Tetrahedron. Vol. 31, pp. 2135 to 2137. Pergamon Press 1975 Printed in Great Britain

HELICENES
PHOTOSYNTHESES OF [11], [12] AND [14]HELICENE

R. H. MARTIN* and M. BAES
Service de Chimie Organique, Faculté des Sciences, Université Libre de Bruxelles,
50 Av. F. D. Roosevelt, B-1050 Bruxelles, Belgique

(*Received in UK* 12 *April*; *Accepted for publication* 25 *April* 1975)

Abstract—[11], [12] and [14]helicene have been synthetised in one operational step by photoinduced double cyclodehydrogenations of bis(arylvinyl)arenes.

With the object of studying further the spectral, chiroptical and physical properties of the helicenes, we have completed the all benzene-helicene series up to [14]helicene, inclusive.†

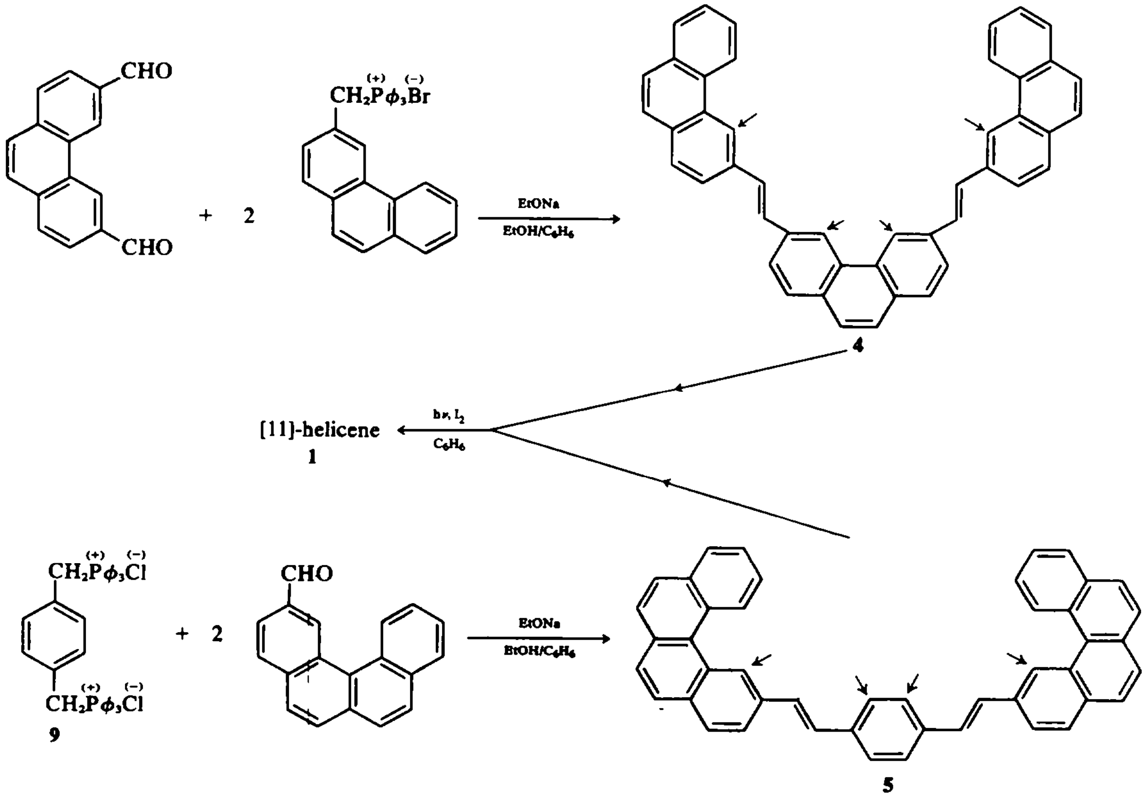
The syntheses of [11], [12] and [14]helicene described in this communication involve double photocyclisations, a process used successfully in earlier work, particularly in the case of [13]helicene, the first member of the multi-layered helicenes.[1]

The photoinduced double cyclodehydrogenations can, in principle give rise to a large number of isomers. However, the double photocyclisation step leading to [13]helicene gave the desired helicene in 52% yield.

Two independent photosyntheses of [11]helicene (Scheme 1), [12] and [14]helicene (Schemes 2 and 3) have been carried out in order to compare the yields and to assign the structures. The structural proofs are based on the fact that, in each case, only the desired helicene is a common isomer of the two synthetic schemes. In the case of [11] and [12]helicene, a third independent photosynthesis has been carried out by Moradpour *et al.*[2] The structures thus assigned are fully confirmed by the study of their ^{1}H-NMR spectra[4] and by GLC. In GLC, [10], [11], [12] and [14]helicene behave as predicted in an earlier publication.[5]

EXPERIMENTAL

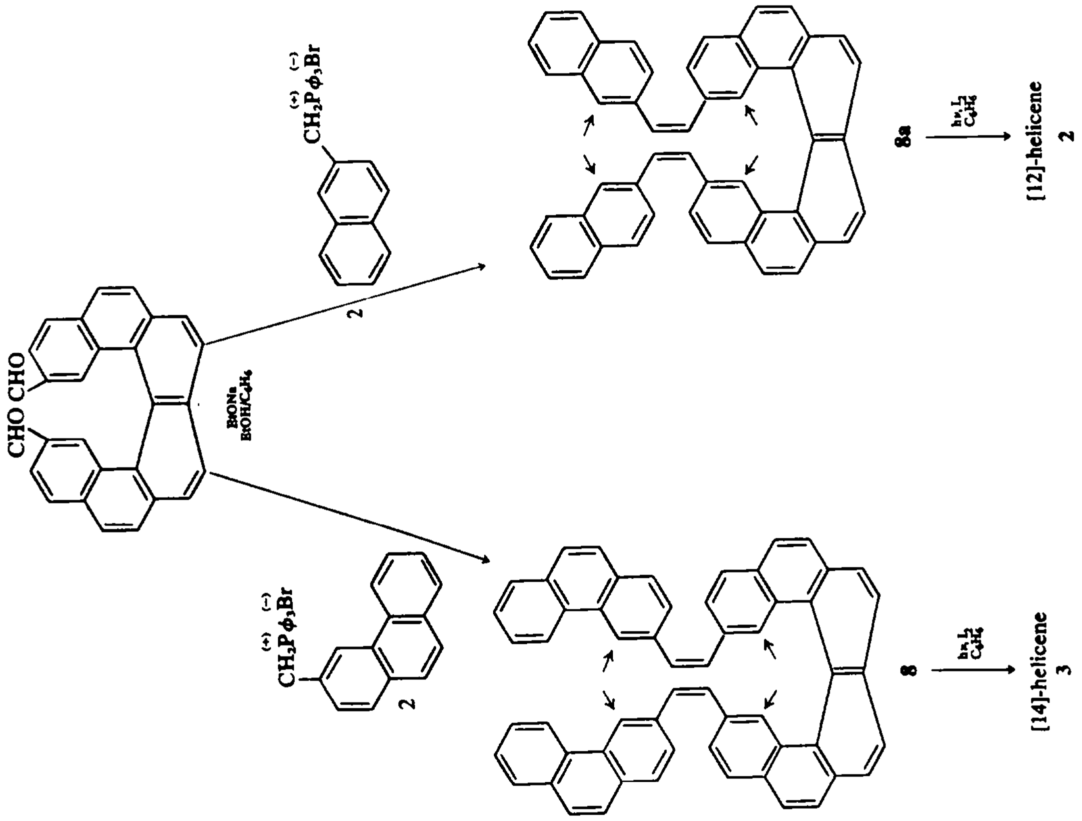
(a) *Wittig reaction.* The precursors **4**, **5**, **6**, **7**, **8** and **8a** of the helicenes are prepared in one operational step by a double Wittig reaction. In the course of this and similar work, we have observed that the yield of the double Wittig reaction is usually better when the dialdehyde is used instead of the bisphosphonium salt; Wynberg *et al.* have reached the same conclusion.[6] For the preparation of **5**, the reverse is however true (97 vs 65%).



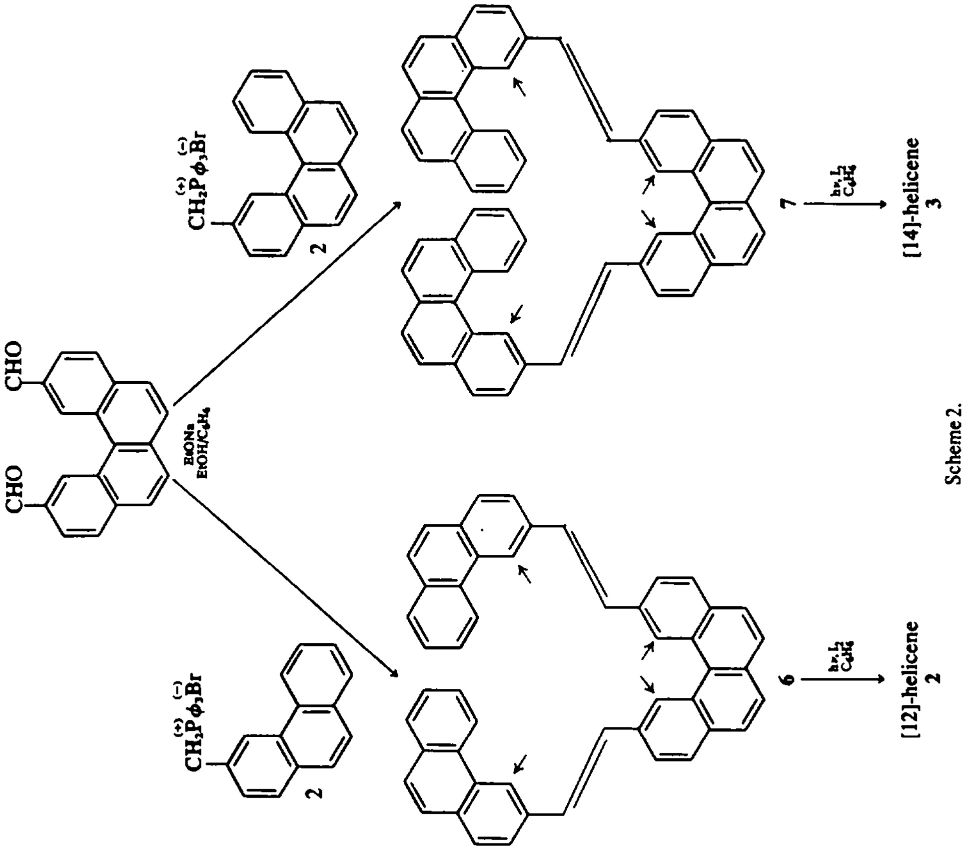
Scheme 1.

---

†Three photosyntheses of [10]helicene are presently known; two of them are described in an accompanying communication,[2] the other one, starting from 2-methoxycarbonyl[6]helicene, will be published shortly.[3]



Scheme 3.



Scheme 2.

Table 1.

	Wittig yield	Time of irradiation	Helicene	Yield	M^+ (m/e)
3– = -3– = -3	96%	1h 40′	[11]	54%	578
4– = -1– = -4	97%	3h	[11]	84%	578
3– = -4– = -3	87%	2h10′	[12]	32%	628
2– = -6– = -2	64%	1h	[12]	42%	628
4– = -4– = -4	84%	4h 30′	[14]	10%	728
3– = -6– = -3	78%	4h 30′	[14]	45%	728

-1–: 1,4-phenylene,
3–: 3-phenanthryl,
-3–: 3,6-phenanthrylene,
4–: 2-benzo[c]phenanthryl,
-4–: 2,11-benzo[c]phenanthrylene,
-6–: 2,15-hexahelicylene.

General procedure. A soln of EtONa in EtOH ($2\cdot5 \times 10^{-3}$ mol of Na in 15 ml EtOH) was added slowly to a boiling soln of the phosphonium bromide ($2\cdot10^{-3}$ mol) and the dialdehyde (10^{-3} mol) dissolved in the minimum amount of EtOH/benzene (N_2 and stirring). The mixture was refluxed during 1 hr and kept at room temp over night (stirring). The yellow ppt was collected and dried under reduced pressure. The mother liquor was concentrated to approximately one quarter of the original volume and MeOH was added to the residue. The ppt was collected and purified by column chromatography (alumina–benzene). This last treatment was repeated, if necessary, to complete the extraction of the desired product. The yields are given in Table 1.

Note. The aldehydes used in this work were prepared either from the corresponding (bis)bromomethyl derivatives by the action of 2-nitropropane in alkaline soln[7] or by oxidation of the corresponding primary alcohols with DDQ (2,15-bisformyl [6]helicene).

(b) *Photocyclisations.* A suspension of the product to be cyclised (0·1 g) in benzene (1 l) containing 8–12 mg of I_2, was irradiated, at room temp, with a Hanovia 450 W high pressure Hg lamp (Pyrex well). The time required to complete the photocyclisation (no more starting material detected by TLC on silica-gel (p.ether 60–70°/ethyl acetate 4:1) is given in Table 1. The product was purified by column chromatography [alumina-p.ether 60–70°; first fluorescent (green) band]. The new helicenes were characterised by MS, GLC and by ^{1}H-NMR spectroscopy.[4] The yields are given in Table 1.

Acknowledgements—Financial support from the "Fonds de la Recherche Fondamentale Collective" is gratefully acknowledged.

REFERENCES

[1] R. H. Martin, G. Morren and J-J. Schurter, *Tetrahedron Letters* 3683 (1969).
[2] A. Moradpour, H. Kagan, M. Baes, G. Morren and R. H. Martin, *Tetrahedron* 31, 2137 (1975).
[3] V. Libert (Brussels), private communication.
[4] R. H. Martin, N. Defay and M. Baes, unpublished results.
[5] J. F. Nicoud, A. Moradpour, G. Balavoine, H. Kagan, R. H. Martin and M. Deblecker, *J. Chromatog.* **66**, 43 (1972).
[6] J. H. Dopper, D. Oudman and H. Wynberg, *J. Am. Chem. Soc.* **95**, 3692 (1973).
[7] H. B. Hass and M. L. Bender, *Ibid.* **71**, 1767 (1949).