Tetrahedron Letters No.42, pp. 3683-3688, 1969. Pergamon Press. Printed in Great Britain.

[13] HELICENE
and
[13] HELICENE-10,21-d_2 (1)

R.H.Martin[*], G.Morren[**] and J.J.Schurter.
Service de Chimie Organique Fac.Sc., Université Libre de Bruxelles,
50, Av.F.D.Roosevelt, Bruxelles 5 - Belgique.

(Received in UK 7 August 1969; accepted for publication 14 August 1969)

Tridecahelicene, the first benzologue of the multilayered helicenes, has been synthesised, in 52 % yield, by the double photocyclisation of IVa.

The cyclodehydrogenation of IVa, involving the loss of 4 hydrogens, can give rise to no less than 12 isomers, if cyclisations of intermediate pentahelicenic structures to perylene systems are considered (2). In order to discard 9 of these possibilities, including all the perylene structures, we have applied the method using partially deuterated derivatives described in the preceeding communication (this issue of Tetrahedron Letters).

The double photocyclisation of IVb (R=D, R'=H) gave the corresponding bisdeuterated hydrocarbon, thus proving that the cyclisations do not involve the labelled positions (β) in the benzo[c]phenanthrene moieties. Of the three remaining hydrocarbons (αβ'/αβ', αβ'/αα' and αα'/αα'), the one resulting from a double cyclisation in the β' positions of the phenanthrene moiety can, moreover, be excluded on the following ground:

- When the photolysis of IVa was stopped after 45 min, two reaction products were isolated by chromatography : the fully cyclised hydrocarbon (ca. 25 %) and a monocyclised product (ca. 50 %). The corresponding bisdeuterated derivatives were obtained from IVb. The N.M.R. spectra (Fig.5 and Fig.6) of the partially cyclised hydrocarbons ($C_{54}H_{32}$ and $C_{54}H_{30}D_2$) showed, without ambiguity, that the first cyclisation had taken place in the 4 position (α') of the phenanthrene moiety to give 1-(2-benzo[c]phenanthryl)-2-(2-octahelicenyl)ethylene (-d_2 respectively).

---

[*] Author to whom inquiries should be addressed.
[**] Titulaire d'une bourse de spécialisation de l'IRSIA.

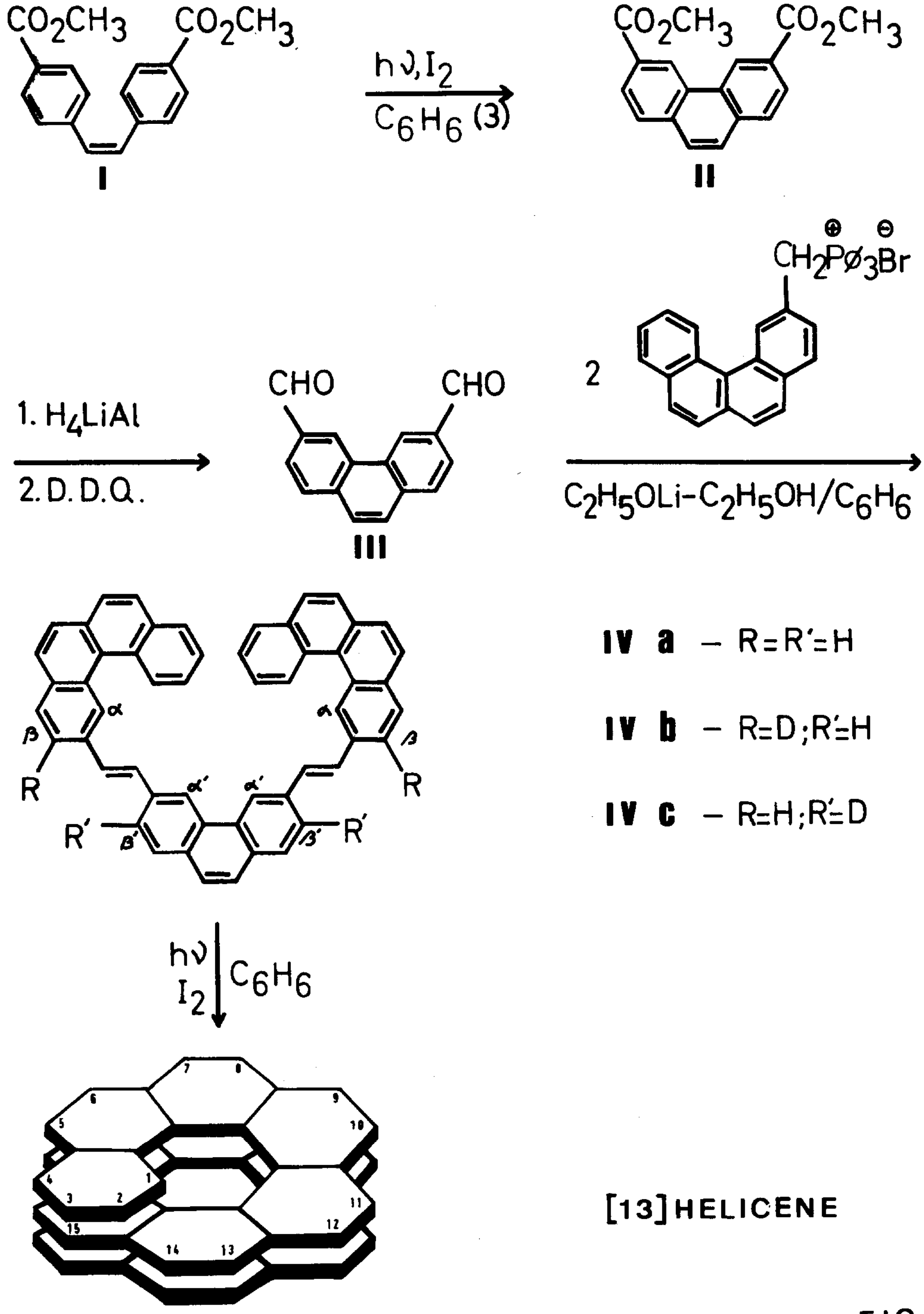
CO2CH3
CO2CH3
I
hν, I2
C6H6 (3)
CO2CH3
CO2CH3
II
1. H4LiAl
2. D.D.Q.
CHO
CHO
III
2
CH2P⊕ø3Br⊖
C2H5OLi-C2H5OH/C6H6
α
β
R
α'
R'
β'
IV a – R=R'=H
IV b – R=D;R'=H
IV c – R=H;R'=D
hν
I2
C6H6
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
[13]HELICENE

FIG.1

[13]helicene

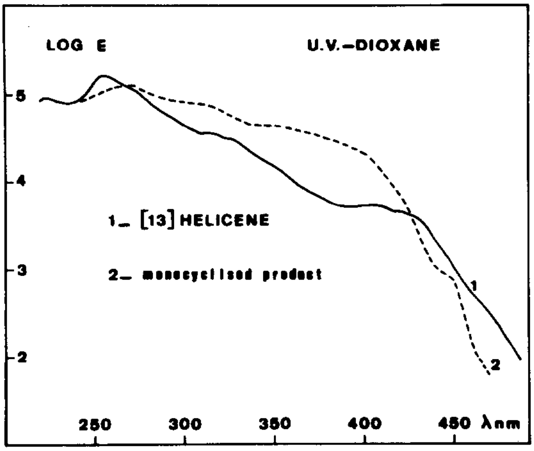

Fig.2

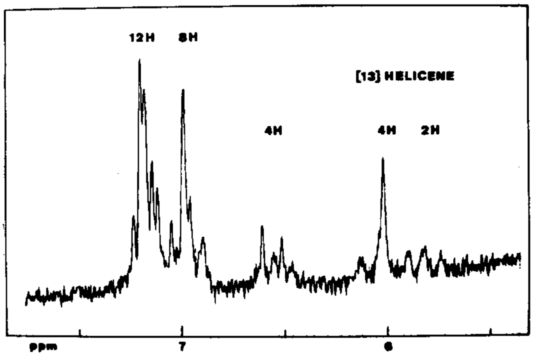

Fig.3 90Mc (CS_2) 584 runs.

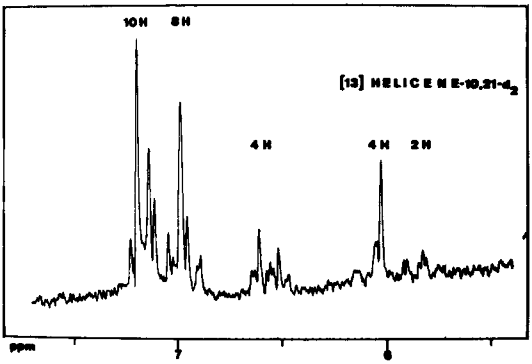

Fig.4 90Mc (CS_2) 255 runs.

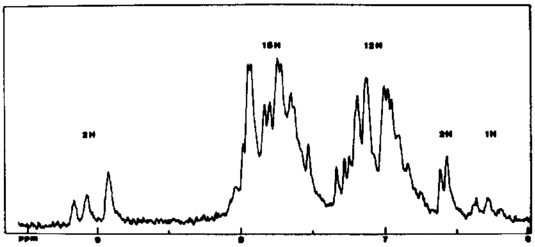

Fig.5 Monocyclised product
90Mc (CS_2) 25 runs.

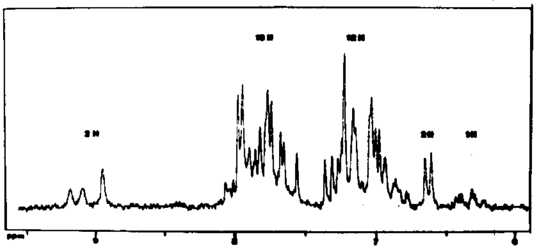

Fig.6 Deuterated monocyclised product
90Mc (CS_2) 40 runs.

The photocyclisation of this 1,2-diarylethylene (R=R'=H) gave the fully cyclised hydrocarbon isolated previously (29 %; identified by N.M.R. spectroscopy).

Of the two hydrocarbons which could result from this last experiment, only [13]helicene ($\alpha\alpha'/\alpha\alpha'$) is fully compatible with the spectral data at hand. The N.M.R. spectrum is indeed incompatible with the isomeric structure ($\alpha\beta'/\alpha\alpha'$). It moreover excludes the two hydrocarbons which could result from a rearrangement of the type described by Mijovic and Coll. (3) (a similar rearrangement, in the case of the monocyclised product, is also excluded by N.M.R. spectroscopy).

The N.M.R. spectrum of [13]helicene in CS_2 (Fig.3) shows the following characteristics*:

- The absence of signals at fields lower than 7.23 ppm. This is clear evidence that every proton in the molecule is under the shielding influence of the induced diamagnetic ring-current of at least one benzenoid ring (4)**.
- A singlet at 6.03 ppm assigned to $H_{15,16}$, the two protons of the middle ring which is overlapped on both sides by the end-rings. The doublet of $H_{1,30}$ at 6.10 ppm, the multiplet of $H_{3,28}$ at 6.55 ppm and the doublet of $H_{14,17}$ at 6.57 ppm.
- The presence of a multiplet at a particularly high field (5.82 ppm). This multiplet is assigned to the end-rings protons $H_{2,29}$, which are located just above two overlapping rings***(the corresponding protons $H_{2,21}$ of [9]helicene resonate at 6.25 ppm in CS_2).

It is interesting to recall that Longone and Chow (5) have observed a similar effect in the N.M.R. spectrum of a multilayered [2,2]paracyclophane.

The modifications observed in the spectra of the deuterated derivatives are in accordance with expectations (Fig.4 and Fig.6).

A detailed analysis of the N.M.R. spectra will be undertaken in collaboration with Dr.N.Defay.

---

* Preliminary assignments based on the study of the lower benzologues (4) and specific solvent effects (CS_2/C_6D_6).

** Among the structures considered in this work, only [13]helicene fulfils this condition.

***The lower benzologue [12]helicene should already show this phenomenon.

The reaction scheme leading to [13]helicene is illustrated in Fig.1 Yields : I→II 51 %, II→III 66 %, III→IV 75 %. The photocyclisation of IVa was carried out in benzene solution (100 mg 950 ml) in the presence of iodine (5 mg) for 105 min at room temperature using a Hanovia 450W medium pressure mercury lamp (Pyrex-well). Essentially the same experimental conditions were used for the synthesis of the deuterated derivatives.

[13]helicene was isolated by column chromatography (alumina p.eth.60-70°) pale green fluorescence on alumina (1st band), yellow crystals (benzene-ethanol), m.p 414-415° (capillary tube).

Found M.W. 678 (m.s);C 95,2 %; H 4,8 %; $C_{54}H_{30}$ requires :
M.W. 678,8 ; C 95,5 %; H 4,5 %; Yield 52 %, U.V. Fig.2

[13]helicene-10,21-d_2. Found M.W. 680 (m.s), $C_{54}H_{28}D_2$ requires 680,8.

1-(2-benzo[c]phenanthryl)-2-(2-octahelicenyl)ethylene, turquoise blue fluorescence on alumina (2nd band). Found M.W. 680 (m.s); $C_{54}H_{32}$ requires : M.W. 680,8. Yield ca 50 % (after 45 min irradiation). U.V.Fig.2

1-(2-benzo[c]phenanthryl-3-d)-2-(2-octahelicenyl-11-d)ethylene, yellow crystals (benzene-ethanol), m.p.299-301° (microscope).

Found M.W. 682 (m.s); C 95,1 %; H 5,2 %; $C_{54}H_{30}D_2$ requires :
M.W. 682,8 ; C 95,0 %; H 5,0 %.

In order to confirm the structure of the hydrocarbons isolated from the photocyclisation of IVa, we are presently working on the synthesis of the bis-deuterated intermediate IVc, required to determine the course of the cyclisation in the phenanthrene moiety.

Spectral, optical and physico-chemical properties of [13]helicene will be reported later. Experiments towards the synthesis of other helicenic structures are in progress.

Acknowledgements : We are grateful to Dr.N.Defay for the recording of the NMR spectra (Bruker HX 90Mc) and for helpful discussions, to Dr.M.Kaisin for the mesurement of the mass spectra (Hitachi Perkin-Elmer) and to (Miss)M.Morren for the drawing of the [13]helicene molecule. We are indebted to the following Belgian Scientific Organisations - IRSIA and FNRS - for financial support.

REFERENCES.

(1) Part XXIX of " Syntheses in the field of polycyclic aromatic compounds ". For part XXVIII see R.H.Martin and J.J.Schurter, preceeding communication in this issue of Tetrahedron Letters.

(2) W.Carruthers, J.Chem.Soc., (C) 1525 (1967).

M.Scholz, M.Mühlstädt and F.Dietz, Tetrahedron Letters, 665 (1967).
F.Dietz and M.Scholz, Tetrahedron, **24**, 6845 (1968).

(3) S.D.Cohen, M.V.Mijovic and G.A.Newman, Chem.Comm., 722 (1968).

(4) " Studies in N.M.R. spectroscopy. The helicenes and lower benzologues " R.H.Martin, N.Defay, H.P.Figeys, M.Flammang-Barbieux, J.P.Cosyn, M.Gelbcke and J.J.Schurter, Tetrahedron Letters, in the press.

(5) D.T.Longone and H.S.Chow, J.Am.Chem.Soc., **86**, 3898 (1964).