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THE PHOTOCYCLISATION OF 1,2-DIARYLETHYLENES: DETERMINATION OF THE CHEMICAL STRUCTURE OF THE CYCLISED PRODUCTS BY DEUTERIUM LABELLING.

HEXAHELICENE-7-d (1).

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The photocyclisations of 1,2-diarylethylenes (2) leading to the helicenes can give rise to isomeric polycyclic aromatic systems and are therefore highly ambiguous. In most cases, the chemical structure of the cyclised products can be deduced from the study of their U.V., N.M.R. and mass spectra (3,4,5)**.

In the present work, we have examined the possibility of getting a simpler and more definite structural proof, by the use of partially deuterated derivatives. The method has been tested in the case of hexahelicene, the structure of which is fully established by Newman's synthesis (6).

On photocyclisation, the monodeuterated 1,2-diarylethylene VII can lose either 2 hydrogens (-2H) to give hexahelicene-7-d (VIII)*** or 1 hydrogen and 1 deuterium (-HD) to give benzo[a]naphto[1,2-h]anthracene (IX). The reaction products can therefore be distinguished by mass spectroscopy (M.W.329 and 328 respectively).

For the synthesis of VII, we have used the scheme illustrated in Chart 1.****

The photocyclisation of III to IV was carried out in cyclohexane solution (1 g;950 ml) in the presence of iodine (10 mg) for 2 hours at room temperature using a Hanovia 450W medium pressure mercury lamp (Pyrex well).

The bromine-deuterium exchange [D_2O, Zn and CaO at 100° for 41 hours (7)] was repeated twice to give a labelled hydrocarbon (V) with an isotopic purity of ca 96 %, as determined by mass spectroscopy.

The final cyclisation, carried out in benzene solution (128 mg;750 ml) in the presence of iodine (4mg) for 75 min at room temperature, gave after chromatography (alumina p.eth.60-70°), an 87 % yield of hexahelicene-7-d, m.p.232-234°.

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[**] The O.R.D. and C.D. curves of the resolved hydrocarbon are also usefull in this respect.

[***] Newman's nomenclature will be used in this and subsequent publications.

[****] The structures have been checked by C.H. analyses, N.M.R. and mass spectroscopy.

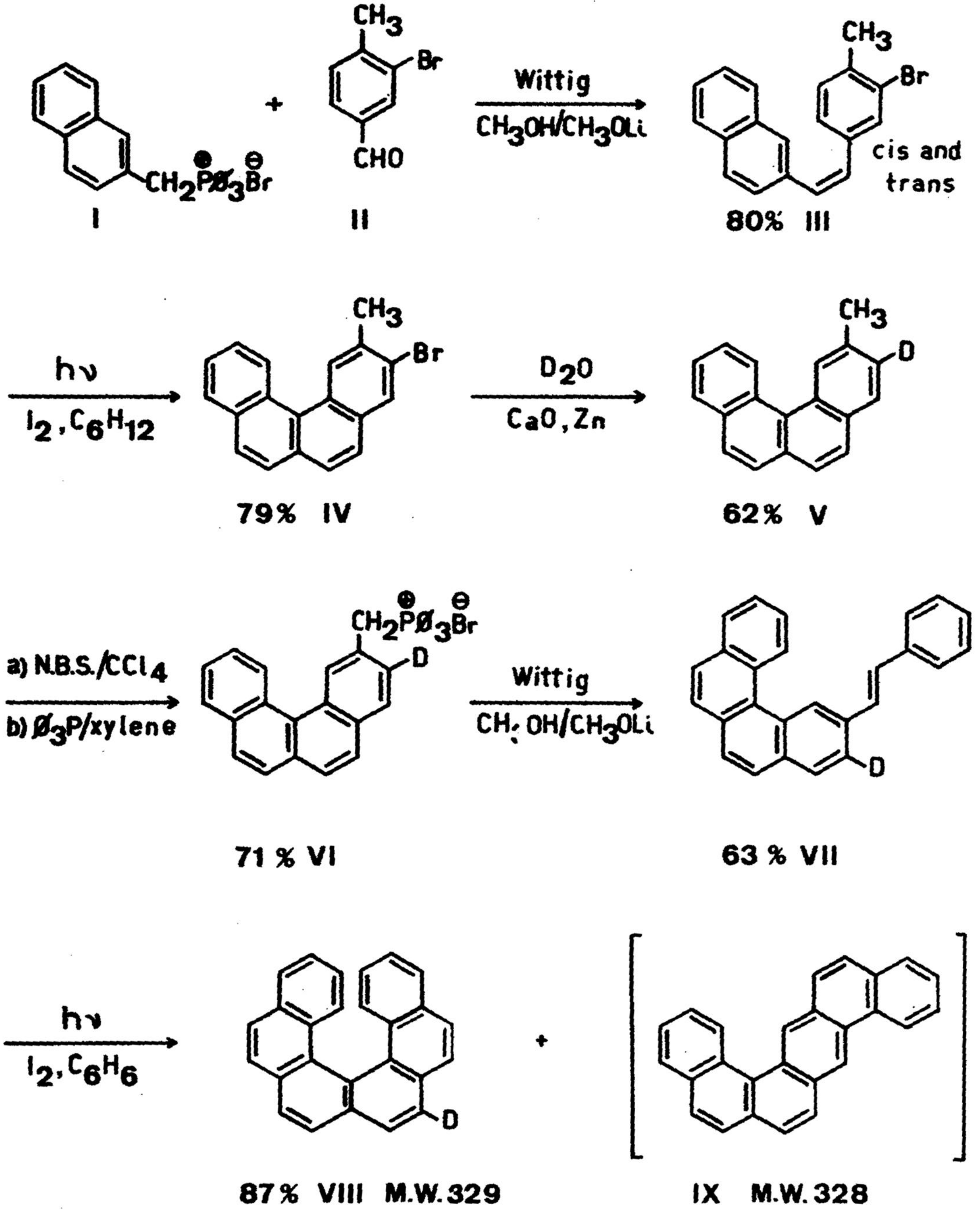
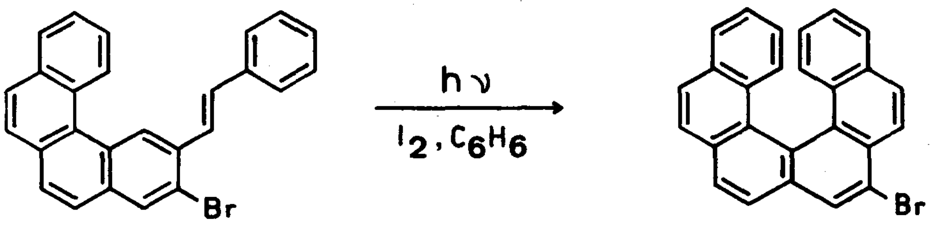

CH3
Br
+
CHO
CH2PØ3Br
I
II
Wittig
CH3OH/CH3OLi
CH3
Br
cis and trans
80% III
hν
I2, C6H12
CH3
Br
79% IV
D2O
CaO, Zn
CH3
D
62% V
a) N.B.S./CCl4
b) Ø3P/xylene
CH2PØ3Br
D
71 % VI
Wittig
CH3OH/CH3OLi
D
63 % VII
hν
I2, C6H6
D
+
87% VIII M.W.329
IX M.W.328

CHART I

A comparison of the mass spectra of hexahelicene-7-d and hexahelicene, recorded on the same instrument under identical conditions, indicates an isotopic purity of ca 96 %. The mass spectrum shows, as expected, an intense ion peak corresponding to coronene-1-d (m/e = 301) (8).

The N.M.R. spectrum of hexahelicene-7-d, was recorded to confirm the structure. It further allowed us to distinguish the signals of $H_{5,6}$ and $H_{7,8}$ respectively, in the N.M.R. spectrum of hexahelicene (4).

Finally, the photocyclisation (benzene-I_2-85 min) of X, prepared by a Wittig reaction [CH_3OH-CH_3OLi-(9)] between benzaldehyde and (3-bromo-2-benzo[c]-phenanthryl)methyl-triphenylphosphonium bromide (CH_3 replaced by $CH_2\overset{(+)}{P}\ \phi_3\overset{(-)}{Br}$ in IV), gave pure 7-bromohexahelicene, m.p.196,5-198°, in 67 % yield.



X

67 % XI

An important application of the above labelling method is described in the following communication . Further work is in progress.

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