Tetrahedron Vol. 28, pp 1749 to 1758. Pergamon Press 1972 Printed in Great Britain

STUDIES IN THE HELICENE SERIES

STRUCTURAL DETERMINATIONS USING DEUTERIUM LABELLING COMBINED WITH ^{13}C-NMR SPECTROSCOPY*

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(*Received in the UK* 12 *November* 1971; *Accepted for publication* 24 *November* 1971)

Abstract—Specific deuterium labelling, combined with ^{13}C-NMR spectroscopy, has been used to study the course of the photocyclodehydrogenetions leading to hexa-, hepta-, octa- and nonahelicene. The case of heptahelicene is a good illustration of the scope and limitations of this technique in this particular field.

THE normal photocyclodehydrogenation of 1,2-diarylethylenes leading to the helicenes[2] can proceed to give many isomers,‡ particularly in the case of the double photocyclizations.[4] The number of possible isomers is still larger if rearrangements of the type described by Cohen, Mijovic and Newman[5] are considered. The structural determination of the reaction products is therefore a crucial problem. The methods used so far in this field are discussed in a recent review.[6]

Among these, deuterium labelling, combined with mass spectrometry, provides more information than any other one on the same scale (fraction of a mg). It is, however, impossible to distinguish by deuterium labelling alone the "normal" and the "rearranged" hydrocarbons which can result from a cyclodehydrogenation involving the same positions in a given 1,2-diarylethylene (e.g. II and III; VIII and IX; XIV and XV; XIX and XX, etc.).

This problem can only be solved, either by rather elaborate experiments based on two independent syntheses involving labelled intermediates or, more simply, by the combined use of deuterium labelling and ^{13}C—NMR spectroscopy. Both schemes are illustrated in the case of heptahelicene.

We wish to emphasise that the following discussion is strictly limited to one aspect of ^{13}C—NMR spectroscopy namely the total number of singlets or in the case of octahelicene the number of singlets due to the protonated carbon atoms, observed in the fully decoupled ^{13}C—NMR spectra of the non-deuteriated hydrocarbons.

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* Part XXXIII, *Syntheses in the field of polycyclic aromatic compounds—XXXII*, see ref. 1.

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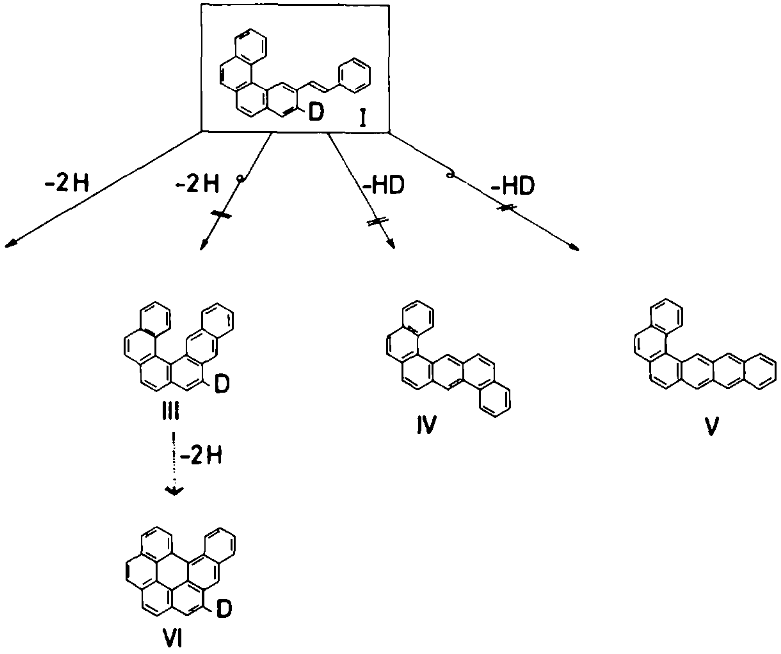
‡ The course of the reaction is much simpler in the heterohelicene series studied by Wynberg and his collaborators,[3] for only one product can result, in most cases, from the "normal" photocyclization process.

I. *Hexahelicene*

Photocyclization of 1-(2-*benzo*[c]*phenanthryl*-3-*d*)-2-*phenylethylene* I (Scheme I). In a preliminary communication,[7] we have shown that deuterium labelling can be used with success to determine the course of the photocyclization of the 1,2-diarylethylene I. This demonstration was, however, over-simplified by the fact that the structure of [6]helicene (II; D=H) was already known from the pioneer work of Newman and Lednicer.[8] It followed that the monodeuteriated hydrocarbon, isolated in 87% yield, could not be the rearranged product III resulting from a cyclization in position 1 of the benzo[*c*]phenanthrene skeleton. The nature of the compound prepared without deuterium labelling can now be determined, very simply, by the study of its ^{13}C—NMR spectrum. Of the four isomers involving the loss of two hydrogens (II, III, IV and V; D=H) only one, namely hexahelicene, has an element of symmetry from the NMR point of view. The fact that the fully decoupled ^{13}C—NMR spectrum[9] of the reaction product contains only 14 singlets (26 singlets are expected in the spectra of III, IV and V; D=H) constitutes an unambiguous proof of its helicene structure.



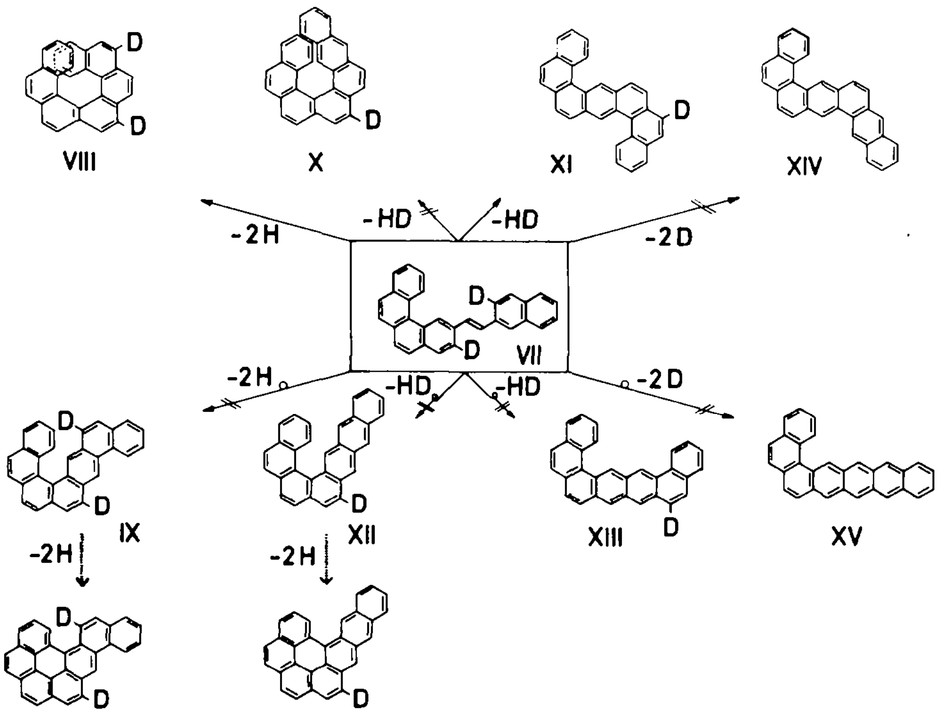
SCHEME 1

II. *Heptahelicene*

a. *Photocyclization of* 1-(2-*benzo*[*c*]*phenanthryl*-3-*d*)-2-(2-*naphthyl*-3-*d*)*ethylene* VII (Scheme 2). As expected,[2b] two hydrocarbons are isolated by chromatography from this reaction. The first one (m.p. 253–254·5°; 20% yield) was shown to contain two deuterium atoms (M$^+$ $m/e = 380$) while the second one (m.p. 225–226°; 67% yield) contains only one deuterium (M$^+$ $m/e = 379$).

The *bisdeuteriated* hydrocarbon could be either VIII or IX.* The isomers VIII and IX can, of course, be distinguished by ^{13}C—NMR spectroscopy. The presence of only 14 singlets (overlap of 2 signals) in the proton decoupled ^{13}C—NMR spectrum of this hydrocarbon (VIII; D=H)[9] fully confirms its helicene structure (without overlap of signals, 30 singlets are expected in the spectra of the three non-deuteriated isomers). It is important to note at this stage that ^{13}C—NMR spectroscopy, without deuterium labelling experiments, could not distinguish two other isomers, namely VIII (D=H) and XI (D=H). Thus, only the combined use of deuterium labelling and ^{13}C—NMR spectroscopy will give an unambiguous answer in this case. In order to solve the problem by deuterium labelling alone, the above experiment must be completed by the study of another photo-synthesis (*vide infra* under *b*).

The *monodeuteriated* hydrocarbon could have one of the four structures X, XI, XII or XIII.† This ambiguity was partially removed by the experiment described in



SCHEME 2

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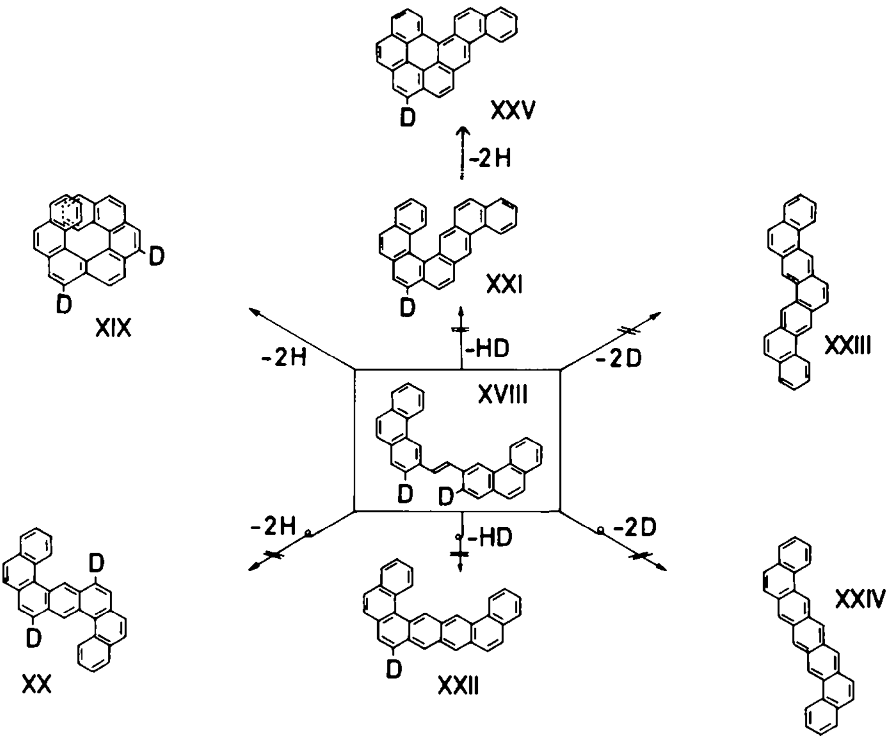
* Structure IX (rearranged product) is very unlikely for it contains a pentahelicene (or dibenzo[*c*,*g*]-phenanthrene) skeleton which usually loses two hydrogens on photolysis[10] to give the corresponding perylene structure (XVI).

† Two of these isomers could be discarded on the following grounds:—The hydrocarbon X (D=H) synthesized by Laarhoven, Cuppen and Nivard[10c] is different from our hydrocarbon.—As already pointed out, structures such as XII are expected to lose two hydrogens to give benzo[*g*,*h*,*i*]naphtho[2,3-*o*]perylene (XVII) on photolysis.

paragraph c (*vide infra*). ^{13}C—NMR spectroscopy could, in this case, distinguish XI (D=H) from X (D=H), XII (D=H) and XIII (D=H).[*] Without deuterium labelling experiments, it could not distinguish XI (D=H) from the helicene structure VIII (D=H).



Scheme 3

b. *Photocyclization of* 1,2-*bis*(3-*phenanthryl*-2-*d*)*ethylene* XVIII (Scheme 3). As expected,[2a] only one product containing two deuterium atoms is isolated from the photolysis of XVIII. That this hydrocarbon and the one described in paragraph a. (m.p. 253·5–255°) have the same skeleton, is evident from their ^{1}H—NMR spectra. Of all the bisdeuteriated hydrocarbons of schemes 2 and 3, only heptahelicene-d$_2$ (VIII and XIX) is common to both. The structural determination of this hydrocarbon is thus completely solved. In this connection, it is worth pointing out: (1) that the two independent syntheses carried out on the non-deuteriated 1,2-diarylethylenes VII (D=H) and XVIII (D=H) would not give an unambiguous answer, for both could also proceed to give dinaphtho[1,2-*a*;1′,2′-*h*]anthracene (XI=XX; D=H); (2) that ^{13}C—NMR spectroscopy alone could not differentiate the normal (XIX; D=H) and the rearranged (XX; D=H) bisdeuteriated hydrocarbons of scheme 3.

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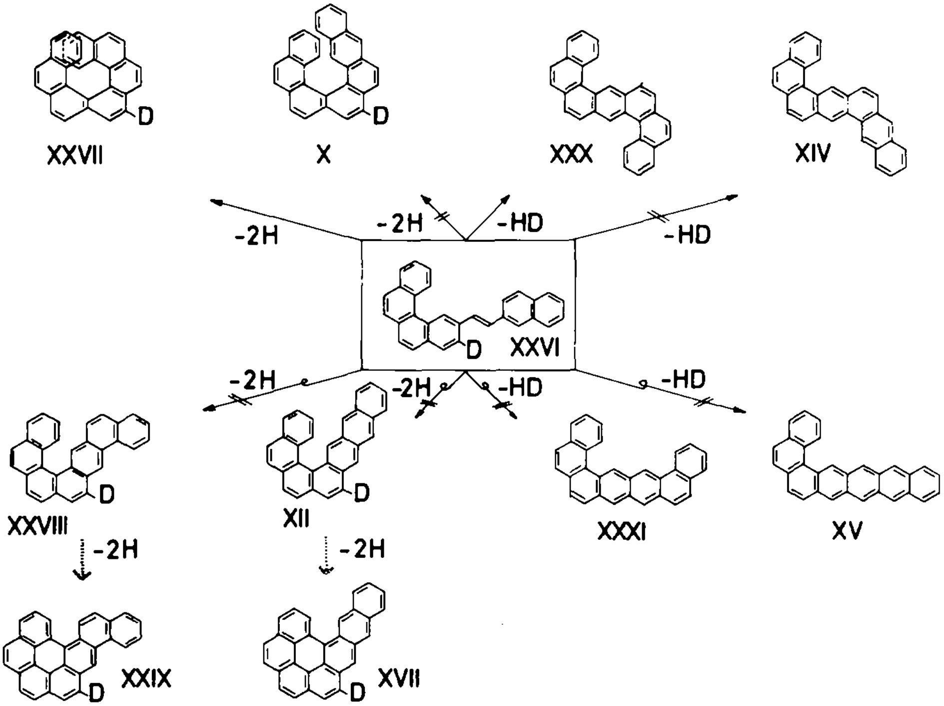
[*] The ^{13}C—NMR spectrum of this hydrocarbon has not yet been recorded. Structure XI is, however, the only one compatible with the ^{1}H—NMR spectrum.

c. *Photolysis of* 1-(2-*benzo*[c]*phenanthryl*-3-*d*)-2-(2-*naphthyl*)*ethylene XXVI* (Scheme 4). This experiment was carried out in order to further elucidate the structure of the monodeuteriated hydrocarbon (m.p. 253–254·5°) isolated from the photolysis of VII (scheme 2). A monodeuteriated hydrocarbon and a nondeuteriated hydrocarbon were obtained. ^{1}H—NMR spectroscopy confirms that the monodeuteriated hydrocarbon is heptahelicene-9-d (XXVII). The combined results of schemes 2 and 4 leave only two alternatives for the non-deuteriated product, namely dinaphtho[1,2-*a*; 1′,2′-h]-anthracene (XXX) and benzo[*a*]naphtho[2,1-*l*]tetracene (XXXI) (common skeletons to both schemes). For a choice between these two structures, see footnote page 1752).

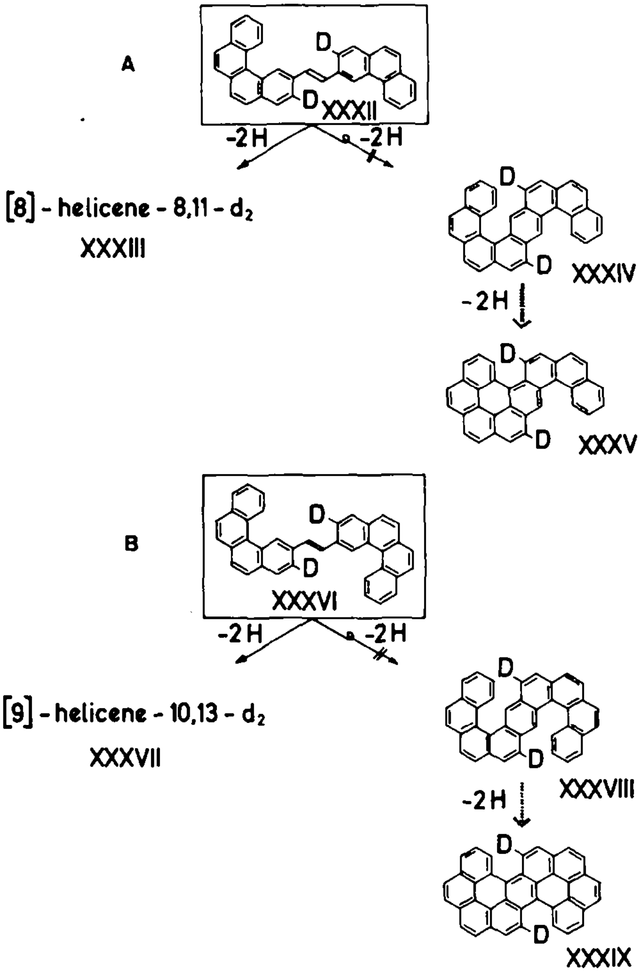


SCHEME 4

It is interesting to note that scheme 4, combined with ^{13}C—NMR spectroscopy, is the simplest scheme available for the unambiguous structural determination of both heptahelicene (XXVII) and its isomer XXX.

III. *Octahelicene and nonahelicene*

Photolysis of 1-(2-*benzo*[c]*phenanthryl*-3-*d*)-2-(3-*phenanthryl*-2-*d*)*ethylene* XXXII (Scheme 5A) *and* 1,2-*bis*(2-*benzo*[c]*phenanthryl*-3-*d*)*ethylene* XXXVI (Scheme 5B).[2b] In both cases, the only hydrocarbon isolated was shown to contain two deuterium atoms (M$^+$ m/e = 430 and 480, respectively). It follows that the cyclized products are either the respective helicenes or the corresponding rearranged hydrocarbons (XXXIV and XXXVIII). A choice based on ^{13}C—NMR spectroscopy is only possible in the case of octahelicene. The ^{13}C—NMR spectrum (unpublished work) of the non-deuteriated hydrocarbon contains the signals of 10 protonated carbon atoms, thus confirming the helicene structure.



SCHEMES 5A and 5B

CONCLUSIONS

The work described in this communication clearly shows the scope and the limitations of the deuterium labelling technique. In the field investigated, the main limitation comes from the fact that the two isomers which can result from a cyclization involving the same positions in the 1,2-diarylethylene are indistinguishable by deuterium labelling alone. However, deuterium labelling combined with ^{13}C—NMR spectroscopy can often yield unambiguous answers. The type of rearrangement[5] discussed above should not be over-stressed (nor should it be overlooked . . .). This assertion is based on the fact that no such rearrangement has yet been observed in the photocyclizations of unsubstituted benzenoid 1,2-diarylethylenes.

EXPERIMENTAL

The NMR spectra were recorded at 60 MHz (Varian A60; $CDCl_3$; TMS = 0). The reported chemical shifts (Hz-60 MHz) correspond to the middle point of the system(s) considered.

The isotopic purities (D) were determined by mass spectrometry (Hitachi Perkin–Elmer RMU-6D) at low potential (*ca* 15 eV).

The m.p. (hot stage microscope) are uncorrected. The microanalyses were carried out either on the non-deuteriated or on the deuteriated derivatives. This is specified in the empirical formulae.

General procedures

a. 1,2-*Diarylethylenes.* The 1,2-diarylethylenes are prepared by the Wittig reaction in an atmosphere of dry N_2. The aldehyde and the phosphonium salt (1 :1 mole ratio) are dissolved in the minimum quantity of anhyd MeOH. 10% excess of freshly prepared MeOLi is added and the mixture is stirred at room temp for 16 h, unless otherwise noted. The ppt is filtered off, the mother liquor is evaporated to dryness and the residue is chromatographed with light petroleum (60–70°) on grade III alumina. The combined products are isomerized in boiling xylene in the presence of iodine.

b. *Photocyclization.* The 1,2-diarylethylenes, dissolved in benzene or cyclohexane, are photolysed in a pyrex well, in the presence of iodine,[11] with a Hanovia 450 W medium pressure mercury lamp. The products are separated and purified by column chromatography on alumina.

1-(3-*Bromo*-p-*tolyl*)-2-*phenylethylene*

A soln of triphenylphosphoniomethylbenzene bromide (17·35 g; $4\cdot10^{-2}$ mole) and 3-bromo-*p*-tolualdehyde[12] (8·37 g; $4\cdot10^{-2}$ mole) in MeOH is treated with MeOLi (10% excess), stirred for 1 hr at room temp and worked up as described. *trans*-1-(3-Bromo-*p*-tolyl)-2-phenylethylene (94%) is recrystallized from MeOH, m.p. 108·5–110°. M^+ *m/e* = 272 and 274 (calc. 272 and 274); NMR: CH_3 (s) 142·5 Hz; ethylenic protons (s) 419 Hz; 7 H_{Ar} at ~ 440 Hz; H_{ortho} to Br (m) 460 Hz. (Found: C, 65·7; H, 4·9. $C_{15}H_{13}Br$ requires: C, 65·90; H, 4·80%).

2-*Bromo*-3-*methylphenanthrene*

A soln of *trans*-1-(3-bromo-*p*-tolyl)-2-phenylethylene (1·5 g) dissolved in cyclohexane (900 ml) containing I_2 (30 mg) is irradiated for ½ hr. Another 20 mg I_2 are added to the soln which has turned yellow and the photolysis is continued for 1½ hr. (no more unchanged 1,2-diarylethylene). The chromatographed (alumina, light petroleum 60–70°) and recrystallized (MeOH) 2-bromo-3-methylphenanthrene (0·64 g; 43%) has a m.p. of 107–110°. M^+ *m/e* = 270 and 272 (calc. 270 and 272); NMR: CH_3 (m) 154 Hz; H_2 (s) 449 Hz; 5 H_{Ar} at ~ 460 Hz; H_4 and H_5 multiplets at ~ 510 Hz. (Found: C, 66·3; H, 4·2. $C_{15}H_{11}Br$ requires: C, 66·50; H, 4·08%).

The residue from the mother liquor of the recrystallization is a 3:1 mixture of 4-bromo-3-methylphenanthrene (CH_3 (s) 160 Hz; H_5, 600 Hz) and 2-bromo-3-methylphenanthrene (CH_3 (m) 154 Hz). Total yield of the cyclization (2-bromo- and 4-bromo-): 63%.

3-*Methylphenanthrene*-2-*d*

A mixture of 2-bromo-3-methylphenanthrene (3·03 g), Zn powder (34 g, washed successively with EtOH, CCl_4, ether and dried at 80° in high vacuum for one night), CaO (3·97 g, heated 18 hr at 900) and D_2O (25 ml, 99·7%) refluxed, with efficient stirring, for 4 days. The product is extracted with $CHCl_3$ and recrystallized from EtOH (1·95 g), m.p. 61–62°; lit.: 3-methylphenanthrene 61–62 .[11]

3-*Triphenylphosphoniomethylphenanthrene*-2-*d bromide*

3-Methylphenanthrene-2-d, dissolved in CCl_4, is brominated in the side chain with NBS in the presence of benzoylperoxide[13] and the bromomethyl derivative (m.p. 116–118°) is treated with triphenylphosphine in boiling xylene,[14] m.p. 273–276°, overall yield: 76%.

3-*Phenanthraldehyde*-2-*d*

The aldehyde is prepared from the corresponding bromomethyl derivative following the procedure of Ried and Bodem.[15] A soln of 3-bromomethylphenanthrene-2-d (0·475 g; $1\cdot68.10^{-3}$ mole) in CCl_4 (20 ml) is treated with NBS (0·315 g; $1\cdot76.10^{-3}$ mole) and benzoylperoxide (52 mg). After 90 min refluxing, the soln is cooled, filtered and the solvent is distilled under reduced pressure. The residue (brownish oil, 0·691 g) is dissolved in 120 ml of a 5:1 EtOH-benzene soln containing 0·4 g of potassium oxalate monohydrate.

After 20 hr refluxing, the solvent is distilled under reduced pressure and the residue is chromatographed on a column of silica gel (benzene). The aldehyde is then sublimed at 60°/0·02 Torr, m.p. 77·5–79° (lit. 3-phenanthraldehyde: 79·5–80°[16]), yield: 90%.

1-(3-*Bromo*-p-*tolyl*)-2-(2-*naphthyl*)*ethylene*

The Wittig reaction is carried out on 9·66 g ($2{\cdot}10^{-2}$ mole) of 2-triphenylphosphoniomethylnaphthalene bromide and 4·18 g ($2{\cdot}10^{-2}$ mole) of 3-bromo-*p*-tolualdehyde for 3 hr at room temp. The ppt of *trans*-1-(3-bromo-*p*-tolyl)-2-(2-naphthyl)ethylene is filtered and recrystallized from benzene, m.p. 176–179° (2·62 g: 41%); M^+ *m/e* = 322 and 324 (calc. 322 and 324); NMR: CH_3 (s) 144 Hz; ethylenic and aromatic protons at ~450 Hz. (Found: C, 71·3; H, 4·70. $C_{19}H_{15}Br$ requires: C, 70·8; H, 4·38%). The mother liquor of the reaction mixture is evaporated to dryness and the residue is chromatographed on alumina (light petroleum 60–70°). *cis*-1-(3-Bromo-*p*-tolyl)-2-(2-naphthyl)ethylene is recrystallized from MeOH, m.p. 70·5–72·5°, yield: 2·62 g; M^+ *m/e* = 322 and 324 (calc. 322 and 324). NMR. CH_3(s) 140 Hz; ethylenic protons (2 doublets) $\nu_A = 404$ Hz, $\nu_B = 393$ Hz, $\Delta_{AB} = 11{\cdot}3$ Hz, $J_{H,H} = 12{\cdot}4$ Hz; 10 H_{Ar} at ~445 Hz; total yield (*cis* + *trans*): 82%.

3-*Bromo*-2-*methylbenzo*[c]*phenanthrene*

cis-1-(3-Bromo-*p*-tolyl)-2-(2-naphthyl)ethylene (1·027 g; $3{\cdot}2.10^{-3}$ mole) in 950 ml cyclohexane containing 11 mg ($4{\cdot}3\,.\,10^{-5}$ mole) I_2 is photolyzed for 2 hr. The reaction is followed by TLC (silica gel impregnated with 2,4,6-trinitrofluorenone) with light petroleum (60–70°). Three to four successive runs are necessary to observe a separation between the 1,2-diarylethylene and the cyclized product. The product is chromatographed on alumina (light petroleum 60–70°) and recrystallized from hexane, m.p. 66·5–68°, yield: 78%; NMR: CH_3 (m) 156 Hz; 7 H_{Ar} at ~456 Hz; H_4 (s) 488 Hz; H_1 and H_{12} multiplets at ~540 Hz. M^+ *m/e* = 320 and 322 (calc. 320 and 322). (Found: C, 70·95; H, 4·1. $C_{19}H_{13}Br$ requires: C, 71·06; H, 4·05%).

2-*Methylbenzo*[c]*phenanthrene*-3-d

The procedure used for the bromine-deuterium exchange is similar to the one described in the case of the corresponding phenanthrene derivative (see above), m.p. 80–82°, yield: 89%; M^+ *m/e* = 243 (calc. 243). (Found: C, 93·7; H, 5·9. $C_{19}H_{15}D$ requires: C, 93·80; H, 6·22%).

2-*Triphenylphosphoniomethylbenzo*[c]*phenanthrene*-3-*d bromide*

A mixture of 2-methylbenzo[*c*]phenanthrene-3-d (1·23 g; $5{\cdot}10^{-3}$ mole), freshly recrystallized NBS (0·93 g; $5{\cdot}6\,.\,10^{-5}$ mole), benzoylperoxide (0·15 g) and CCl_4 (50 ml) is refluxed for 2 hr. The cooled soln is filtered and evaporated to dryness. The residue is treated with triphenylphosphine (1·38 g; $5{\cdot}6.10^{-3}$ mole) for 3 hr. The ppt formed on cooling is filtered and washed with ether, m.p. 311·5–315° (2·32 g, 78%).

2-*Formylbenzo*[c]*phenanthrene*-3-*d*

2-Bromomethylbenzo[*c*]phenanthrene-3-d (0·453 g; m.p. 94–96°) is treated with NBS as described. The oily product is dissolved in EtOH-benzene (5:1), 0·33 g potassium oxalate monohydrate are added and the mixture is refluxed for 42 hr. The oily aldehyde is chromatographed on silica gel in benzene (yellow-green fluorescent band) and recrystallized from EtOH, m.p. 94–96°, overall yield from 2-methylbenzo[c]phenanthrene-3-d: 77%; M^+ *m/e* = 257 (calc. 257). (Found: C, 89·0; H, 4·8. $C_{19}H_{12}O$ requires: C, 89·0; H, 4·68%).

Methyl 2-*naphthoate*-3-d

A stirred mixture of methyl 3-bromo-2-naphthoate (0·82 g), Zn powder (9·72 g), CaO (1 g) and D_2O (99·7%) is refluxed for 190 hr. Two further portions of D_2O (5–7 ml each) are added during the refluxing period. The Zn is destroyed with HCl and the products are extracted ($CHCl_3$) and reesterified (MeOH-HCl), m.p. 72–73° (lit. methyl 2-naphthoate: 73·2°); M^+ *m/e* = 187 (calc. 187), yield: 96%.

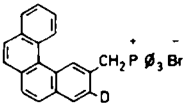
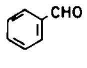
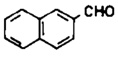
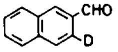
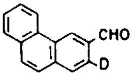
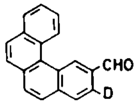
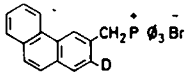
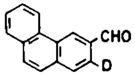
2-*Naphthaldehyde*-3-*d*

Methyl 2-naphthoate-3-d is reduced to the corresponding alcohol (LAH–ether) which is oxidized with 2,3-dichloro-5,6-dicyano-*p*-quinone (DDQ) in benzene soln (16 hr reflux). The mixture is filtered and the aldehyde is chromatographed on silica gel (benzene). The aldehyde is recrystallized from water, m.p. 57–58° (lit. 2-naphthaldehyde 57–58°); M^+ *m/e* = 157 (calc. 157); overall yield: 84%.

Deuteriated trans *1,2-diarylethylenes* (I, VII, XVIII, XXVI, XXXII and XXXVI)

The results of the Wittig reactions, carried out by the general procedure described above, are collected in Table 1.

TABLE 1

Phosphonium bromide	Aldehyde	Trans 1,2 - diarylethylene m p	Yield %
		I. 142.5 - 143.5°	63
″		XXVI 201 - 202°	84
″		VII 201 - 202°	84
″		XXXII 199 -200°	82 5
″		XXXVI 227 - 229°	86
		XVIII. 295 - 295.5	87.5

Isotopic purity of the deuteriated trans *1,2-diarylethylenes*

trans-1,2-Diarylethylene	% d_2	% d_1	No deuterium
I	—	93·5	6·5
XXVI	—	95	5
VII	93	7	0
XXXII	93	7	0
XXXVI	93	7	0
XVIII	93	7	0

These purities were determined by mass spectroscopy at low potential.

Photoinduced syntheses of the deuteriated helicenes

The photocyclizations were carried out by the general procedure described above, in benzene solution.

trans-1,2-Diarylethylene	Time of irradiation	helicene	Yield %
I	75 min.	[6] d_1 II	87
VII	90 min.	[7] d_2 VIII	14
XVIII	30 min.	[7] d_2 XIX	61
XXVI	90 min.	[7] d_1 XXVII	14
XXXII	75 min.	[8] d_2 XXXIII	68
XXXVI	2 hr.	[9] d_2 XXXVII	61

Acknowledgements—The financial support of the "Fonds de la Recherche Fondamentale Collective" (contract 994) is gratefully acknowledged. The authors are indebted to Mr C. Moulard and Mr R. Polain for the recording of the mass spectra and NMR spectra.

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