mg) and isonuatigenin (3 mg) was accomplished by C_{18} reverse-phase HPLC [Microsorb (5 μm), Rainin, 10 × 250 mm; UV detection, 210 nm] using MeOH/H_2O (88:12), flow rate 1.7 mL/min, yielding isonuatigenin as a white powder: mp 212–215 °C; $[\alpha]_D$ −82° (c = 0.177) and nuatigenin as a white powder: mp 206–210 °C; $[\alpha]_D$ −62° (c = 0.092). Literature values for (25S)-isonuatigenin: mp 215–218 °C; $[\alpha]_D$ −140° (c = 2.00).[11] Literature values for (25S)-nuatigenin: mp 210–214 °C; $[\alpha]_D$ −94° (c = 2.0).[11] The lower optical rotations recorded on the aglycons isolated in this work in comparison with those reported in the literature are most likely due to concentration differences.[31]

D-Glucose and L-Rhamnose.[24] Saponin **7** (5.5 mg) was refluxed in aqueous HCl (1 N, 6 mL) for 7 h. After cooling, the reaction mixture was extracted with $CHCl_3$ (2 × 5 mL) to remove the diosgenin, and the aqueous layer was neutralized to pH 7 with Amberlite IRA68 ion-exchange resin and filtered, and the solution was transferred to a glass ampoule. The solvent removed by lyophilization, (+)-(*S*)-2-butanol (0.5 mL) and trifluoroacetic acid (5 drops) were added, and the ampuole was sealed. After standing overnight (12 h) at 100 °C in a steam bath, the solvent was removed in vacuo at 40 °C, and the residue was transferred to a screw-cap vial. To the residue was added anhydrous pyridine (1 mL), hexamethyldisilazane (0.2 mL), and trimethylchlorosilane (0.1 mL). The vial was shaken vigorously for 30 s and allowed to stand at 50 °C in a water bath. After cooling, the solvent was removed in vacuo, and the residue was dissolved in petroleum ether (bp 35–60 °C) and filtered, and the solvent was removed in vacuo for NMR analysis as described in the text, or used directly for GC–MS analysis as described below. Standard persilylated 2-butyl glycosides were prepared from commercially available D-glucose, L-glucose, and L-rhamnose with both (+)-(*S*)-butanol and (±)-2-butanol by a strictly identical procedure, which included exposure to the initial hydrolysis step.

GC–MS analysis was performed on the Finnigan MAT-90 using an HP-1 methyl silicane capillary column (30 m × 0.32 mm × 0.50 μm film thickness) with helium as carrier gas: flow rate of 6 mL/min. A temperaturee gradient was employed: 135 °C for 2 min, then a ramp of 1 °C/min to a final temperature of 200 °C. Retention times of persilylated glycosides: (+)-(*S*)-2-butyl D-glucoside, 33.91 min and 40.78 min (α- and β-anomers were not distinguished); (+)-(*S*)-2-butyl L-glucoside, 35.03 and 40.78 min (α- and β-anomers not distinguished); (+)-(*S*)-2-butyl L-rhamnoside, 16.61 min (major, α-anomer) and 19.08 min (minor, β-anomer); (+)-(*S*)-2-butyl D-rhamnoside, 16.08 min (major, α-anomer) and 18.72 min (minor, β-anomer).

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Supplementary Material Available: Double relayed coherence transfer spectrum of saponin **9** showing rhamnose H-6 through H-3 mapping, HETCOR and fixed evolution HETCOR spectra of **7**, and the 2D NOE spectra of saponin **8** at ambient and 5 °C (5 pages). Ordering information is given on any current masthead page.

(31) In support of this assumption, we measured the optical rotation of the diosgenin and isonuatigenin we had isolated at decreasing concentrations. In both cases, decreasing concentration led to a reduced specific rotation. Diosgenin: $[\alpha]_D$ −119° (c = 0.350), $[\alpha]_D$ −103° (c = 0.012). Isonuatigenin: $[\alpha]_D$ −82° (c = 0.177), $[\alpha]_D$ −71° (c = 0.021). For other examples of dramtic variation in optical rotation withh concentration, see: (a) Horn, D. H. S.; Pretorius, Y. Y. *J. Chem. Soc.* **1954**, 1460. (b) Horeau, A. *Tetrahedron Lett.* **1969**, 3121. (c) Kumata, Y.; Furukawa, J.; Fueno, T. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3920. (d) Meyers, A. I.; Roth, G. P.; Hoyer, D.; Barner, B. A.; Laucher, D. *J. Am. Chem. Soc.* **1988**, *110*, 4611.

Formation of 5,6- and 7,8-Dihydrohexahelicene: Mechanistic Details of the Rearrangement of the Primary Photocyclization Product of 2-Styrylbenzo[*c*]phenanthrene in the Presence of a Base

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Irradiation of 2-styrylbenzo[*c*]phenanthrene (**1**) in alkylamines or basic alcoholic solution results in the formation of a mixture of two dihydrohexahelicenes (5,6- and 7,8-dihydrohexahelicene, **5** and **6**). The ratio of **5** and **6** depends on the kind of solvent. In alkylamine **6** is the favored dihydrohexahelicene. In basic alcoholic solution **5** is the preferred product. Deuteration of the solvent causes a change in the ratio of **5** and **6** in favor of **5**. The reaction starts with the deprotonation of the primary formed, unstable 16d,16e-dihydrohexahelicene (**2**), followed by a protonation step. The site of this protonation determines the ratio of **5** and **6** and depends upon the acidity of the protonating agent, an alkylammonium cation or solvent molecule, and the electron densities at the various possible sites for protonation in the intermediate. Irradiation of **1** in several chiral alkylamines yielded optically enriched **6**.

Introduction

The photodehydrocyclization of 2-styrylbenzo[*c*]-phenanthrene (**1**) into hexahelicene (**3**) is a well-known photochemical reaction (Scheme I). *trans*-16d,16e-Dihydrohexahelicene (**2**) has been accepted as the primary photoproduct.[1-4] The oxidation of **2** occurs in the presence of O_2, I_2, TCNE, and other dehydrogenating reagents.[2-4]

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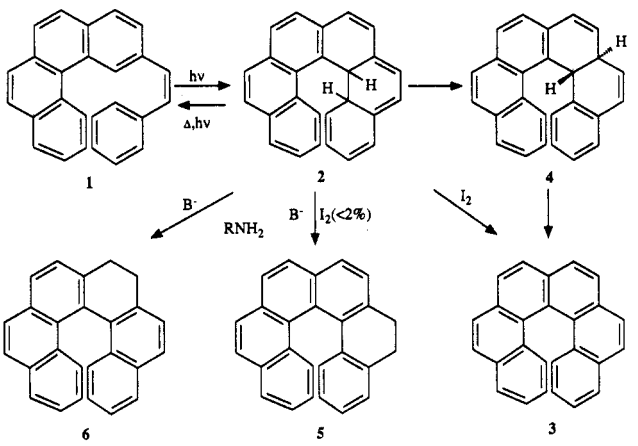
Scheme I



Besides the oxidative reaction, 2 undergoes, thermally as well as photochemically, a ring-opening reaction back to 1.

The unstable primary photocyclization product 2 can be converted into more stable isomers. The rearrangement of 2 by a [1,5]-suprafacial hydrogen shift to *trans*-6a,16d-dihydrohexahelicene (4), a compound sensitive to oxidation, has been reported under anaerobic conditions.[5,6] The presence of only a tiny amount of I_2 alters the reaction pathway, resulting in the formation of 5,6-dihydrohexahelicene (5), a stable isomer of 2.[7] When the photocyclization of 1 is performed in the presence of amine, besides 5, a second stable isomer of 2, 7,8-dihydrohexahelicene (6), is found in the irradiation mixture. The structure and conformation of 6 have been elucidated by NMR and X-ray analysis and by force-field calculations.[8]

To elucidate the mechanistic details of the rearrangement of 2 into 5 and 6, the photocyclization of 1 has been studied in several amines as well as in basic alcoholic solution.

Results

Experiments in Amines. A solution of 1 in *n*-butylamine ($c = 10^{-3}$ mol/L) in a Pyrex tube was irradiated at 300 nm for 16 h. After evaporation of the solvent followed by flash chromatography on silica gel (Merck Kieselgel 60H, eluent: *n*-hexane) of the reaction mixture, 80% of the precursor 1 was recovered as a mixture of hexahelicene (3), 5,6-dihydrohexahelicene (5), and 7,8-dihydrohexahelicene (6). These compounds could not be separated preparatively by chromatography on conventional stationary phases. Silica gel coated with the chiral complexing agent 2-(2,4,5,7-tetranitro-9-fluorenylideneaminooxy)-propionic acid (TAPA), designed for the separation of the enantiomers of hexahelicene by Newman,[9] proved to be an excellent stationary phase for the separation of the irradiation mixture.[10]

The results of the photocyclization of 1 in some amines have been collected in Table I. The compositions of the

Table I. Composition of the Mixtures of Hexahelicene (3), 5,6-Dihydrohexahelicene (5), and 7,8-Dihydrohexahelicene (6) from 2-Styrylbenzo[*c*]phenanthrene (1) Irradiated at 300 nm in Amine, Basic Alcoholic Solutions, and Deuterated Solvents

amine	3, %	5, %	6, %	ratio 6/5
n-propylamine	15	7	78	11
isopropylamine	18	11	71	6.5
isopropylamine (argon)	2	14	84	6
n-butylamine	16	16	68	4.3
n-butylamine (argon)	5	18	77	4.3
n-butylamine-d_2	3	47	50	1.06
tert-butylamine	24	13	63	4.8
triethylamine	15	5	80	16
(1-phenylethyl)amine	19	10	71	7
2-amino-1-butanol	15	4	81	20
K *tert*-butoxide/MeOH	9	66	25	0.38
K *tert*-butoxide/MeOD	22	70	8	0.11

Table II. Ratio of 7,8-Dihydrohexahelicene (6) and 5,6-Dihydrohexahelicene (5) (6/5) Formed in Amine Diluted with *n*-Hexane or Diisopropyl Ether

solvent	(v/v)	yield 6, %	6/5
isopropylamine/*n*-hexane	(1:25)	85	9
n-octylamine/*n*-hexane	(1:25)	91	23
(1-phenylethyl)amine/*n*-hexane	(1:25)	83	7
triethylamine/*n*-hexane	(1:25)	87	12
2-amino-1-butanol/diisopropyl ether	(1:4)	90	20
2-amino-1-butanol/diisopropyl ether	(1:10)	89	18
ephedrine (10 g/L)/diisopropyl ether		86	8
(1-phenylethyl)amine/diisopropyl ether	(1:10)	86	9

product mixtures were determined by HPLC analysis of reaction mixtures after flash chromatography. Relatively small amounts of hexahelicene (3) were formed, even when oxygen was not removed from the solution before or during irradiation, indicating that the rearrangement of 2 in amine is faster than dehydrogenation by oxygen. The data presented in Table I demonstrate that the ratio 6/5 depends on the kind of amine. Compound 6 is the favored rearrangement product in all amines, however.

The ratio 6/5 is little affected by the presence of oxygen as is demonstrated by the results of the photocyclization in *n*-butylamine and isopropylamine, where oxygen has been removed by flushing with argon.

Pure samples of the dihydrohexahelicenes 5 and 6 were irradiated in *n*-propylamine in the presence of oxygen for 24 h at 300 nm to assess their stability under these conditions. Neither conversion of 5 into 6 nor any conversion of 6 into 5 could be detected. Both dihydrohelicenes were very resistant to oxidation. After irradiation for 24 h in *n*-propylamine in the presence of oxygen only 1.5% of 6 and 2% of 5 proved to be converted into hexahelicene (3).

The rearrangement of the primary photocyclization product 2 does not necessarily need pure amine. The rearrangement also proceeds efficiently when the amine has been diluted with *n*-hexane or diisopropyl ether, provided the oxygen has been removed by flushing with argon to prevent excessive formation of hexahelicene. In Table II the results of the photocyclization of 1 in several amines diluted with *n*-hexane or diisopropyl ether have been collected. The application of a solvent to dilute the amine is necessary when using a solid amine like ephedrine. Moreover it allows the use of expensive amines. Diisopropyl ether is better than hexane for dilution of amines. Due to its polarity it dissolves amines like aminobutanol and ephedrine better than *n*-hexane, and polarity is in favor of the rearrangement which involves polar intermediates.

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Table III. Incorporation of Deuterium in 5,6-Dihydrohexahelicene (5) and 7,8-Dihydrohexahelicene (6) Obtained from the Photocyclization of 2-Styrylbenzo[c]phenanthrene (1) in Deuterated Solvents (the Data of D-Incorporation Were Calculated from the Mass Spectra)

medium	compd	ratio D/H[a]	number of D incorporated, % 0	1	2	3
KOtBu/MeOD	5	0.82	1	31	55	13
KOtBu/MeOD	6	0.81	1	34	50	15
n-BuND$_2$	5	0.60	1	52	43	4
n-BuND$_2$	6	0.55	7	48	41	4

[a] In alicyclic part.

Formation of Dihydrohexahelicenes in Basic Alcoholic Solution. Irradiation for 50 h at 300 nm of a 0.002 M, deaerated solution of 2-styrylbenzo[c]phenanthrene (1) in methanol, being 0.3 M in KOtBu, yielded a complex mixture of compounds. Apart from the expected compounds hexahelicene (3), 5,6-dihydrohexahelicene (5), and 7,8-dihydrohexahelicene (6), several unidentified compounds were formed. Contrary to the irradiation of 1 in amines, 5,6-dihydrohexahelicene (5) was the main product in basic alcoholic solution. It was estimated that about 70% of the precursor 1 was converted into 9% hexahelicene (3), 66% 5, and 25% 6. Removal of oxygen during or before the irradiation was necessary, otherwise no trace of the dihydrohelicenes 5 and 6 could be detected and only hexahelicene 3 was isolated from the irradiation mixture.

Irradiations in Deuterated Media. The results reported above show that in amines 7,8-dihydrohexahelicene (6) is the favored product, while in basic alcoholic solution 5,6-dihydrohexahelicene (5) is the main product. To study the mechanistic details causing this difference in behavior, 2-styrylbenzo[c]phenanthrene (1) was irradiated with 300-nm UV light in N-deuterated n-butylamine (n-BuND$_2$), and in O-deuterated methanol being 0.3 M in KOtBu (KOtBu/MeOD). The results have been included in Table I. An increase in the formation of 5,6-dihydrohexahelicene (5) was observed in the deuterated alcohol as well as in the deuterated amine.

The mixtures of deuterated compounds were separated on silica gel coated with (R)-(−)-TAPA. The purified samples of deuterated 5,6- and 7,8-dihydrohexahelicene (5 and 6) were analyzed by NMR spectroscopy and mass spectrometry. The data of D-incorporation calculated from the mass spectra have been collected in Table III.

The NMR spectral details of 5 and 6 have been discussed previously.[7,8] The NMR spectra in $CDCl_3$ at 500 MHz of the alicyclic regions of the products obtained from the photocyclizations of 1 in n-BuNH$_2$ and n-BuND$_2$ are presented in Figure 1.

From the alicyclic regions of the NMR spectra of the purified samples of deuterated 5,6- and 7,8-dihydrohexahelicene obtained from the irradiation of 1 in deuterated media, the positions of amounts of D-incorporation in 5 and 6 were determined. The results have been collected in Table IV. The amount of pure 7,8-dihydrohexahelicene (6) obtained from the photocyclization in KOtBu/MeOD was insufficient to be analyzed by NMR spectroscopy.

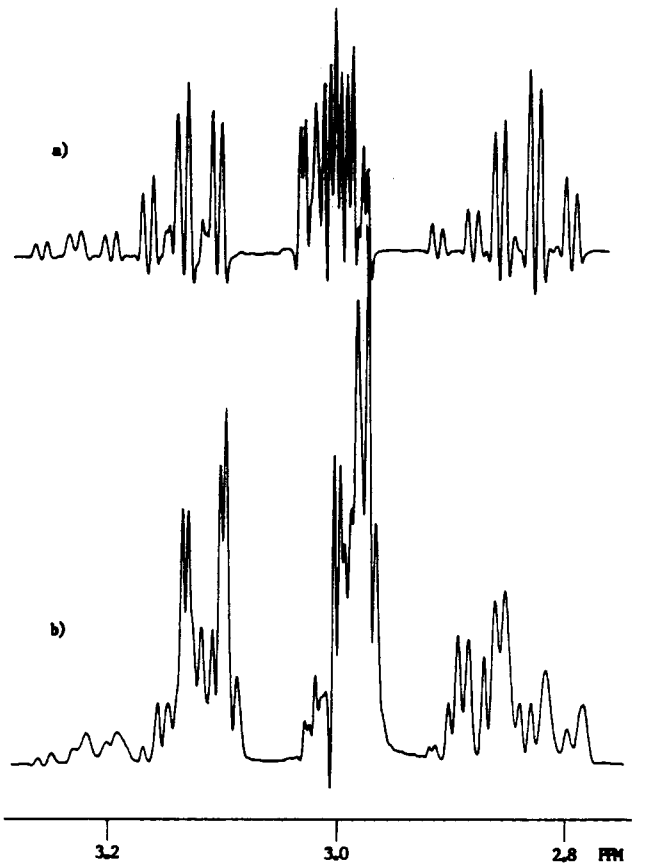


Figure 1. The alicyclic region of the NMR spectra in $CDCl_3$ at 500 MHz of mixtures obtained from the photocyclization of 1. (a) In n-BuNH$_2$, (b) in n-BuND$_2$.

Optically Enriched 7,8-Dihydrohexahelicene in Chiral Amines. As reported above, the enantiomers of hexahelicene (3) and 7,8-dihydrohexahelicene (6) are resolved by HPLC on silica gel coated with (R)-(−)-TAPA.[10] This HPLC method is suitable for the determination of the enantiomeric excess (ee) of 3 and 6. We studied the possibility of the asymmetric synthesis of 6 by using a chiral amine as the solvent. The results collected in Table V indicate that indeed an asymmetric amine induces the formation of enantiomerically enriched 6 and even an increase of the chiral discrimination by the chiral amine upon dilution with diisopropyl ether. The combination of a chiral amine with a chiral solvent shows a relatively large ee value.

Discussion

The rearrangement of 2 into 5 and 6 resembles closely that of 4a,4b-dihydrophenanthrene into 1,4- and 9,10-dihydrophenanthrene.[11] In the present case, however, the

Table IV. Incorporation of Deuterium in 5,6-Dihydrohexahelicene (5) and 7,8-Dihydrohexahelicene (6) Obtained from the Photocyclization of 2-Styrylbenzo[c]phenanthrene (1) in Deuterated Solvents (Calculated from the NMR Spectra)

medium	compd	ratio D/H[a]	position, % H_{5a}	H_{6e}	H_{5e}	H_{6a}
KOtBu/MeOD	5	0.82	75	30	15	60
n-BuND$_2$	5	0.60	80	30	20	20
			H_{7a}	H_{8e} and H_{7e}		H_{8a}
n-BuND$_2$	6	0.57	25	30		60

[a] In alicyclic part.

Table V. Asymmetric Synthesis of 7,8-Dihydrohexahelicene (6) in Chiral Amines

solvent	(v/v)	ee_{HPLC}[a] chirality	%
(*S*)-(−)-(1-phenylethyl)amine		M	0.5
(*S*)-(−)-(1-phenylethyl)amine/diisopropyl ether	(1:10)	M	2.2
(*R*)-(−)-2-amino-1-butanol		P	0.6
(*R*)-(−)-2-amino-1-butanol/diisopropyl ether	(1:10)	P	1.6
(*R*)-(−)-2-amino-1-butanol/diisopropyl ether	(1:20)	P	2.6
(*R*)-(−)-2-amino-1-butanol/(*S*)-(+)-ethyl *O*-benzoyllacetate	(1:10)	P	7.8
(−)-ephedrine (10 g/L)/diisopropyl ether		P	2.7
(−)-ephedrine (10 g/L)/(−)-bornyl acetate		P	6.8

[a] ee_{HPLC} = enantiomeric excess determined by HPLC; ee_{HPLC} ± 0.5%. Chirality: the chiral configuration of the enantiomer of 6 formed in excess, either P or M.[1]

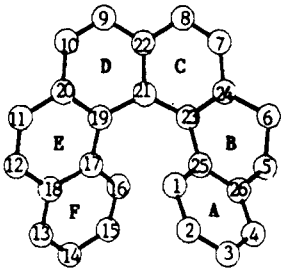
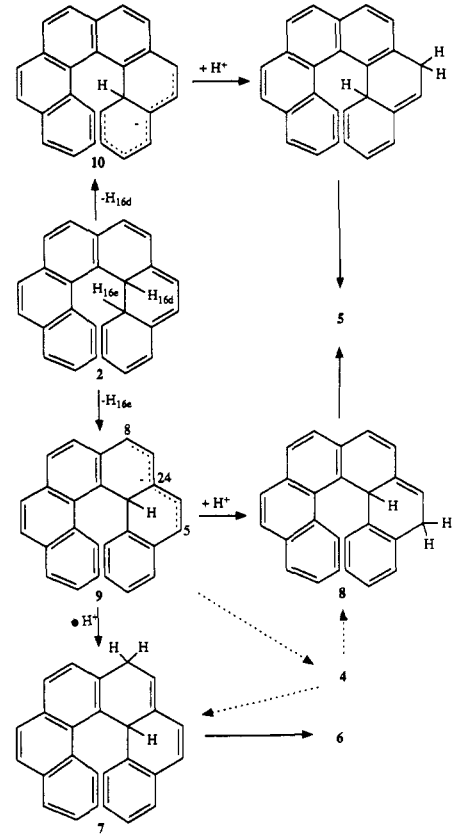


Figure 2. The numbering and indexing of the hexahelicene skeleton.

conformational aspects are more pronounced and have to be taken into consideration. Therefore, before discussing the mechanistic details of the rearrangement of **2** into **5** or **6**, it is appropriate to establish the conformations of the intermediates and products of the reaction. In principle the two stable dihydrohexahelicenes **5** and **6** can exist in two possible conformations. From the NMR data of the two compounds it has been deduced that in both compounds one conformation is strongly favored.[8] The occurrence of a second conformation could not be detected. The X-ray analyses of **5** and **6** demonstrated again that in the solid phase only one conformation occurs.[8] For the analysis of the mechanism of the rearrangement of the primary photocyclization product, *trans*-16d,16e-dihydrohexahelicene (**2**), knowledge of the configuration of this compound is necessary, too. The two hydrogens H16d and H16e of **2** occupy trans positions, as is to be expected for a conrotatory ring closure of a hexatriene system, and firmly established for the configuration of *trans*-4a,4b-dihydrophenanthrene, the primary photocyclization product of stilbene.[1,2] This reduces the number of possible configurations for **2** to two, when mirror images are counted simply. The two configurations are not interconvertible, unless a bond of the helicene skeleton is broken. In one configuration H16d is positioned at the inside of the inner helix, C(1)–C(25)–C(23)–C(21)–C(19)–C(17)–C(16) (see Figure 2 for the numbering of the hexahelicene skeleton), and H16e is situated outside of the inner helix. In the other one H16e is situated inside of the inner helix, while H16d is at the outside.

It is not possible to isolate the highly unstable dihydrohexahelicene **2**, so no direct information about its real configuration is at hand. The *trans*-6a,16d-dihydrohexahelicene (**4**), which originates from **2** via a [1,5]-suprafacial

Scheme II



hydrogen shift, can be isolated, however. The configuration of **4** has been deduced from its NMR spectrum.[5] The chemical shift of proton H16d is found at lower field (δ 5.2 ppm) than calculated by the Shoolery rules (4.1 ppm). Proton H6a absorbs at δ 3.2 ppm in accordance with the calculated value (3.1 ppm). The high value of the chemical shift of proton H16d must be due to the result of deshielding by the ring current of the opposite ring, implying that H16d is located at the inside of the inner helix. This conclusion is corroborated by a strong NOE enlargement of the signal of proton H16 when H16d is irradiated.[5] Because **4** is formed from **2** via a [1,5]-suprafacial shift of hydrogen H16e, H16d in **2**, which does not change position, must be located at the inside of the inner helix of **2** as in **4**. This configuration is also the one which can be expected to be formed from the photocyclization of the preferred conformer of *cis-syn*-**1**.

The rearrangement of **2** into **5** or **6** starts with the abstraction of a proton and a subsequent or simultaneous protonation. Previously it has been demonstrated that primary amines deprotonate and reprotonate the DHP of 1,2-di-2-naphthylethylene in its ground state.[11] As is shown in Scheme II, abstraction of proton H16d from **2** should yield the intermediate **10**, which cannot be converted into **6** but only into **5**. Abstraction of H16e, on the other hand, yields the intermediate **9**, which can lead to both **5** and **6**. The configuration of *trans*-16d,16e-dihydrohexahelicene (**2**) implies that H16d, located at the inside of the inner helix, is more difficult to be reached by a base than H16e. Moreover abstraction of H16e is promoted by the formation of a benzene moiety, leading to a higher increase of resonance energy than the conversion of a phenanthrene moiety into a benzo[*c*]phenanthrene moiety upon abstraction of H16d. For these reasons we assume that H16e is abstracted first, in accordance with the high yield of **6** observed in amines. Moreover, when the rearrangement

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of **2** would proceed via **10**, the experiments in deuterated solvents should have shown D-incorporation in the terminal ring of **5**, which was not observed.

When H16e has been abstracted from **2**, most of the developing negative charge is found at the positions C5, C24, and C8 of **9**. Protonation at C24 would yield compound **4**, which is known to be formed under nonoxidative conditions, without the interaction of a base, by a suprafacial [1,5]-hydrogen shift from **2**. Protonation at position C5 of **9** yields **8**, the precursor of **5**. Protonation at position C8 of **9** results in **7**, the precursor of **6**. No trace of the less stable compound **4** is found in the irradiation mixture after workup. Probably **4** is converted quickly into either compound **7** or compound **8**, due to the presence of a base. By a second deprotonation and reprotonation **7** and **8** are converted into their stable isomers **6** and **5**, respectively (see Scheme II). We propose that the steps depicted in Scheme II are not reversible in view of the loss of resonance energy and that interconversion of the isomers **7** and **8** will be negligible, because the methine hydrogen of these compounds is much more acidic than their methylene hydrogens. Bearing in mind that interconversion of **5** and **6** has not been observed in amine, nor that the ratio **6**/**5** is affected by the presence of oxygen in amine, it can be stated that the protonation at C5 or C8 of the intermediate **9** determines the ratio of the final products **5** and **6**.

The results obtained from the experiments in deuterated amine and deuterated methanol demonstrate that the "axial" position is clearly preferred over the "equatorial" position at both C5 of **5** and C8 of **6** with respect to incorporation (see Table IV). The "axial" position at C5 of **5** is located at the opposite side of the molecule in comparison with H16e of **2**. The "axial" position at C8 of **6** is located at the same side of the molecule as H16e of **2**.[8] From these observations we conclude that protonation at the same side of the molecule as occupied by H16e yields preferentially **7**, which eventually is converted into **6**. On the other hand, protonation at the opposite side of the molecule favors **8**, which results eventually in **5**.

In relatively weak bases like amines the abstraction of proton H16e is facilitated by more or less simultaneous protonation of the developing anion **9**. The protonation is not provided for by the surrounding amine molecules but rather by the more acidic alkylammonium cation, formed at the same side of the inner helix as H16e. Immediate protonation at this side of the molecule, which is in favor of the formation of **6**, is fast. Protonation at the other side of the molecule, which yields **5** preferentially, requires either protonation by a weaker acidic amine molecule, or actual migration of the cation to this side of the molecule, or by proton transfers between amine molecules. Compared with the immediate protonation by the abstracting amine molecule itself, protonation at the opposite side of the molecule is slow. Therefore, in amine the formation of **6** is favored over that of **5**. Molecule models show that also the "axial" proton H5a of **8** is located at the opposite side of the molecule as H16e in **2**. The "axial" proton H8a of **7**, on the other hand, is located at the same side as H16e in **2**.

In deuterated amines substantially more **5** is formed than in unlabeled amines. A significant amount of D-incorporation is found at the opposite side of the position of H16e. From these facts we conclude that the immediate protonation by the abstracting molecule is slower in deuterated amine than in nondeuterated amines. This is understandable because protonation now involves breaking of an N–D bond. The delayed protonation allows for more migration of the ammonium cation or transfer of a proton between the ammonium cation and an amine molecule, which results in more protonation at the opposite side of the molecule, and a higher yield of **5**.

We noticed that in amines the amount of D-incorporation at C5 of **5** and C8 of **6** (0.9–1.0 D) differs significantly from the amount of D-incorporation at C6 of **5** and C7 of **6** (0.5 D) (see Table IV). This indicates the possibility of a [1,3]-H shift besides proton transfer by amine for the conversions of **8** into **5** and **7** into **6**.

The values of the ratio **6**/**5** found in different amines (Table I) indicate that a delicate interaction between the basicity of the amine and steric factors is involved in the first deprotonation/reprotonation step of the rearrangement. This is emphasized by the values for the ratio **6**/**5** obtained in *n*-propylamine, isopropylamine, *n*-butylamine, *tert*-butylamine, and triethylamine (Table I). The values of the dissociation constants of these amines in aqueous solution lie in a small range (pK_a = 10.7–10.8 at 20 °C).[12] Yet the ratio **6**/**5** varies from 4.3 to 16.

In basic alcoholic solutions we are dealing with different conditions for the rearrangement of **2**. The abstraction of the proton H16e is now performed by a stronger base, and the proton needed for the reprotonation is furnished by methanol molecules. Abstraction of proton H16e by the stronger base is faster. The reprotonation step is slower because methanol is less acidic than an ammonium cation. The lifetime of the intermediate anion **9** is longer in methanol than in amines. The site of reprotonation of the intermediate **9** is only determined by the electron densities at the various positions in the anion **9**; the solvent molecules are all equally capable of furnishing the desired proton. From the results obtained in basic alcoholic solution we conclude that reprotonation at C5 is favored over reprotonation at C8, indicating that C5 has the higher electron density.

The experiments in O-deuterated methanol demonstrate that most of the D-incorporation is found at the "axial" positions of C5 and C6 of **5**. Contrary to the results obtained in deuterated amines both deprotonation/reprotonation steps involved in the rearrangement of **2** are solvent-mediated as is evidenced by the high amount of D-incorporation in both **5** and **6** (1.8 D). The observation that the ratio **6**/**5** obtained in deuterated methanol is changed in favor of **5** in comparison with common methanol is explained by the difference in bond energy between an O–H and an O–D bond. The influence of the isotope is more pronounced when the O–D bond is more broken in the transition state. This is the case at the position with lower electron density, i.e. position C8. Therefore the reprotonation at C8 is more sensitive to the primary isotope effect than reprotonation at C5, resulting in a smaller **6**/**5** ratio in deuterated methanol.

The formation of the dihydrohexahelicenes **5** and **6** has been realized via an alternative reaction pathway, which involves the intermediacy of radicals.[7] The rearrangement occurred when **2** was generated by the photocyclization of **1** in benzene in the presence of a very small amount of iodine under nonoxidative conditions. The iodine abstracts a hydrogen atom from **2**, preferentially H16e for the same reasons as given above for the rearrangement in amines. This results in an intermediate radical, which is normally converted fast into hexahelicene **3** by abstraction of a second hydrogen. The low concentration of iodine gives the intermediate helicene radical the opportunity to capture a hydrogen from the formed HI or a solvent molecule, which yields **8** or **7**, the precursors of **5** or **6**. In benzene

(12) Perrin, D. D. *Dissociation Constants of Organic Bases in Aqueous Solution*; Butterworths: London, 1965.

only 5 has been found; in this solvent only the abstraction of an H atom from HI seems possible, not from the solvent. Experiments to verify this failed. (Addition of amines give rise to 5 and 6; addition of 18-crown-6 to dissolve added carbonate or bicarbonate leads only to 3.) Photocyclization of 1 in various cholesteric phases and chiral solvents yields both 5 and 6.[13]

Experimental Section

General Methods. ^{1}H NMR spectra were recorded on a Bruker WM-500 spectrometer operating in the Fourier transform mode and interfaced to an Aspect 2000 computer equipped with a real-time pulser board. Samples were measured in $CDCl_3$ using tetramethylsilane (0 ppm) as an internal standard. UV spectra were measured with a Perkin-Elmer 555 spectrometer. Mass spectra were recorded on a VG 7070E spectrometer. Melting points were determined by using a Leitz melting point microscope and are uncorrected. HPLC analysis was performed on a Spectra-Physics HPLC system: it was made up of a solvent delivery system (SP8700) equipped with a 254-nm UV detector (SP8300) and a computing integrator (SP4100). Stainless-steel columns (length, 20 or 25 cm; i.d., 0.46 cm) were slurry packed using carbon tetrachloride to suspend the silica particles (Lichrosorb Si60/5; Merck, Darmstadt, G.F.R.).

The modification of the HPLC columns with (*R*)-(−)-TAPA and details of the chromatographic separation of 3, 5, and 6 have been reported elsewhere.[10]

Product compositions, which have been collected in Tables I and II, were determined by HPLC analysis of the reaction mixtures after flash chromatography (silica gel, *n*-hexane). Stationary phase: 13 mg of (*R*)-(−)-TAPA on 1 g of Lichrosorb Si60/5, 25 cm × 0.46 cm i.d. Mobile phase: diethyl ether–petroleum ether (bp 60–80 °C) (5:95). Linear velocity: μ = 0.19 cm/s. The data collected in Table V have been determined under the following chromatographic conditions: Stationary phase: 15 mg of (*R*)-(−)-TAPA on 1 g of Lichrosorb Si60/5, (20 + 25 cm) × 0.46 cm i.d. Mobile phase: diethyl ether–petroleum ether (bp 60–80 °C) (5:95). Linear velocity: μ = 0.12 cm/s.

All irradiations were carried out in a Rayonet RPR-100 photoreactor, fitted with 300-nm lamps, through Pyrex.

The amines were dried over molecular sieves (4 Å) or refluxed over potassium hydroxide and distilled immediately before use.

Starting Materials and Products. The synthesis of 2-styrylbenzo[*c*]phenanthrene (1) and its photodehydrocyclization to hexahelicene (3) have been published previously.[15-17]

n-Butylamine was deuterated by decomposition of the tetra-arsenic–hexa-*n*-butyl imide complex in D_2O according to Vetter[18] and Kahntlehner.[19] The NMR spectrum revealed besides full N-deuteration the presence of 25% D at the α-C atom (CH_3C-$H_2CH_2CHDND_2$).

A solution of 1 (15 mg) in 50 mL of an amine, either pure (Table I) or diluted with *n*-hexane or diisopropyl ether (Table II), was irradiated through Pyrex at 300 nm for 16 h. After evaporation of the solvent followed by flash chromatography on silica gel (Merck Kieselgel 60H, eluent: *n*-hexane) a mixture of hexahelicene (3) and 5,6- and 7,8-dihydrohexahelicene (5 and 6) was isolated. The structure elucidations and experimental data of 5 and 6 have been described in detail.[7,8] The total yield of 3, 5, and 6 recovered from the irradiation mixture after flash chromatography was 60–70% (relative to the precursor 1) for amines diluted with *n*-hexane (Table II), and 70–80% for pure amines and amines diluted with diisopropyl ether (Tables I and II).

A deaerated solution of 5 mg of the precursor 1 in 10 mL of solvent consisting of the chiral amine, either pure or diluted with diisopropyl ether, was irradiated at 300 nm in a Pyrex vessel for 24 h. The resulting mixture was purified by flash chromatography on silica gel using *n*-hexane as the eluent. Further purification by chromatography on a reversed-phase column (Lobar RP8, 10% water in methanol) yielded samples of 6 contaminated with some 3 and 5. From these purified samples the data collected in Table V were obtained.

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