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# PHOTOCHEMISTRY WITH CIRCULARLY POLARISED LIGHT.
# II) ASYMMETRIC SYNTHESIS OF OCTA AND NONAHELICENE[1].

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In a recent publication (1), some of us have described the first example of an asymmetric synthesis using circularly polarised light ; optically active hexahelicene was obtained from two independent syntheses (best optical yield : 0,2%). We have now extended these experiments to two higher benzologues of hexahelicene, namely octa and nonahelicene.

The photolyses were carried out in the 290-370nm region with light circularly polarised at 313nm (ellipticity of |1.16| at 290nm and |0.79| at 390nm.) as described earlier (1).

The 1.2-diarylethylenes (ca. 50mg) were photolysed in benzene solution (740ml) in the presence of iodine (10mg) (scheme I). The course of the reaction was followed by G.L.C. (3) (3 to 6 hours irradiation were needed for complete reaction) and the helicene isolated by column chromatography (alumina). The final products (helicenes) were never recrystallised, but their purity was controlled by G.L.C. The first peak of the O.R.D. curves of the helicenes obtained from these experiments were compared with the curves (2) of authentic samples. The results are collected in tables I and II.

Two independent syntheses of octahelicene, have been studied, one starting from the prochiral molecule 1, the other one from the racemic 1,2-diarylethylene 2. Octahelicene 3, prepared in 80% yield by the first synthesis (1→3), shows a very high specific rotation $[\alpha]_D = (\pm)\ 21 \pm 1°$. The (+) and (-) antipodes are obtained respectively with left and right circularly polarised light.

The specific rotation $[\alpha]_D = +\ 30,4°$ (LCP) of nonahelicene 5, prepared from 4 in 50% yield

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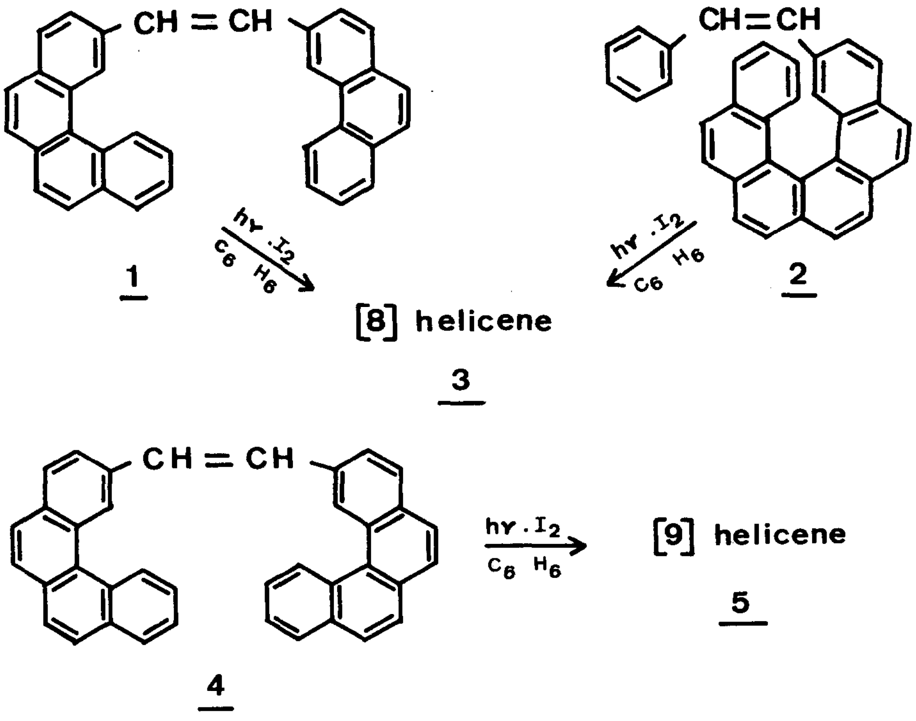
## TABLE I

OPTICAL ROTATIONS OF OCTAHELICENE AND NONAHELICENE
OBTAINED BY THE PHOTOCYCLISATION OF 1 AND 4.

| 1,2-Diarylethylene | Light polarisation* | Helicene | yield % | $[\alpha]^{23}_{589}$ (chloroform) |
|---|---|---|---|---|
| 1 | RCP | [8] 3 | 80 | -21 ± 1° (c 1,22) |
| 1 | LCP | [8] 3 | 80 | +20,2 ± 1° (c 1,12) |
| 4 | LCP | [9] 5 | 50 | +30,4 ± 1,5° (c 0,65) |

*RCP : right circularly polarised light.
LCP : left circularly polarised light.

## SCHEME I



is approximately 50% higher than the specific rotation of octahelicene. It is interesting to recall that the specific rotation of hexahelicene, prepared by a similar asymmetric synthesis, was much smaller $[\alpha]_D$ = (±) 7° and that this value corresponds to a 0,2% optical yield. It is unfortunately impossible to calculate the optical yield of the syntheses described in this communication ; this is due to the fact that the specific rotations of the pure antipodes are still unknown.It is however probable that the optical yields of the syntheses described here are of the same magnitude as the one observed in the case of hexahelicene*.

In the second synthesis of octahelicene, starting from the racemic 1,2-diarylethylene <u>2</u>, no optical activity is observed when the reaction is <u>complete</u>. This is in accordance with expectation, since the starting material cannot racemise. However, when the reaction is stopped before the complete transformation of <u>2</u>, the octahelicene formed has a low, but significant, optical activity (see table II).

TABLE II

OPTICAL ROTATION OF OCTAHELICENE OBTAINED BY ASYMMETRIC PHOTODESTRUCTION OF RACEMIC <u>2</u>.

| 1,2-diarylethylene destruction ratio (%) | light polarisation | $[\alpha]^{23}_{546}$ (chloroform) |
|---|---|---|
| 30 | LCP | + 5,1 ± 1,3° (c = 0,217) |
| 75 | | + 3,7 ± 1,3° (c = 0,188) |
| 100 : complete reaction | | 0,0° (c = 0,932) |
| 45 | RCP | - 7,6 ± 1,3° (c = 0,250) |

These results show clearly that the observed optical activity of the helicenes is not due to an induced asymmetric degradation of the latter, as had already been demonstrated in the case of hexahelicene (1). The photolysis of dl <u>2</u> can thus be described as an "asymmetric destruction".

A possible mechanism for this type of asymmetric synthesis was previously discussed (4) in the case of hexahelicene :

$$\begin{tikzcd}
\underline{\text{cis}}\text{ diarylethylene M} \arrow[r, leftrightarrow] \arrow[d, shift left] & \text{dihydrohelicene M} \arrow[r] & \text{Helicene M} \\
\underline{\text{cis}}\text{ diarylethylene P} \arrow[r, leftrightarrow] \arrow[u, shift left] & \text{dihydrohelicene P} \arrow[r] & \text{Helicene P}
\end{tikzcd}$$

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*) By assuming an optical yield of 0,2%, the calculated specific rotations of the pure antipodes are : octahelicene : $[\alpha]_D = \pm$ 10.000° ; nonahelicene : $[\alpha]_D = \pm$ 16.000°.

The cis 1,2-diarylethylene can hardly be planar and is therefore a labile racemic mixture. One enantiomer can then photocyclise faster than the other, if irradiated at the wavelength of a CD band, giving rise to optical activity in the final helicene. This mechanism postulates the thermal racemisation equilibrium to be much faster than the ring closure rate.

CONCLUSION : The exceptionally high optical activity of the helicenes made it possible to demonstrate for the first time without ambiguity* the possibility of inducing asymmetric syntheses with circularly polarised light, a phenomenon of theoretical importance in the problem of the origin of optical activity on the earth.

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## REFERENCES

1) For the first paper in this series see : A.MORADPOUR, J.F.NICOUD, G.BALAVOINE, H.KAGAN and G.TSOUCARIS. J. Amer. Chem. Soc. in press.

2) Unpublished results (Brussels University).

3) Manuscript concerning the G.L.C. of helicenes- in preparation.

4) G.TSOUCARIS, G.BALAVOINE, A.MORADPOUR, J.F.NICOUD, H.KAGAN C.R. Acad. Sc. Paris, in press

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*Dr. O. BUCHARDT and Prof. M. CALVIN have informed us in a personal communication that successful asymmetric syntheses of helicenes have independently been carried out in Prof. CALVIN's laboratory.