation of "traces of coronene" (loss of C_2H_4) in the thermolysis of [6] helicene (sealed evacuated tube heated at 485° for 2 hr).
2. An intramolecular 4+2 cycloaddition involving a helicene skeleton will be described shortly.
3. The rearrangement does not occur when a solution of 1 in naphthalene is heated at 200° for 30 min. The formation of 2 is however observed when 1 is heated 30 min at 200° in hexachlorobutadiene, either in the presence or in the absence of a trace of CF_3CO_2H.