Tetrahedron Letters No.31, pp. 3507-3510, 1968. Pergamon Press. Printed in Great Britain.

# 1- SYNTHESIS OF OCTA- AND NONAHELICENES.
# 2- NEW SYNTHESES OF HEXA- AND HEPTAHELICENES.
# 3- OPTICAL ROTATION AND O.R.D. OF HEPTAHELICENE (1).

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(Received in UK 1 May 1968; accepted for publication 6 May 1968)

1- Octahelicene (IV) and Nonahelicene (V) have been synthetized by the photo-induced cyclization of II and III, following the procedure described by Wood and Mallory (2) for the preparative-scale photoconversion of stilbene to phenanthrene.

The cyclizations were carried out in a pyrex well, using a Hanovia 450W medium pressure mercury lamp.

Octahelicene : a solution of 309 mg of II (m.p.199-200°) in benzene (730 ml) containing a few crystals of iodine, was irradiated for 2 1/2 h at room temperature. The reaction mixture was chromatographed on alumina (p.eth.60-70°) and the first fraction (pale blue fluorescence) collected. After crystallization from benzene-ethanol, octahelicene (naphtho[2,1-c]phenanthro[4,3-g]phenanthrene) had m.p.330-331° (62%) - yellow crystals. Found: C 95.5 H 4.6 M.W. 428 (m.s.) $C_{34}H_{20}$ requires C 95.3 H 4.7 M.W. 428.

Nonahelicene : irradiation of III [170 mg (m.p.229-230°) in benzene (700 ml) containing iodine] for 5 hours, followed by column chromatography (alumina-hexane) gave nonahelicene (bisphenanthro[3,4-c;4',3'-g]phenanthrene) which, after crystallization from benzene-ethanol, had m.p.359-360° (48%) - yellow crystals. Found: C 95.2 H 4.6 M.W. 478 (m.s.) $C_{38}H_{22}$ requires C 95.4 H 4.6 M.W. 478.

The proposed structures are fully substanciated by their N.M.R. (3) (Fig.I and II) and U.V. (Fig.III) spectra [compare hexahelicene (4) and heptahelicene (5) ]. In particular, the absence of signals at fields lower than 480 c/s in the 60 Mc N.M.R. spectra recorded in $CDCl_3$, fully excludes the isomeric structures which could result from the above cyclizations.

Work on the spectral and optical properties of these new highly overcrowded aromatic hydrocarbons and on the synthesis of higher members of the helicene series is under way.

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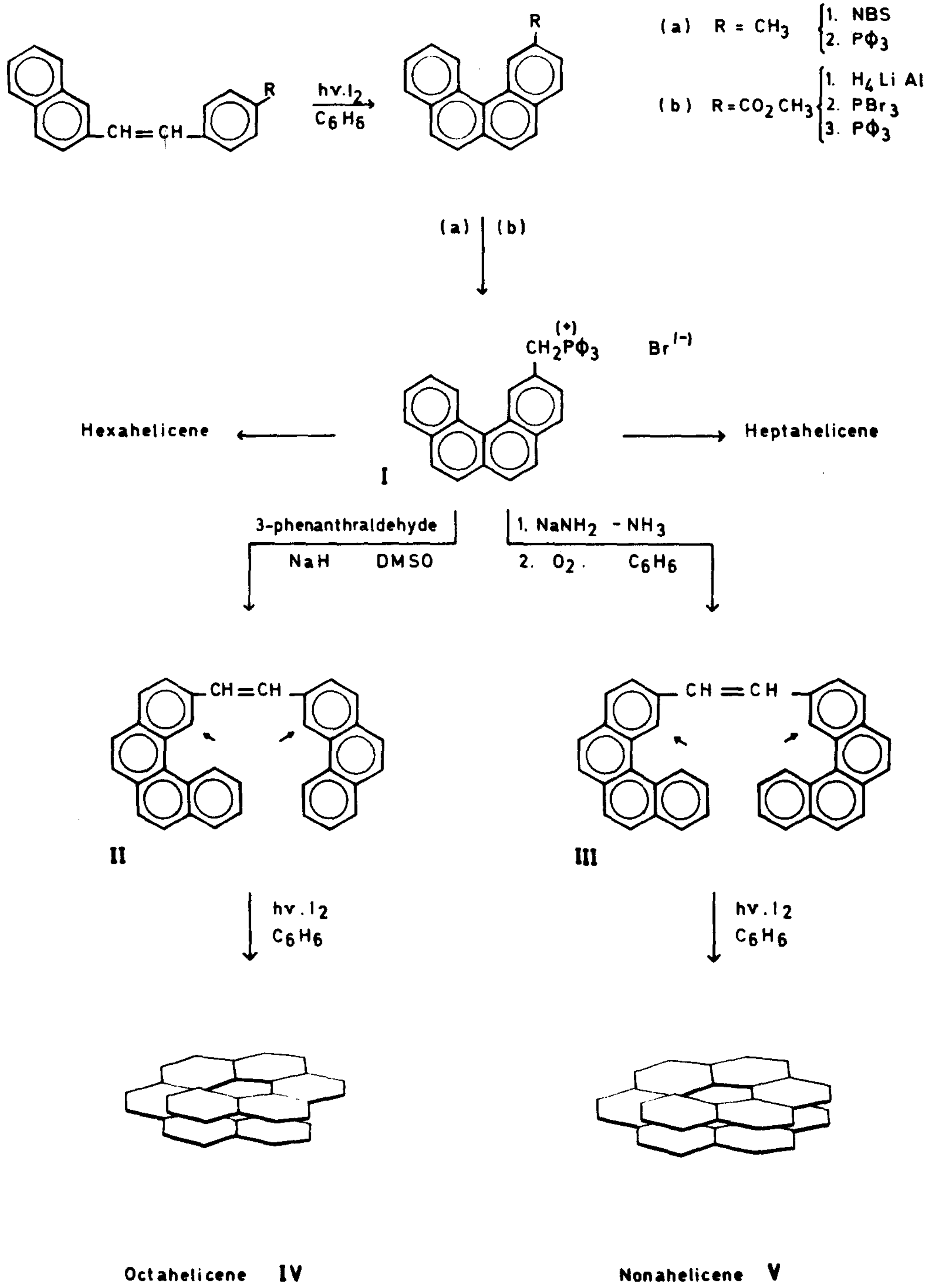
R
CH=CH
hv.I2
C6H6
R
(a) R = CH3 {1. NBS 2. PΦ3
(b) R=CO2CH3 {1. H4LiAl 2. PBr3 3. PΦ3
(a) (b)
(+)
CH2PΦ3
Br(-)
Hexahelicene
Heptahelicene
I
3-phenanthraldehyde
NaH DMSO
1. NaNH2 - NH3
2. O2. C6H6
CH=CH
CH=CH
II
III
hv.I2
C6H6
hv.I2
C6H6
Octahelicene IV
Nonahelicene V

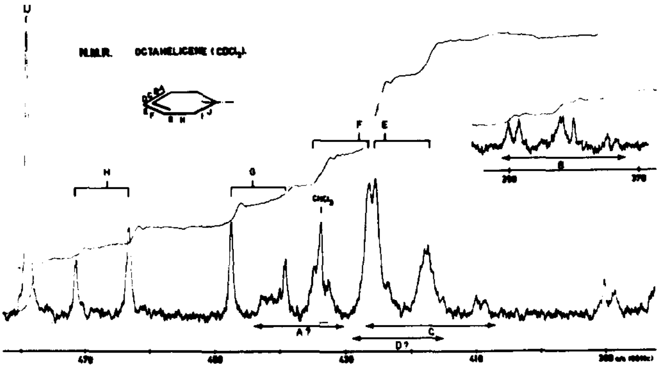

FIG.1

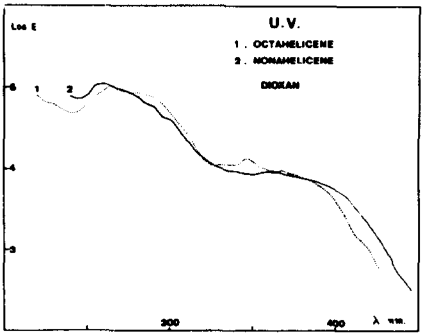

FIG. 3

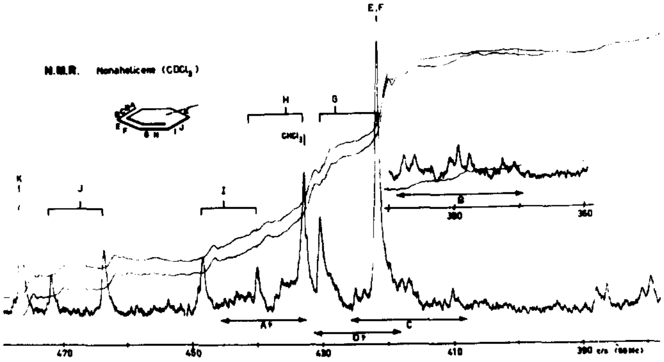

FIG. 2

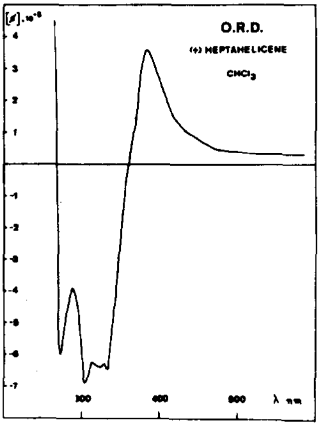

FIG. 4

2- Wittig condensations of I with benzaldehyde and 2-naphthaldehyde gave the corresponding 1,2-diarylethylenes [m.p.144-145° (cis + trans) and 200-201°] which where cyclized (1 and 1 1/2 hours irradiation respectively) to give hexahelicene (80%) and heptahelicene (20%)*. The structure of heptahelicene is thus fully confirmed by a new synthesis which cannot give the isomeric hydrocarbons liable to be formed in the cyclization of 1,2-bis(3-phenanthryl)ethylene (5).

3- Following a suggestion made by Dr.G.M.J.Schmidt (6), who had observed that our specimen of heptahelicene, crystallized from benzene-alcohol,*"belongs to the non-centric* $P2_1$ *space group with two molecules per asymetric unit"*, we have examined the optical properties of solutions of single crys-

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* Dinaphtho[1,2-a;1',2'-h]anthracene (m.p.230-231°), was also isolated (67% yield) in this experiment.

tals (grown by slow crystallization from benzene) of this hydrocarbon. As expected, all of them were optically active, the highest value yet observed being $[\alpha]_D^{20} = + 6200 \pm 200$ ($CHCl_3$)!

The O.R.D. curve (7) (Fig.IV) of a dextrorotatory specimen of heptahelicene $[\alpha]_D^{20} = + 5200 \pm 200$ ($CHCl_3$) , is closely related to the O.R.D. curve of dextrorotatory hexahelicene, recorded in the same solvent ($CHCl_3$) (8).

Further work on the properties of heptahelicene is in progress.

The authors are indebted to the following Belgian scientific Organizations - IRSIA, FNRS and FRFC - for financial support.

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(7) The O.R.D. curve was kindly measured, on a spectropolarimeter "Polarmatic 62" Bellingham and Stanley (Bendix), in the Department of Prof.J.LEONIS, Brussels University.

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