PHOTODEHYDROCYCLIZATIONS OF STILBENE-LIKE COMPOUNDS VIII¹

Synthesis of hexaheliceno[3,4-*c*]hexahelicene

BY

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The synthesis of a new double helicene, hexaheliceno[3,4-*c*]hexahelicene, has been described. Of two possible diastereomers only one has been obtained. Presumably the product has the racemic configuration but this assignment is not yet definite.

In previous papers we reported on the syntheses and conformational properties of two double helicenes. This name is used for molecules containing two coils of angular condensed benzene rings, not belonging to the same helix as *e.g.* in tridecahelicene².

In one of our previous examples being a diphenanthrochrysene³, there is a change, halfway through the molecule, in the normal condensation pattern of true helical molecules in that the molecule has an S shape. In the other, 2,2'-bihexahelicyl⁴, two relatively independent helical parts are connected by a single bond only.

In view of the fascinating structures and remarkable conformations which permit *e.g.* relatively easy isomerization, we investigated a third type of double helicene, hexaheliceno[3,4-*c*]hexahelicene I, in which there are two interruptions in the condensation pattern of true helicenes.

Irradiation of a properly substituted 1,8-bis(arylethenyl)naphthalene (IIc) did not appear very promising for the synthesis of I. It is known that 1,8-bis(phenylethenyl)naphthalene⁵ (IIa) and 1,8-bis(β -naphthylethenyl)naphthalene⁶ (IIb) yield mainly cyclobutane derivatives on irradiation due to an intramolecular cycloaddition.

¹ Part VII: Recl. Trav. Chim. Pays-Bas **92**, 553/1973)

² R. H. Martin, G. Morren and J. J. Schurter, Tetrahedron Letters **1969**, 3683.

³ W. H. Laarhoven and Th. J. H. M. Cuppen, *ibid.* **1971**, 165, and ref. 1.

⁴ W. H. Laarhoven and R. G. M. Veldhuis, Tetrahedron **28**, 1823 (1972).

⁵ J. Meinwald and W. Young, J. Am. Chem. Soc. **93**, 725 (1971).

⁶ Unpublished results.

IIa Ar = phenyl

IIb Ar = β -naphthyl

IIc Ar = 2-benzo[*c*]phenanthryl

Therefore, we followed a pathway (see Scheme) in which in 1,8-dimethylnaphthalene the helical parts were introduced one after the other.

The individual steps are side-chain brominations of methyl substituted aromatics, Wittig reactions of the corresponding triphenylphosphonium halides with aldehydes proper, and photodehydrocyclizations. All these reactions have been used in many of our previous investigations⁷.

The photocyclization of 1-methyl-8-(2-benzo[*c*]phenanthrylethenyl)naphthalene (VII) yielded mainly the methyl substituted benzo[*h*]hexahelicene VIII, although the more planar dinaphtho-anthracene derivative IX might have been expected to be the main product. This result may be due partly to the strong oxydisability of anthracene-like compounds as IX. However, another cause might be that *cis*-VII occurs predominantly in the overcrowded conformation which is most useful for cyclization into VIII. This will be illustrated in a subsequent paper.

The product VIII could be identified simply by comparing its NMR spectrum with that of benzo[*m*]hexahelicene. Both spectra have already been described⁸. Its monobromo derivative X revealed an AB pattern for the methylene group as expected for diastereotopic protons in an asymmetrical compound.

IX was characterized by two low-field singlets from the anthracene moiety ($\delta = 9.15$ and 9.52) and by three low-field doublets ($\delta = 8.72$,

⁷ W. H. Laarhoven, Th. J. H. M. Cuppen and R. J. F. Nivard, *Tetrahedron* **26**, 4865 (1970).

⁸ W. H. Laarhoven and R. J. F. Nivard, *ibid.* **28**, 1803 (1972).

Scheme 1. Synthetic pathway to hexaheliceno[3,4-*c*]hexahelicene (I).

8.82 and 9.20) typical for the angular protons in the phenanthrene-like parts of the molecule.

Photocyclization of the diarylolefin XI proceeded very rapidly; after irradiation of 50 mg of XI during 15 min. no residual starting

compound could be found. Two cyclization products had been formed, XII and the title compound I, in 70% and 15% yield, respectively. Purification of the pyrene derivative XII was rather difficult because of rapid oxidation and persistent contamination with traces of XI. In the NMR spectrum only peaks at low field from angular protons, and from protons in overcrowded regions could be assigned. They characterise the compound, however, very well. Signals at $\delta = 9.48$ and 9.20 belong to the angular protons of the benzo[*c*]phenanthryl residue, the singlet $\delta = 8.79$ is from the uncoupled proton (F') in the benzopyrene moiety, the AB pattern at $\delta = 7.24$ and 7.42 represents the protons A' and B' in the overcrowded pyrene part, and the peaks at $\delta = 6.36$ and 7.08 come from the protons B and C in the terminal ring.

Theoretically, the double helicene I can exist in two diastereomeric forms, *meso*- and *rac*.-I. From the irradiation mixture we could isolate, however, only one product corresponding to I. The presence of more than 0.5% of a second isomer could be excluded by NMR. So, it seemed that only one isomer had been formed.

The melting point, determined in an electric furnace, is about 410°C . During heating the originally prismatic crystals change into needles between 250 and 385° . The needles remain unchanged on cooling, but give back the prismatic form on crystallization from carbon disulfide. Both types of crystals give identical UV and NMR spectra. Therefore, it is unlikely that the change in crystal form is due to isomerization, which has been found in the other double helicenes. Hence the product should be the more stable form, probably the racemic one.

Table I

Chemical shifts in ppm of hexaheliconohexahelicene (I) and some related compounds.

proton	hexaheliconohelicene		hexahelicene		benzo[<i>m</i>]hexahelicene CS ₂
	solvent		AsCl ₃	CS ₂	
A		AsCl ₃	CS ₂		
B		7.71	7.51	7.57	7.49
C		6.47	6.24	6.70	6.42
D		7.00	6.82	7.26	7.08
E, F		7.87	7.68	7.86	7.67
G, H		7.92	7.72	7.96	7.77
G', H'		8.13	7.92	8.02	7.82
F'		8.08	7.87		7.93
E'		8.19	7.98		8.07
B'		9.34	9.11		8.74
A'		6.78	6.58		6.85
		7.63	7.41		7.43

In Table I the chemical shifts of various protons in I have been tabulated and compared with those of corresponding protons in hexahelicene and benzo[*m*]hexahelicene⁸. It appears that the protons B, B' and C in I are shifted upfield in comparison with the single helicenes, whereas the protons A, A' and D have nearly unchanged δ -values. This may be due to a ring current effect of the terminal ring in the second coil.

The NMR data are insufficient to assign either the *meso* or the *rac*. configuration to our product. The signal of the E'-protons ($\delta = 9.11$ in CS₂) is at low field in comparison with the corresponding proton in benzo[*m*]hexahelicene. The value is nearly equal to that of corresponding α_4 -protons in IX ($\delta = 9.20$), XII ($\delta = 9.20$) and *trans*-VII ($\delta = 9.10$ and 9.14) although a lower δ -value should have been expected in view of the presence of additional rings in I. This may point to a relatively small van der Waals interaction and a relatively large distance between the E'-protons in I. The racemic configuration fits better into this picture.

Fig. 1. NMR spectrum of hexahelieno[3,4-*c*]hexahelicene (I) in AsCl₃.

Experimental

For spectral data a Varian SM2B mass spectrometer, a Beckmann DK2a or Cary 15 UV spectrophotometer, a Perkin Elmer 257 IR instrument and a Varian HA100 or T60 NMR apparatus were used.

Melting points were measured with a melting point microscope, and are uncorrected.

Irradiations were carried out in pyrex tubes surrounded by four Sylvania fluorescence lamps with $\lambda_{\text{max}} = 360$ nm.

1,8-Dibromomethylnaphthalene (III) was obtained from 1,8-naphthoic anhydride as described by Sondheimer⁹. M. p. 131–132°.

1,8-Dimethylnaphthalene (IV) was prepared by reduction of III with lithiumtetrahydridoaluminate under conventional conditions. M.p. 61–63° (Lit.¹⁰ 62–63°).

⁹ R. H. Mitchell and F. Sondheimer, *Tetrahedron* **24**, 1397 (1968).

¹⁰ G. Ghilardi and G. Kalopissis, *Bull. Soc. Chim. France* **1952**, 217.

1-Bromomethyl-8-methylnaphthalene (V) was synthesized by bromination of the foregoing compound with one equivalent of *N*-bromosuccinimide (NBS). From NMR it appeared that 60% of the monobromo and 20% of a dibromo product had been formed, and 20% of the unsubstituted product (IV) had been left. By crystallization from pentane IV could be removed; by subsequent distillation (b.p. 100°C/0.15 mm) nearly pure V with m.p. 172–174° was obtained. The NMR spectrum showed that about 2% of III was present.

1-(2-Benzo[c]phenanthryl)-2-[α-(8-methylnaphthyl)]ethene (VII)

To an ethereal solution of V an equivalent amount of triphenylphosphine was added. After some days the triphenylphosphonium salt VI separated as a colourless solid. By a Wittig reaction of VI with 2-benzo[c]phenanthraldehyde⁴ in DMF and sodium methoxide as base the product VII was obtained in 74% yield. By column chromatography on alox the *cis*- and *trans*-isomers could be partially separated. *Trans*-VII had m.p. 143.5–144.5° after crystallization from ethanol/ethyl acetate; mol. weight 394; UV λ max in nm (log ε) in methanol: 445 (3.79); [336 (4.27)]; [322 (4.38)]; [309 (4.44)]; 289 (4.65); [260 (4.49)]; [254 (4.54)]; [248 (4.62)]; 237 (4.71); 220.5 (4.77); 204.5 (4.98); IR ν in cm⁻¹: 975; 841; 770; 767; 742.

Pure *cis*-VII could be obtained from the *trans*-isomer by irradiation in a nitrogen atmosphere. M.p. 162–163° (from methanol); *m/e* 394; UV λ max in nm (log ε) in methanol: [336 (4.13)]; [320 (4.28)]; [310 (4.35)]; 288.5 (4.62); [257 (4.42)]; 236 (4.63); 222.5 (4.74). IR ν in cm⁻¹: 1600, 1500, 1450, 920, 855, 848, 813, 800, 779, 763, 747. Isomerization by boiling a solution of *cis*-VII in carbon tetrachloride with iodine again gave the *trans*-isomer with m.p. and UV spectrum identical with those already given.

The NMR spectra of the isomers will be published elsewhere, together with a discussion on their preferred conformations.

4-Methylbenzo[m]hexahelicene (VIII)

Irradiation of a solution of *cis*- or *trans*-VII in benzene with added iodine gave VIII in 55% yield. The *cis*-isomer was cyclized more rapidly than *trans*-VII. Product formation has to be followed by UV during irradiation, because too long irradiation lowers the yield. The product VIII was isolated from the irradiation mixture by column chromatography on alox and elution with benzene-carbon tetrachloride. M.p. 216° (from carbon disulfide); *m/e* 392; UV λ max (log ε) in CH₂Cl₂: [415 (2.95)]; [390 (3.21)]; [350 (4.18)]; 334 (4.48); 326 (4.48); [285 (4.61)]; 270.5 (4.85); [2.46 (4.59)]; 240 (4.61); NMR as published in ref. 8.

Naphtho[1,2-a]-8-methylnaphtho[2,1-b]anthracene (IX) was obtained in 7% yield as a second product in the foregoing synthesis, by elution of the column with benzene. It was purified by sublimation at 225°/0.1 mm. UV λ max (log ε) in CH₂Cl₂: 417 (3.58); [399 (3.88)]; 392.5 (3.96); 379.5 (4.05); 362 (4.09); [350 (4.12)]; 330 (5.03); 317 (5.01); [305 (4.74)]; [293 (4.44)]; [283 (4.29)]; 266 (4.44); 257.5 (4.46); [249 (4.51)]; 228 (4.61); NMR (CS₂) δ = 3.13 s, 3H (CH₃).

Bromomethylbenzo[m]hexahelicene (X) was prepared by bromination of VIII with NBS. In the NMR spectrum the methylene protons show an AB pattern because of the asymmetry of the molecule.

1-(Benzo[m]hexahelicyl)-2-(2-benzo[c]phenanthryl)ethene (XI)

The bromide X dissolved in xylene, was refluxed for three hours with an equivalent amount of triphenylphosphine. The phosphonium salt, thus obtained, was used in a

Wittig reaction with 2-benzo[c]phenanthraldehyde in DMF and with sodium methoxide as base. After completion of the reaction, the solvent was evaporated and the residue separated by column chromatography on silica and elution with carbon tetrachloride. The yield was 57%. Because of rapid isomerization of *cis*-XI in solution, only *trans*-XI was obtained pure. M.p. 173–176°; *m/e* 630 (C₅₀H₃₀); UV λ max (log ϵ) in CH₂Cl₂: 447 (3.20); [358 (4.60)]; 344 (4.63); 327 (4.62); 270 (4.87); NMR (in CS₂): 6.46 (B); 6.78 (B'); 7.00 (C); 8.17 (olefinic protons, *J* = 16 cps); 8.90 (E'); 9.15 (α_4 -proton); 9.21 (α_4 -proton).

8-(Benzo[c]phenanthryl)(benzo[c]phenanthro[2,1-b]pyrene (XII)

A solution of XI in benzene to which some iodine had been added was irradiated, and after evaporation of the solvent the irradiation mixture was separated as described previously. XII appeared to be the main product (70% yield). It had m.p. 208–214°; *m/e* 628 (C₅₀H₂₈); UV λ max (log ϵ) in CH₂Cl₂: [450 (3.19)]; 416 (3.95); 355.5 (4.57); 330 (4.57); 314 (4.57); 273 (4.85); 235 (4.77); NMR in CS₂: 7.42 (A'); 7.24 (B'); 6.36 (B); 7.08 (C); 8.79 (γ); 9.20 (m, α_4); 9.48 (s, α_4).

Hexahelieno[3,4-c]hexahelicene (I) was the second product, isolated from the foregoing irradiation mixture (15% yield). Its parent peak was at 628 (C₅₀H₂₈), UV λ max (log ϵ) in CH₂Cl₂: [370 (4.62)]; 359 (4.67); [344 (4.61)]; [327 (4.57)]; 275 (4.83); [238 (4.67)]; NMR data (Table I and Fig. 1) and m.p. have been discussed in the text.

Acknowledgement

The authors are indebted to Mrs. *L. van Herpen-de Cock* for measuring the NMR spectra and to Mr. *F. Gerhartl* for the mass spectra.

(Received September 28th, 1972)