Stereochemical Dichotomy in the Stevens Rearrangement of Axially Twisted Dihydroazepinium and Dihydrothiepinium Salts. A Novel Enantioselective Synthesis of Pentahelicene†

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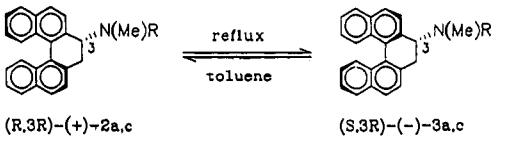
Abstract: Evidence is presented indicating that the stereochemistry of the Stevens rearrangement of the axially chiral onium salts **1a–d** and **5** is dramatically structure-dependent. Thus, the binaphthyl ammonium salts (*S*)-(+)-**1a–c** react with a strong base with exclusive (100% de) formation of the corresponding rearranged amines (*R*,3*R*)-(+)-**2a–c**, demonstrating a complete transfer of the (*S*) axial dissymmetry/asymmetry into (*R*) asymmetry of the newly formed carbon center. Exactly opposite stereochemistry was established in an earlier study by Mislow of the biphenyl analogue (*S*)-(+)-**5**, yielding the rearranged products (*S*,9*S*)-(+)-**6** and (*R*,9*S*)-(–)-**7** with exclusive (*S*) configuration at the carbon center. Rearrangement of the sulfonium salt **1d** is found to be intermediate between the two extremes, yielding a mixture of diastereoisomeric products **2d** and **3d**, which differ in configuration at the asymmetric carbon center. A direct proof is thus provided that two stereochemically different pathways can participate in the Stevens rearrangement. An explanation is suggested in terms of competition between suprafacial (concerted) and antarafacial (nonconcerted) mechanism.

The mechanism of chirality transfer as well as prediction of the absolute configuration in stereoselective (asymmetric) reactions represent topics of growing interest.[1] 2,2′-Disubstituted 1,1′-binaphthyl auxiliaries have often been invoked in this context, providing well-defined model systems and at the same time extraordinarily effective chiral inducers.[2] One specific feature of the binaphthyl models which so far remained unexplored is the ability of a controlled *intramolecular* transfer of *axial* into *central* chirality.[3] In this article we describe a pertinent case of such transfer in the Stevens rearrangement[4] of the 4,5-dihydro-4,4-dimethyl-3*H*-dinaphth[2,1-*c*:1′,2′-*e*]azepinium salt **1a** and some of its congeners. At the same time, we report our discovery of a stereochemical dichotomy in the rearrangement reaction.

We have found that the racemic dihydroazepinium bromide[5a,b] (±)-**1a** with potassium *tert*-butoxide affords cleanly a single pair of enantiomers (*R**,3*R**)-**2a** regardless of reaction temperature (Table 1, entries 1 and 2). The identical product has also been obtained with sodium amide and alkyl/aryllithium (Table 1, entries 3–5), indicating that neither temperature nor base strength and cation affect the stereoselectivity of the reaction.

In a parallel experiment, we found that the optically pure dihydroazepinium iodide[5c] (*S*)-(+)-**1a** furnished the optically active product (*R*,3*R*)-(+)-**2a** (Table 1, entry 6). Similarly, we have found that the *n*-butyl and isopropyl homologues[5c] (*S*)-(+)-**1b** and (*S*)-(+)-**1c** afford the corresponding products (*R*,3*R*)-(+)-**2b** and (*R*,3*R*)-(+)-**2c**, respectively, suggesting that steric bulk of the alkyl substituent on the nitrogen atom also does not affect the steric course of the reaction.

With regard to the configuration of the products, it can be assumed that the absolute twist at the binaphthyl axis remains preserved during the rearrangement.[6] Supporting evidence has been obtained from an epimerization study indicating that the resulting amines (*R*,3*R*)-(+)-**2a,c** are stable under the conditions of the Stevens rearrangement and slowly epimerize *via* rotation around the binaphthyl axis only in refluxing toluene (eq 1).



(R,3R)-(+)-2a,c (S,3R)-(–)-3a,c (1)

R = Me 48 : 52
i-Pr 45 : 55

Direct proof of the configurational stability of the binaphthyl axis has been provided by comparison of CD spectra of the educt (*S*)-(+)-**1a** and product (*R*,3*R*)-(+)-**2a** (Figure 1) and by an independent chemical correlation with (+)-pentahelicene of known (*P*) absolute configuration.[7] Smooth conversion of the rearranged amine (*R*,3*R*)-(+)-**2a** to (*P*)-(+)-pentahelicene (**4**) has been attained either on reaction with *m*-chloroperoxybenzoic acid (*via* Cope elimination) or on treatment with a strong base (*via* base-induced 1,2-elimination). Also, direct treatment of the optically

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(1) (a) *Asymmetric Synthesis*; Morrison, J. D., Scott, J. V., Eds.; Academic Press: Orlando, FL, 1983–1985; Vols. 1–5. (b) For recent examples, see the special issue on enantioselective synthesis: *Chem. Rev.* **1992**, *92*, 739–1140. (c) For industrial applications, see: Crosby, J. *Tetrahedron* **1991**, *47*, 4789.

(2) (a) Rosini, C.; Franzini, L.; Raffaelli, A.; Salvadori, P. *Synthesis* **1992**, 503. (b) Blaser, H. U. *Chem. Rev.* **1992**, *92*, 935. (c) Whitesell, J. K. *Chem. Rev.* **1989**, *89*, 1581.

(3) No precedent concerning formation of a new asymmetric carbon center in proximity to a chiral 1,1′-binaphthyl moiety has so far been reported.

(4) For a recent review, see: Markó, I. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, U.K., 1991; Vol. 3, pp 913–973.

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(6) Although the educts (*S*)-(+)-**1a–c** and the products (*R*,3*R*)-(+)-**2a–c** are of the same absolute twist at the binaphthyl pivot axis, the pertinent configurational symbols assigned by the Cahn–Ingold–Prelog (CIP) nomenclature[15] are opposite. In contrast, the corresponding biphenyl series, in which the educt (*S*)-(+)-**5** and the product (*S*,9*S*)-(+)-**6** are of the same absolute twist (*vide infra*), are given identical configurational symbols. This nomenclature anomaly concerns only the biaryl axis; symbols describing configurations at the newly formed asymmetric centers are not affected.

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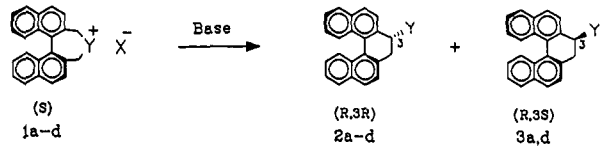
Table 1. Stevens Rearrangement of Ammonium and Sulfonium Salts **1a–d**



entry	educt (X)[a]	Y	base[b]	temp	product(s)[a,c] (total yield, %)	ratio[d] 2:3
1	(±)-**1a** (Br)	NMe_2	^{t}BuOK	rt	(*R**,3*R**)-**2a** (99)	100:0
2	(±)-**1a** (Br)	NMe_2	^{t}BuOK	−50 °C	(*R**,3*R**)-**2a** (99)	100:0
3	(±)-**1a** (Br)	NMe_2	$NaNH_2$[e]	−40 °C	(*R**,3*R**)-**2a** (72)	100:0
4	(±)-**1a** (Br)	NMe_2	^{n}BuLi	−20 °C	(*R**,3*R**)-**2a** (71)[f]	100:0
5	(±)-**1a** (Br)	NMe_2	PhLi[g]	rt	(*R**,3*R**)-**2a** + (*R**,3*S**)-**3a** (89)	>95:<5
6	(*S*)-(+)-**1a** (I)	NMe_2	^{t}BuOK	rt	(*R*,3*R*)-(+)-**2a** (99)	100:0
7	(*S*)-(+)-**1b** (Br)	N(Me)Bu^n	^{t}BuOK	rt	(*R*,3*R*)-(+)-**2b** (99)	100:0
8	(*S*)-(+)-**1c** (I)	N(Me)Pr^i	^{t}BuOK	rt	(*R*,3*R*)-(+)-**2c** (99)	100:0
9	(±)-**1d** (ClO_4)	SMe	^{t}BuOK	0 °C	(*R**,3*R**)-**2d** + (*R**,3*S**)-**3d** (47)[h]	66:34
10	(±)-**1d** (ClO_4)	SMe	^{t}BuOK	−78 °C	(*R**,3*R**)-**2d** + (*R**,3*S**)-**3d** (56)[i]	83:17

[a] For racemic substrates, only one enantiomer is shown in the heading. [b] Base (1.0–3.0 equiv), THF, 30 min. [c] Isolated. [d] Determined by ^{1}H NMR. [e] Liquid NH_3. [f] 4,5-Dihydro-3*H*-4-methyldinaphth[2,1-*c*:1′,2′-*e*]azepin[5a,c] (8%) identified by ^{1}H NMR. [g] Et_2O. [h] Pentahelicene (37%) isolated. [i] After 10 min; unreacted **1d** (44%) determined by ^{1}H NMR.

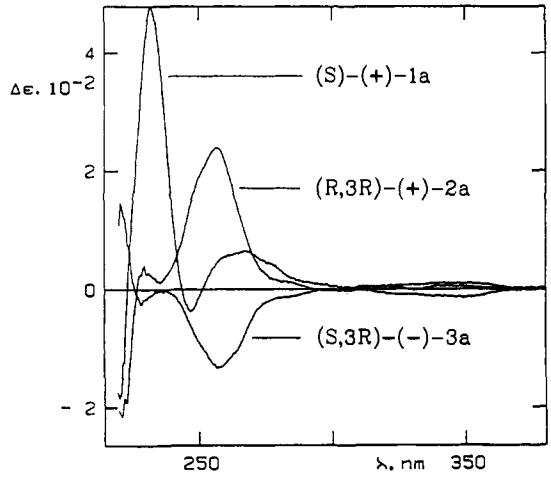
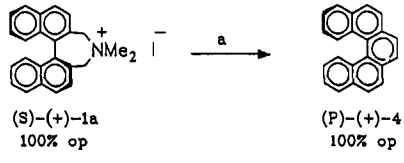


Figure 1. CD spectra of (*S*)-(+)-**1a**, (*R*,3*R*)-(+)-**2a**, and (*S*,3*R*)-(−)-**3a**.

pure quaternary salt (*S*)-(+)-**1a** with an excess of *n*-butyllithium has afforded (*P*)-(+)-pentahelicene (**4**) with >99% enantioselectivity[8] in a one-pot reaction (eq 2).



(2)

[a] n–BuLi (3.1 equiv.), THF, −30 to −20°C, 1 h

Configuration at the C-3 center in the products **2a–c** has been unambiguously inferred from their ^{1}H NMR spectra. The absence of a diaxial-like spin–spin interaction in the ABM proton system at the ethane junction[9] led us to assign a pseudoaxial orientation (Figure 2) to the amino group at the newly formed chiral center at C-3. The experimentally determined vicinal coupling constants fit well with the calculated values[9] (Table 2). Hence, the C-3 substituent in the products (+)-**2a–c** has (*R*) configuration, the overall absolute configuration[6] being (*R*,3*R*).

Significantly, a comparison can be made between the present stereochemical results and the Stevens rearrangement of an analogous biphenyl-substituted dihydroazepinium salt **5** (eq 3) investigated earlier by Mislow.[10] The optically pure quaternary

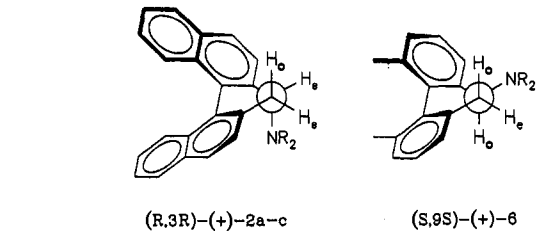
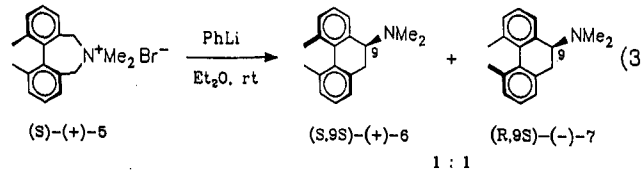


Figure 2. Conformation of the rearrangement products.



bromide (*S*)-(+)-**5** (the atropoisomer of the same twist as (*S*)-(+)-**1a**) on treatment with phenyllithium yielded two diastereoisomers, (*S*,9*S*)-(+)-**6** and (*R*,9*S*)-(−)-**7**, interconverting rapidly by low-energy torsion around the biphenyl pivot axis under the rearrangement conditions.[11] Assuming that the interconversion represents merely a subsequent step in the reaction, the rearrangement of (*S*)-(+)-**5** can be viewed as a stereochemically uniform process proceeding with configurational retention at the biaryl axis, analogous to that now demonstrated for the binaphthyl model (*S*)-(+)-**1a**. Surprising stereochemical differences[12,13] between the rearrangements **5** → **6** and **1a** → **2a** appear, however, in the configurational correlation of the educts with the newly formed carbon center, which show that the correlated configurations are consonant in the former ((*S*)-(+)-**5** → (*S*,9*S*)-(+)-**6**) but dissonant[6] in the latter ((*S*)-(+)-**1** → (*R*,3*R*)-(+)-**2**) reactions.

(8) Optical purity of (*P*)-(+)-pentahelicene (**4**) was determined by chromatography on a triacetylcellulose column at 0 °C in ethanol and/or by comparison of the measured rotations with the published values.[7]

(9) The values of coupling constants found for **2a–c** at the ethane junction are typical for H_e/H_e and H_e/H_{ax} interactions.

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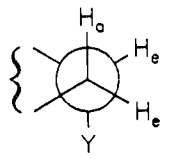
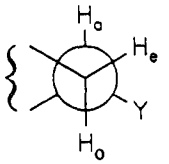
(11) The rearrangement of (±)-**5** as well as the interconversion (*S*,9*S*)-(+)-**6** ⇌ (*R*,9*S*)-(−)-**7** occur at room temperature.[10] Our attempts to suppress the latter process at lower temperature (−78 °C to 0 °C) failed owing to the unreactivity of (±)-**5**.

(12) The configurational difference between the products obtained from the corresponding educts (*S*)-(+)-**1a–c** and (*S*)-(+)-**5** is apparent from the NMR spectra. The pseudoaxial orientation of the NR_2 group in the binaphthyl products (*R*,3*R*)-(+)-**2a–c** contrasts with the pseudoequatorial orientation established in the biphenyl product (*S*,9*S*)-(+)-**6** (see Figure 2).

(13) In addition to their stereochemical differences, the reactivities of the binaphthyl and biphenyl derivatives in the Stevens rearrangement are also strikingly different, the former (**1a–c**) being more reactive than the latter (**5**) by several orders of magnitude.

Table 2. Calculated and Observed Parameters for Structures of (*R*,3*R*)-(+)-**2a–c**, (*R**,3*R**)-**2d**, (*S*,3*R*)-(−)-**3a,c**, and (*R**,3*S**)-**3d**[a]

structure[b]	dihedral angle	calcd value[c] (deg)	observed coupling constants (Hz) 2a	3a	2b	2c	3c	2d	3d
	H_a–C_4–C_3–H_e	47	4.3 (3)[d]		4.6	4.0		4.5	
	H_e–C_4–C_3–H_e	−71	1.8 (1)[d]		1.8	1.8		1.7	
(R,3R)-2									
	H_a–C_4–C_3–H_a	173		13.6 (9)[d]			12.7		12.8
	H_e–C_4–C_3–H_a	−66		4 (1)[d]			4.6		5.5
(S,3R)-3									

[a] For racemic (*R**,3*R**)-**2d** and (*R**,3*S**)-**3d**, only one enantiomer was considered. [b] Y = NR_2 or SMe. [c] Calculated for **2a** and **3a** (Y = NMe_2). [d] Calculated value in parentheses.

Such a striking discord could have an important bearing on the mechanism of the Stevens rearrangement, suggesting the possibility of two distinct pathways in the reaction. Strong support in favor of such a possibility is found in the rearrangement of the dihydrothiepinium salt[14] **1d**, a sulfur analogue of **1a**. We have found that the sulfonium salt (±)-**1d** on treatment with potassium *tert*-butoxide affords two diastereoisomeric products, (*R**,3*R**)-**2d** and (*R**,3*S**)-**3d**, differring in configuration at the asymmetric carbon center (Table 1, entries 9 and 10). This may be taken as a consequence of a *mechanistic dichotomy*.

The operation of a mechanistic dichotomy in the Stevens rearrangement has already been examined in the reaction of optically active acyl-stabilized ammonium ylides, and a possible competition between stereoselective (retention) and nonselective (racemization) mechanisms has been suggested.[16,17] In contrast to the earlier evidence, our present findings indicate dichotomy of *two stereoselective mechanisms* in the rearrangement of the biaryl azepinium and thiepinium salts. The first mechanism transfers biaryl chirality with *configurational retention* (**5** → **6**), whereas the other occurs with *inversion* (**1a–c** → **2a–c**). A simultaneous operation of both divergent mechanisms is postulated in the reaction **1d** → **2d** + **3d**. Following the accepted symbolism of concerted sigmatropic transformation,[18] the former mechanism can be viewed as a *suprafacial* and the latter as an *antarafacial* mode of the rearrangement pathway.

A similar situation has been previously encountered in this laboratory in the base-promoted olefin-forming 1,2-elimination of several alkyl- and cycloalkyltrimethylammonium salts.[19–24] Employing stereospecific deuterium labeling, we have demonstrated that *trans*-olefins are formed by syn elimination and *cis*-olefins by anti elimination. In our original analysis[25] of the phenomenon (called syn–anti dichotomy[24]), we suggested that the dichotomy is the result of "the operation of some effect which has so far escaped notice" and proposed tentatively that diastereotopicity of the hydrogens at C(β) could be the factor responsible. This proposal has been further elaborated by Wolfe[26] and treated theoretically in terms of the rotation-inversion behavior of a carbanion adjacent to a chiral center.

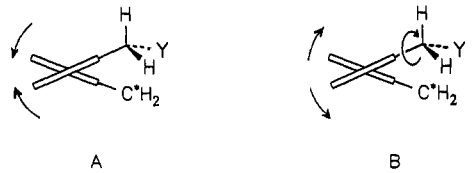


Figure 3. Proposed pathways in the Stevens rearrangement (Y = NR_1R_2 or SR; C^*H_2 denotes a radical or carbanion).

It would be premature at this stage to speculate about the applicability of such a concept to the rearrangement reaction. However, it may be noted that an alternative rationale can be proposed in terms of a simple bond rotation (torsion). As examination of a model suggests, a partial rotation around the biaryl axis in the direction diminishing the twist angle (Figure 3A) drives the benzylic grouping -C^*H_2 along the N–C bond to the new terminus in a suprafacial motion. In contrast, rotation around the biaryl axis in the opposite direction, accompanied by simultaneous rotation (180°) around the aryl–enammonium bond (Figure 3B), corresponds to an antarafacial motion. Differences in steric strain[28] and electron delocalization[29] may well be responsible for the dual course. Conceivably, narrowing the biaryl twist angle increases steric strain in the more congested binaphthyl system and thus disfavors the suprafacial path. Widening the biaryl twist angle, on the other hand, relieves strain in the system and promotes the antarafacial path. Implicit in the concept is the assumption that the two competing pathways differ in the

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(15) The IUPAC rules, Section E (Fundamental Stereochemistry). In *J. Org. Chem.* **1970**, *35*, 2849.
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(17) Dolling, U. H.; Closs, G. L.; Cohen, A. H.; Ollis, W. D. *J. Chem. Soc., Chem. Commun.* **1975**, 545.
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(28) Mislow, K.; Glass, M. A. V.; Hopps, H. B.; Simon, E.; Wahl, G. H. *J. Am. Chem. Soc.* **1964**, *86*, 1710.
(29) It was observed previously (ref 30) that ylides derived from the corresponding allylic ammonium and sulfonium cations lead to different rearranged products. Stabilization by d_π–p_π interaction in the latter cation has been proposed as the factor responsible. Such a stabilization may also explain the observed stereochemical difference in the rearrangement of the binaphthyl dihydrothiepinium and dihydroazepinium salts.
(30) Jemison, R. W.; Ollis, D. W. *Chem. Commun.* **1969**, 294.

timing of bond changes, the former representing a concerted and the latter a nonconcerted (radical pair or ion pair) reaction.[27]

Experimental Section

(*R,3*R**)-3-(*N*,*N*-Dimethylamino)-3,4-dihydrodibenzo[*c*,*g*]phenanthrene ((±)-2a). Method A.** Potassium *tert*-butoxide (75 mg, 0.668 mmol, 3 equiv.) was added to a suspension of quaternary salt (±)-**1a** (0.222 mmol) in THF (2 mL). After the mixture was stirred under argon at room temperature for 1 h, the solvent was evaporated, and the residue was partitioned between water (5 mL) and chloroform (5 mL). The aqueous layer was extracted 3 times with chloroform (3 × 5 mL), the combined organic layers were washed with water (5 mL) and dried (Na_2SO_4), and the solvent was evaporated to give 71 mg (99%) of (*R**,3*R**)-**2a**.

Method B. Quaternary salt (±)-**1a** (100 mg, 0.222 mmol) was added to sodium amide in liquid ammonia (prepared from sodium (40 mg, 1.74 mmol, 7.8 equiv) and ammonia (10 mL) in the presence of $FeCl_3$). After the mixture was stirred for 30 min at −30 °C, the ammonia was evaporated, and the residue was mixed with water (5 mL) and extracted with ether (2 × 5 mL). The ethereal extract was washed with water and dried (Na_2SO_4), and the solvent was evaporated. The residue in light petroleum–benzene (10:1) was filtered through a short column of alumina, yielding 52 mg (72%) of product (*R**,3*R**)-**2a**.

Method C. A suspension of quaternary salt (±)-**1a** (100 mg, 0.222 mmol) in THF (2 mL) was stirred in an argon atmosphere at −20 °C with 2.4 M *n*-butyllithium in hexane (0.150 mL, 0.360 mmol, 1.6 equiv) for 30 min. Workup of the reaction mixture (see method A) afforded 55 mg (75%) of a mixture of (*R**,3*R**)-**1a** and 4,5-dihydro-3*H*-4-methyldinaphth[2,1-*c*:1′,2′-*e*]azepin[5a,c] (92:9, ^{1}H NMR).

Method D. A suspension of quaternary salt (±)-**1a** (100 mg, 0.222 mmol) in ether (1 mL) was stirred with 1.8 M phenyllithium in ether (0.200 mL, 0.360 mmol) at room temperature for 3 days under argon and worked up as described in method A to yield 64 mg (89%) of a mixture of (*R**,3*R**)-**2a** and (*R**,3*S**)-**3a** (>95:<5, ^{1}H NMR), mp 146–147 °C (light petroleum–ether 3:1): ^{1}H NMR ($CDCl_3$) δ 2.16 (s, 6 H, CH_3), 3.07 (dd, J_{gem} = 15.9 Hz, *J* = 4.1 Hz, 1 H, ArC*H*HC), 3.35 (dd, J_{gem} = 15.9 Hz, *J* = 2.0 Hz, 1 H, ArCH*H*C), 3.46 (dd, *J* = 4.1 Hz, *J* = 2.0 Hz, 1 H, ArCHN), 7.10–8.07 (m, 12 H, arom); IR (CCl_4), ν 2982 (CH_3), 2956 (CH_2), 2896 (CH in $CHNMe_2$), 2859 (CH_2), 2812 and 2767 (CH_3 in $(CH_3)_2N$), 1375 (CH_3); EIMS *m*/*z* 323 ($M^{\bullet+}$), $C_{24}H_{21}N$, 58), 322 ($C_{24}H_{20}N$, 23), 308 ($C_{23}H_{18}N$, 15), 280 (34), 279 ($C_{22}H_{15}$, 100), 278 (66), 277 (87), 276 (65), 265 ($C_{21}H_{13}$, 21), 264 (20), 263 (22), 252 (7). Anal. Calcd for $C_{24}H_{21}N$: C, 89.12; H, 6.53; N, 4.33. Found: C, 88.95; H, 6.40; N, 4.19.

(*R*,3*R*)-(+)-3-(*N*,*N*-Dimethylamino)-3,4-dihydrodibenzo[*c*,*g*]phenanthrene ((*R*,3*R*)-(+)-2a). The title compound was prepared from quaternary salt (*S*)-(+)-**1a** analogously as described for (*R**,3*R**)-**2a** (method A, −50 °C to −20 °C); mp 171–173 °C (benzene–ether 1:2), optically pure (^{1}H NMR with (*S*)-(+)-2,2,2-trifluoro-1-(9-anthryl)-ethanol): $[\alpha]^{28}_{589}$ +843°, $[\alpha]^{28}_{578}$ +884°, $[\alpha]^{28}_{546}$ +1018°, $[\alpha]^{28}_{436}$ +1746° (*c* 0.78, chloroform); CD (*c* 0.3302 mmol·L^{-1}, $CHCl_3$) $\Delta\epsilon_{347}$ −13.3, $\Delta\epsilon_{257}$ +238.3, $\Delta\epsilon_{235}$ +12.6 L·mol^{-1}·cm^{-1}.

(*R*,3*R*)-(+)-3-[[*N*-(1-Butyl)-*N*-methyl]amino]-3,4-dihydrodibenzo[*c*,*g*]phenanthrene ((*R*,3*R*)-(+)-2b). A mixture of quaternary salt (*S*)-(+)-**1b** (200 mg, 0.448 mmol), potassium *tert*-butoxide (75 mg, 0.668 mmol), and THF (4 mL) was stirred under argon at room temperature for 20 min. The solvent was evaporated, and the residue was partitioned between water (5 mL) and chloroform (5 mL). The aqueous layer was extracted with chloroform (3 × 5 mL), the combined organic layers were washed with water and dried (Na_2SO_4), and the solvent was evaporated to give the product (160 mg, 98%) as an amorphous solid: $[\alpha]^{25}_{589}$ +655°, $[\alpha]^{25}_{578}$ +687°, $[\alpha]^{25}_{546}$ +792°, $[\alpha]^{25}_{436}$ +1343° (*c* 1.82, chloroform); ^{1}H NMR ($CDCl_3$) δ 0.66 (t, *J* = 7.2 Hz, 3 H, $(CH_2)_2CH_3$), 0.91–1.09 and 1.18–1.33 (m, 4 H, $(CH_2)_2CH_3$), 1.92 (s, 3 H, CH_3N), 2.38 (t, *J* = 7.2 Hz, 2 H, $NCH_2(CH_2)_2$), 3.02 (dd, J_{gem} = 15.9 Hz, *J* = 4.6 Hz, 1 H, ArC*H*HC), 3.33 (dd, J_{gem} = 15.9 Hz, *J* = 1.8 Hz, 1 H, ArCH*H*C), 3.77 (dd, *J* = 4.6 Hz, *J* = 1.8 Hz, 1 H, ArCHN), 7.18–7.96 (m, 12 H, arom); IR (CCl_4) ν 2959 (CH_3), 2933 (CH_2), 2900 (CH in CHNMeBu), 2872 and 2863 (CH_3 in CH_2CH_3), 2843 (CH_2), 2787 (CH_3 in CH_3N), 1375 (CH_3); EIMS *m*/*z* 365 ($M^{\bullet+}$), $C_{27}H_{27}N$, 30), 350 (5), 336 (2), 322 ($C_{24}H_{20}N$, 10), 308 (5), 294 (5), 279 ($C_{22}H_{15}$, 100), 278 (44), 277 (56), 276 (50), 267 ($C_{21}H_{15}$, 4), 263 (17), 252 (6), 98 ($C_6H_{12}N$, 3). Anal. Calcd for $C_{27}H_{27}N$: C, 88.72; H, 7.45; N, 3.83. Found: C, 88.70; H, 7.51; N, 3.78.

(*R*,3*R*)-(+)-3-[[*N*-Methyl-*N*-(2-propyl)]amino]-3,4-dihydrodibenzo[*c*,*g*]phenanthrene ((*R*,3*R*)-(+)-2c). A mixture of quaternary salt (*S*)-(+)-**1c** (100 mg, 0.209 mmol), potassium *tert*-butoxide (70 mg, 0.624 mmol, 3 equiv), and THF (2 mL) was stirred under argon at room temperature for 30 min. After evaporation of the mixture to dryness, the residue was partitioned between a saturated solution of NaCl (5 mL) and ether (5 mL). The aqueous layer was extracted with ether (3 × 5 mL), and the combined ethereal extracts were washed with saturated NaCl solution (5 mL) and dried (Na_2SO_4). Evaporation of the solvent gave 72 mg (99%) of oily product (*R*,3*R*)-(+)-**2c**: $[\alpha]^{28}_{589}$ +657°, $[\alpha]^{28}_{578}$ +690°, $[\alpha]^{28}_{546}$ +795°, $[\alpha]^{28}_{436}$ +1370° (*c* 0.28, chloroform); ^{1}H NMR ($CDCl_3$) δ 0.81 (d, *J* = 6.4 Hz, 3 H, CH_3CHCH_3), 0.90 (d, *J* = 6.4 Hz, 3 H, CH_3CHCH_3), 1.85 (s, 3 H, CH_3N), 3.01 (dd, J_{gem} = 15.4 Hz, *J* = 4.0 Hz, 1 H, ArC*H*HC), 3.03 (h, *J* = 6.4 Hz, 1 H, $(CH_3)_2CH$), 3.28 (dd, J_{gem} = 15.4 Hz, *J* = 1.8 Hz, 1 H, ArCH*H*C), 3.87 (dd, *J* = 4.0 Hz, *J* = 1.8 Hz, 1 H, ArCHN) 7.16–7.94 (m, 12 H, arom); IR (CCl_4) ν 2966 (CH_3), 2935 (CH_2), 2897 and 2873 (CH_3 in $(CH_3)_2CH$), 2843 (CH_2), 2789 and 2776 (CH_3 in CH_3N), 1375, 1369 and 1361 (CH_3 in $(CH_3)_2CH$); EIMS *m*/*z* 351 ($M^{\bullet+}$, $C_{26}H_{25}N$, 56), 350 ($C_{26}H_{24}N$, 27), 336 ($C_{25}H_{22}N$, 14), 308 ($C_{23}H_{18}N$, 18), 294 (7), 292 (5), 279 ($C_{22}H_{15}$, 100), 277 (85), 266 (12), 265 ($C_{21}H_{13}$, 22), 252 (9). Anal. Calcd for $C_{26}H_{25}N$: C, 88.83; H, 7.17; N, 4.00. Found: C, 88.75; H, 7.31; N, 3.82.

Thermal Equilibration of (*R,3*R**)-3-(*N*,*N*-Dimethylamino)-3,4-dihydrodibenzo[*c*,*g*]phenanthrene ((±)-2a). Preparation of (*S**,3*R**)-3-(*N*,*N*-Dimethylamino)-3,4-dihydrodibenzo[*c*,*g*]phenanthrene ((±)-3a).** A solution of compound (*R**,3*R**)-**2a** (130 mg) in toluene (3 mL) was boiled for 8 h. After evaporation of the solvent, the ratio of (*R**,3*R**)-**2a**:(*S**,3*R**)-**3a** (48:52) was determined by ^{1}H NMR spectroscopy. Flash chromatography in pentane–ether–acetone (96:2:2 and 80:10:10) gave 58 mg of compound (*R**,3*R**)-**2a** and 63 mg of compound (*S**,3*R**)-**3a** (total yield 93%).

(*S**,3*R**)-**3a**: ^{1}H NMR ($CDCl_3$) δ 2.50 (s, 6 H, CH_3), 2.81 (dd, J_{gem} = 13.7 Hz, *J* = 13.4 Hz, 1 H, ArC*H*HC), 2.99 (dd, J_{gem} = 13.7 Hz, *J* = 4.0 Hz, 1 H, ArCH*H*C), 3.94 (dd, *J* = 13.4 Hz, *J* = 4.0 Hz, 1 H, ArCHN), 7.14–8.10 (m, 12 H, arom); IR (CCl_4) ν 2974 (CH_3), 2938 (CH_2), 2895 (CH in $CHNMe_2$), 2861 (CH_2), 2825 and 2783 (CH_3), 1351 (CH_3) cm^{-1}; EIMS identical with the spectrum of (*R**,3*R**)-**2a**. Anal. Calcd for $C_{24}H_{21}N$: C, 89.12; H, 6.55; N, 4.33. Found: C, 89.05; H, 6.65; N, 4.18.

Thermal Equilibration of (*R*,3*R*)-(+)-3-(*N*,*N*-Dimethylamino)-3,4-dihydrodibenzo[*c*,*g*]phenanthrene ((*R*,3*R*)-(+)-2a). Preparation of (*S*,3*R*)-(−)-3-(*N*,*N*-Dimethylamino)-3,4-dihydrodibenzo[*c*,*g*]phenanthrene ((*S*,3*R*)-(−)-3a). Compound (*S*,3*R*)-(−)-**3a** was prepared from amine (*R*,3*R*)-(+)-**2a** as described for (*S**,3*R**)-**3a**: $[\alpha]^{30}_{589}$ −419°, $[\alpha]^{30}_{578}$ −438°, $[\alpha]^{30}_{546}$ −499° (*c* 0.36, chloroform); CD (*c* 0.3862 mmol·L^{-1}, $CHCl_3$) $\Delta\epsilon_{347}$ +10.8, $\Delta\epsilon_{257}$ −133.8, $\Delta\epsilon_{238}$ +0.6, $\Delta\epsilon_{235}$ −3.2 L·mol^{-1}·cm^{-1}.

Thermal Equilibration of (*R*,3*R*)-(+)-3-[[*N*-Methyl-*N*-(2-propyl)]-amino]-3,4-dihydrodibenzo[*c*,*g*]phenanthrene ((*R*,3*R*)-(+)-2c). Preparation of (*S*,3*R*)-(−)-3-[[*N*-methyl-*N*-(2-propyl)]amino]-3,4-dihydrodibenzo-[*c*,*g*]phenanthrene ((*S*,3*R*)-(−)-3c). Compound (*R*,3*R*)-(+)-**2c** (100 mg) was equilibrated as described in the above-mentioned experiments. The obtained mixture of (*R*,3*R*)-(+)-**2c** and (*S*,3*R*)-(−)-**3c** (45:55, ^{1}H NMR) on flash chromatography in light petroleum–ether–acetone (96:2:2 and 80:10:10) afforded 110 mg (51%) of compound (*S*,3*R*)-(−)-**3c**: $[\alpha]^{20}_{589}$ −609°, $[\alpha]^{20}_{578}$ −635°, $[\alpha]^{20}_{546}$ −719°, $[\alpha]^{20}_{436}$ −971° (*c* 0.28, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.17 (d, *J* = 6.7 Hz, 3 H, CH_3CHCH_3), 1.20 (d, *J* = 6.7 Hz, 3 H, CH_3CHCH_3), 2.34 (s, 3 H, CH_3N), 2.89 (dd, J_{gem} = 13.1 Hz, *J* = 4.6 Hz, 1 H, ArC*H*HC), 2.98 (dd, J_{gem} = 13.1 Hz, *J* = 12.7 Hz, 1 H, ArCH*H*C), 3.12 (h, *J* = 6.7 Hz, 1 H, $(CH_3)_2CH$), 4.10 (dd, *J* = 12.7 Hz, *J* = 4.6 Hz, 1 H, ArCHN), 7.15–8.10 (m, 12 H, arom); IR (CCl_4) ν 2965 (CH_3), 2934 (CH_2), 2905 (CH in CHNMePr), 2874 (CH_3 in $(CH_3)_2CH$), 2850 (CH_2), 2799 and 2786 (CH_3 in CH_3N), 1385, 1374 and 1360 (CH_3 in $(CH_3)_2CH$) cm^{-1}; EIMS identical with the spectrum of (*R*,3*R*)-(+)-**2c**. Anal. Calcd for $C_{26}H_{25}N$: C, 88.83; H, 7.17; N, 4.00. Found: C, 89.01; H, 7.30; N, 3.84.

(*R,3*R**)-3-(Methylthio)-3,4-dihydrodibenzo[*c*,*g*]phenanthrene ((±)-2d) and (*R**,3*S**)-3-(Methylthio)-3,4-dihydrodibenzo[*c*,*g*]phenanthrene ((±)-3d).** A solution of potassium *tert*-butoxide (27 mg, 0.241 mmol, 1.03 equiv) in THF (2 mL) was added dropwise at 0 °C under argon to a suspension of perchlorate (±)-**1d** (100 mg, 0.234 mmol) in THF (3 mL). After being stirred at the same temperature for 30 min, the mixture was mixed with water (1 mL), warmed to room temperature, and concentrated in vacuo. The residue was partitioned between water (4 mL) and chloroform (4 mL), and the aqueous layer was extracted with chloroform (3 × 4 mL). The combined chloroform extracts were washed with water (2 × 4 mL) and dried (Na_2SO_4), and the solvent was evaporated

to give a mixture of compounds (*R**,3*R**)-**2d**, (*R**,3*S**)-**3d**, and **4** (37:19:44, ^{1}H NMR). Flash chromatography in light petroleum–ether–acetone (96:2:2) afforded 24 mg (31%, oil) of sulfide (*R**,3*R**)-**2d**, 12 mg (16%, oil) of sulfide (*R**,3*S**)-**3d**, and 24 mg (37%) of pentahelicene **4**. The same reaction at –78 °C was carried out analogously. After 10 min, the reaction mixture was worked up to yield a mixture of compounds (*R**,3*R**)-**2d**, (*R**,3*S**)-**3d**, and **1d** (47:9:44, ^{1}H NMR).

(*R**,3*R**)-**2d**: ^{1}H NMR ($CDCl_3$) δ 1.95 (s, 3 H, CH_3), 3.20 (dd, J_{gem} = 15.6 Hz, J = 1.5 Hz, 1 H, ArC*H*HC), 3.43 (dd, J_{gem} = 15.6 Hz, J = 4.3 Hz, 1 H, ArCH*H*C), 4.22 (dd, J = 4.3 Hz, J = 1.5 Hz, 1 H, ArCHS), 7.19–7.97 (m, 12 H, arom); IR (CCl_4) ν 2944 (CH_2), 2915 (CH_3), 2882 (CH in CHSMe), 2858 (CH_2), 2827 (CH_3), 1318 (CH_3), 704 (S-CH_3), 674 and 663 (S-CH) cm^{-1}; EIMS *m*/*z* 326 ($M^{\cdot+}$, $C_{23}H_{18}S$, 18), 279 ($C_{22}H_{15}$, 100), 278 ($C_{22}H_{14}$, 38), 277 (56), 276 (57), 265 (4), 263 (12), 252 (4). Anal. Calcd for $C_{23}H_{18}S$: C, 84.62; H, 5.56; S, 9.82. Found: C, 84.80; H, 5.42; S, 10.01.

(*R**,3*S**)-**3d**: ^{1}H NMR ($CDCl_3$) δ 2.19 (s, 3 H, CH_3), 3.08 (dd, J_{gem} = 14.3 Hz, J = 12.0 Hz, 1 H, ArC*H*HC), 3.18 (dd, J_{gem} = 14.3 Hz, J = 5.5 Hz, 1 H, ArCH*H*C), 3.95 (dd, J = 12.8 Hz, J = 5.5 Hz, 1 H, ArCHS), 7.19–8.20 (m, 12 H, arom); IR (CCl_4) ν 2949 (CH_2), 2922 (CH_3), 2898 (CH in CHSMe), 2856 (CH_2), 2835 (CH_3), 1321 (CH_3), 710 (S-CH_3), 661 (S-CH) cm^{-1}; EIMS identical with the spectrum of (*R**,3*R**)-**2d**. Anal. Calcd for $C_{23}H_{18}S$: C, 84.62; H, 5.56; S, 9.82. Found: C, 84.50; H, 5.70; S, 9.88.

(*P*)-(+)-Dibenzo[*c*,*g*]phenanthrene ((*P*)-(+)-4). Method A. *m*-Chloroperoxybenzoic acid (120 mg, 50–60%, 1.1 equiv) was added to a solution of amine (*R*,3*R*)-(+)-**2a** (100 mg, 0.309 mmol) in chloroform (2 mL). After being stirred under argon at –30 °C to –20 °C for 1 h, the mixture was poured onto ice and worked up rapidly at 0 °C. The separated organic phase was washed with 5% HCl (4 mL), water (5 mL), and a saturated solution of $KHCO_3$ and dried over Na_2SO_4. Evaporation of the solvent afforded the product (*P*)-(+)-**4** (82 mg, 95%), optically pure according to HPLC on triacetylcellulose in ethanol at 0 °C.

Method B. A mixture of amine (*R*,3*R*)-(+)-**2a** (100 mg, 0.309 mmol), *n*-butyllithium (0.400 mL, 2.4 M solution in hexane, 3.1 equiv) and THF (2 mL) was stirred in an argon atmosphere at –30 °C to –20 °C for 1 h and then processed as described for method A to yield 71 mg (83%) of optically pure (*P*)-(+)-**4**.

Method C. A solution of *n*-butyllithium (0.460 mL of 2.4 M solution in hexane, 5.0 equiv) was added dropwise to quaternary salt (*S*)-(+)-**1a** (100 mg, 0.222 mmol) in THF (3 mL) under argon at –30 °C to –20 °C. After being stirred at this temperature for 30 min, the mixture was rapidly (over 56 min) worked up at 20 °C. The solvent was evaporated in vacuo, and the residue was dissolved in pentane–dichloromethane (4:1, 5 mL), filtered through a short column of alumina, and eluted with the same solvent mixture (20 mL). Evaporation of the solvents in vacuo gave 54 mg (87%) of (*P*)-(+)-**4**: $[\alpha_{extrapol}]^{20}_{589}$ +2430°, $[\alpha_{extrapol}]^{20}_{578}$ +2581°, $[\alpha_{extrapol}]^{20}_{546}$ +3109°, $[\alpha_{extrapol}]^{20}_{436}$ +7774° (*c* 0.57, dichloromethane); EIMS *m*/*z* 280 (1.8), 279 (14.5), 278 ($M^{\cdot+}$, 70.5), 277 (100), 276 (87.0), 275 (12.5), 274 (22.0), 273 (3.5), 272 (4.1), 265 (0.3), 264 (1.5), 263 (7.1), 262 (0.9), 261 (1.0), 252 (0.3), 251 (0.4), 250 (1.4), 249 (1.6), 248 (2.5), 247 (1.0), 246 (0.9), 139 (13.7), 138 (67.0), 137 (36.5), 136 (11.5), 135 (1.4).

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