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Confirmation of the Sector Rule of the Benzenoid Chromophore

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1,2,3,4,4a,9,9a,10-Octahydroanthracene and tetralin derivatives with known absolute configurations were synthesized to estimate the contribution of a methyl substituent at the third sphere to the Cotton effect induced in the benzenoid transitions. The contributions were estimated from the CD spectra obtained based on the conformation of the skeleton deduced by Force Field Theory and the assumption that the contributions are additive. A large contribution was observed for the 1-*quasiequatorial*-methyl group in the ${}^1L_b$ benzenoid transition and for the 2-*axial*-methyl group in the ${}^1L_a$ benzenoid transition. The sign agreed well with the rule proposed by Snatzke except for the contribution of ring B in the ${}^1L_a$ benzenoid transition.

Snatzke *et al.* have proposed a refined sector rule for the benzene chromophore.[1,2] Although they described the sign of the contribution of the substituent in each section, the magnitude remained unclear. CD spectra of tetralin derivatives have been reported[3,4] but the data could not give the contribution of the substituent itself, owing to the ambiguity of the contribution of the tetralin skeleton. Further, the sign of the ${}^1L_b$ CD band could not be predicted in the molecule, which is complicated because of the presence of two rotational contributions of opposite signs, as in the case of (*S*)-(−)-anhalonine.[5] The present work studied the contributions of the chiral second and third spheres on the assumption that the contributions are additive. We chose substituted 1,2,3,4,4a,9,9a,10-octahydroanthracenes to find the contribution of 1-*quasiaxial*, 1-*quasiequatorial*, and 2-*axial* substituents,** since ring B would be fastened in the half chair conformation[6] due to ring C. Further, to find the contributions of the 2-*equatorial*-methyl group and the chiral second sphere, (+)-2,3-dimethyltetralin was synthesized and the CD spectrum was compared with that of (−)-2-methyltetralin.[4,7]

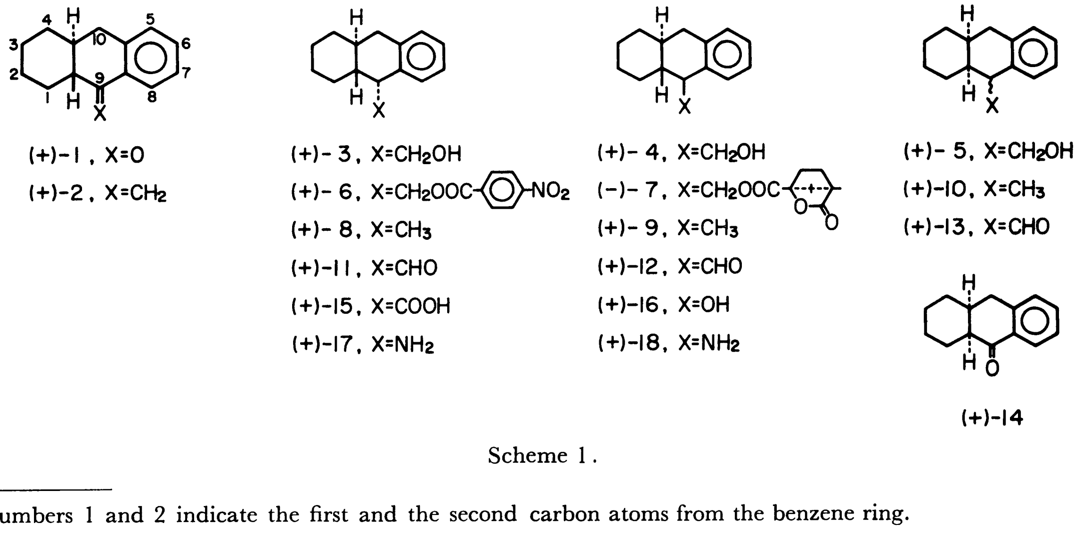
Synthesis

Wittig reaction of (4a*S*,9a*R*)-(+)-1,2,3,4,4a,9,9a,10-octahydro-9-anthracenone[1] [(+)-**1**] gave (+)-exo-olefin (+)-**2** in fairly good yield. Hydroboration of (+)-**2** gave three isomers: the first isomer (+)-**3** was isolated as the *p*-nitrobenzoate (+)-**6**; the second (+)-**5** was purified by preparative TLC and the third (+)-**4** was obtained as the (−)-ω-camphanic ester (−)-**7**.

Methyl derivatives (+)-**8**, (+)-**9**, and (+)-**10** were obtained by reduction of the tosylate of (+)-**3**, (+)-**4**, and (+)-**5**, respectively. The configuration of the methyl group and the ring juncture could be determined as follows.

Pyridinium chlorochromate oxidation of alcohol derivatives, (+)-**3**, (+)-**4**, and (+)-**5** gave the expected aldehyde (+)-**11**, (+)-**12**, and (+)-**13**, respectively. Further as a by-product, the *trans*-ketone (+)-**1** was obtained from (+)-**3** and (+)-**4**. The other isomer of the ketone (+)-**14** was isolated from (+)-**5**. The structure of (+)-**14** was assigned to be the *cis*-ring juncture by comparison with the physicochemical properties of (+)-**1**, since the C-9a position was only possible place to change. Then we could decide that (+)-**3** and (+)-**4** had the *trans*-ring juncture and (+)-**5** had the *cis*-ring juncture.

Further, the first isomer (+)-**3** was oxidized with the Jones' reagent giving the carboxylic acid (+)-**15** and (+)-**1**. From (+)-**15** the amino derivative (+)-**17** was obtained by the Curtius rearrangement. The coupling constant was 5 Hz between the protons at 9 and 9a of the carboxylic acid (+)-**15**. And the signal of the proton at 9 was observed as singlet in the amino derivative (+)-**17**. This small coupling constant led us to deter-



(+)-1, X=O
(+)-2, X=CH2
(+)-3, X=CH2OH
(+)-6, X=CH2OOC-C6H4-NO2
(+)-8, X=CH3
(+)-11, X=CHO
(+)-15, X=COOH
(+)-17, X=NH2
(+)-4, X=CH2OH
(−)-7, X=CH2OOC-
(+)-9, X=CH3
(+)-12, X=CHO
(+)-16, X=OH
(+)-18, X=NH2
(+)-5, X=CH2OH
(+)-10, X=CH3
(+)-13, X=CHO
(+)-14

Scheme 1.

** Numbers 1 and 2 indicate the first and the second carbon atoms from the benzene ring.

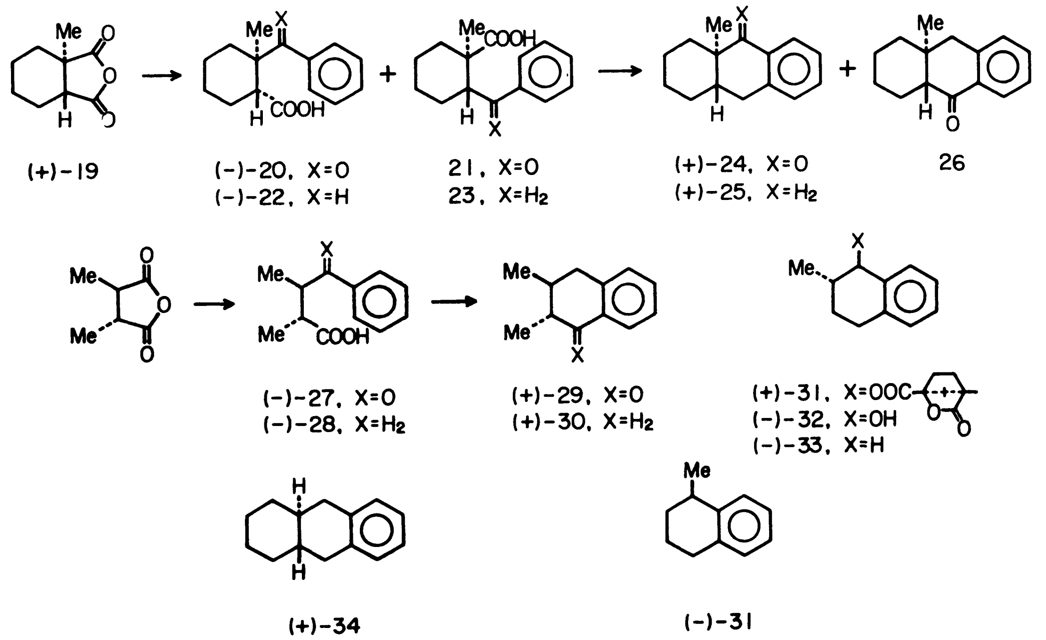
Table 1. UV and CD spectra

Compd	Solvent	UV		CD		
		λ/nm	ε	λ/nm	$\Delta\varepsilon$	$R\times10^{42}$
(+)-**3**	MeOH	273	619	272	+0.406	+76.65
		266	556	265	+0.439	
		261.5	390			
		260	377			
		217^{sh}	7060			
		213	9010	210	+2.55	+200.96
		197	45600			
		195	46200			
(+)-**4**	MeOH	273	536	270	+0.0424	+5.37
		266	530	264	+0.0363	
		260^{sh}	388	255.5	+0.0272	
		217^{sh}	8330	222.5	+0.188	+16.30
		212	9600			
		196	45700			
		195	45300			
(+)-**8**	Hexane	273	735	273	+0.568	+96.0
		266	631	266	+0.558	
		261.5	431			
		259	412			
		217	7720	215^{sh}	+2.21	+296.3
		213	9240			
		209	9240			
		197	77600			
		194	77100			
(+)-**9**	Hexane	273	578	272.5	−0.0576	−3.37
		266	526	270	+0.0121	
		262	365	265	−0.0333	
		260	353	257.5	−0.0273	
		252^{sh}	207			
		217^{sh}	7780	214	+1.35	+206.2
		212.5	9050			
		197	46500			
		195	46500			
(+)-**25**	Isooctane	273.5	859	272.5	+0.303	+57.65
		266.5	704	265	+0.330	
		262	477			
		260	464			
		254^{sh}	243			
		217	8720	215	+2.142	+331.91
		213	10400			
		208	10500			
		197	58700			
		194	57700			
(+)-**30**	Hexane	273.5	703	272	+0.191	+45.2
		266	593	264.5	+0.248	
		262	413			
		260	396			
		216.5	7690	217	+1.43	+185.7
		212.5	9100			
		208	9020			
		196.5	51600			
		193	53000			
(+)-**33**[E)]	Hexane	274	746	272	+0.161	+33.9
		266.5	595	265	+0.176	
		262	414			
		260	396			
		217	7980	217	+0.548	+78.3

TABLE 1. (Continued)

Compd	Solvent	UV		CD		
		λ/nm	ε	λ/nm	Δε	$R\times10^{42}$
		209	9120			
		197	50700			
		194	50400			
(+)-**34**	Isooctane	274	746	273	+0.267	+51.69
		267	611	265.5	+0.288	
		262	419			
		260	401			
		253^{sh}	247			
		217	6930	215	+2.03	+318.5
		212.5	8140			
(−)-**35**[a)]	Hexane	273	289	272.5	+0.226	+37.64
		266	276	264.5	+0.233	
		262	202			
		260	193			
		217	7830	220	−0.604	−30.70
		213	9210			

sh: Shoulder. E): Enantiomer was measured. !: Lowest recorded value, not a maximum. a) The compound of 75.4% e.e. was measured and corrected to the optical purity.



Scheme 2.

mine the configuration of the first isomer (+)-**3** to be 4a*S*, 9*R*, 9a*R* as shown in (+)-**3** of Scheme 1.

Reduction of the oxime of (+)-**1** gave almost selectively one *trans*-amino derivative (+)-**18**. The coupling constant was 8 Hz between the protons at **9** and **9a** and larger than that of the above amino isomer (+)-**17**. Further, reduction of (+)-**1** gave almost selectively one *trans*-isomer (+)-**16** of the alcohols with $NaBH_4$ or by the Meerwein-Pondorf-Verley method. The coupling constant was 6 Hz. Though the other *trans*-isomer could not be isolated, the signal of the proton at 9 was observed as singlet. Thus we can deduce that both major isomers have *quasiequatorial* substituent as (+)-**18** and (+)-**16**. The signals in a region of the methylene group of (+)-**17** and (+)-**18** showed quite similar pattern to those of (+)-**4**, (+)-**7** and (+)-**9**. This led us to determine their configuration to be 4a*S*, 9*S*, 9a*R*.

The second isomer (+)-**5** was deduced to have the *cis*-ring juncture as mentioned above and from the signals in a region of the methylene group in the NMR spectrum but the configuration of the substituent was remained unclear.

Friedel-Crafts reaction of benzene with (+)-(1*R*,2*R*)-*trans*-1-methyl-1,2-cyclohexanedicarboxylic anhydride[8)] [(+)-**19**] gave two isomers, **20** and **21** in a 10 : 1 ratio. Racemic **20** could be isolated by fractional recrystallization but not the optically active form. However, since both (−)-**20** and (−)-**21** lead to the same object compound **25**, the mixture of (−)-**20** and (−)-**21** was employed for further reaction without separation. Thus,

Table 2. Temperature-dependent CD spectra in methylcyclohexane–isopentane (85 : 15)

Compd	25 °C			−68 °C			−190 °C		
	λ/nm	$\Delta\varepsilon$	$R\times10^{42}$	λ/nm	$\Delta\varepsilon$	$R\times10^{42}$	λ/nm	$\Delta\varepsilon$	$R\times10^{42}$
(+)-**8**	272.5	+0.491	+92.2	272.5	+0.479	+90.5	271.5	+0.436	+96.6
	265.5	+0.579		265	+0.633		265	+0.700	
(+)-**9**	273.5	−0.036		277	−0.006				
	269.5	+0.009		270	+0.061		270	+0.148	+26.95
	265	−0.047	−5.07	263	+0.027	+4.78	264.5	+0.175	
	259.5	−0.030		254.5	+0.015				
	253	−0.012		248.5	+0.009				
(−)-**35**	272.5	+0.217	+29.9	272.5	+0.177	+28.9	272.5	+0.117	+33.1
	265	+0.209		264.5	+0.197		264	+0.221	

the angular methyl compound (+)-**25** was obtained as shown in Scheme 2.

(+)-(2*S*,3*S*)-2,3-Dimethyltetralin (+)-**30** was prepared from (+)-(2*R*,3*R*)-dimethylsuccinic acid[9] according to the procedure cited for racemic **30**.[10] The synthesis of partially optical active (−)-(1*R*,2*S*)-2-methyl-1-tetralol (−)-**32** has been reported previously,[4,7] but we obtained optically pure (−)-**32** from the *ω*-camphanic ester (+)-**31** more easily.

Results and Discussion

CD and UV spectra of the prepared compounds are shown in Table 1 with the data for (+)-(4a*S*,9a*S*)-*trans*-1,2,3,4,4a,9,9a,10-octahydroanthracene[2] [(+)-**34**] and (−)-(1*R*)-1-methyltetralin [(−)-**35**],[4] which we also prepared. Four benzenoid transitions, $^1\mathrm{L}_\mathrm{b}$, $^1\mathrm{L}_\mathrm{a}$, $^1\mathrm{B}_\mathrm{b}$, and $^1\mathrm{B}_\mathrm{a}$, were found for the UV spectra and two, $^1\mathrm{L}_\mathrm{b}$ and $^1\mathrm{L}_\mathrm{a}$, for the CD spectra. Assuming that the contributions of the substituent are additive, we can obtain the contributions, $\delta\Delta\varepsilon$ and δR, by subtracting the $\Delta\varepsilon$ values and rotational strengths, R, of (+)-**34** from the substituted 1,2,3,4,4a,9,9a,10-octahydroanthracenes. Further we can estimate the contribution of the 2-*equatorial*-methyl group by subtracting the Cotton effect of (+)-**33** from that of (+)-**30**. The contribution of ring B can be calculated by subtracting the contribution of the 2-*equatorial*-methyl group from the Cotton effect of (+)-**33**. However, *trans*-1,2,3,4,4a,9,9a,10-octahydroanthracene is not always rigid in conformation. Substituent groups often exert an influence on the conformation of ring B for deformation from a half-chair conformation. We deduced the stable conformation using the Force Field Theory, MMl,[11] with the results shown in Fig. 1. The 2-*equatorial*-methyl group in **30** and **33** does not cause the deformation of ring B from a half-chair form, and the *equatorial*-methyl forms **30a** and **33a** were more stable than the *axial*-methyl forms **30b** and **33b**, respectively. Also, the 2-*axial*-methyl group in compound **25** does not lead to as much deformation.

The 1-*quasiaxial*-methyl form **35a** was more stable than the 1-*quasiequatorial* **35b** as pointed out before[4,12] and the deformation from the half-chair form is smaller in the 1-*quasiaxial*-methyl **35a** than in 1-*quasiequatorial* **35b**. Further, ring B of **8a** is more twisted from the half-chair form than that of **35a** owing to an additional peri-effect.

The theory suggests that the 1-*quasiequatorial*-methyl compound **9** has a twist-boat conformation **9a** rather than a half-chair form.

We measured the temperature-dependent CD spectra of (+)-**8**, (+)-**9**, and (−)-**35**, which are shown in Table 2. The rotational strength of (+)-**8** and (−)-**35** were constant within experimental error with temperature changes, although the band at 272 nm became smaller at lower temperature in (−)-**35**. Next, (−)-**35** was

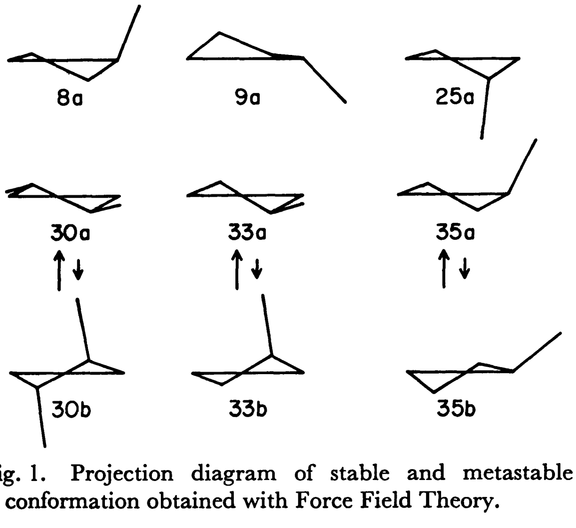


Fig. 1. Projection diagram of stable and metastable conformation obtained with Force Field Theory.

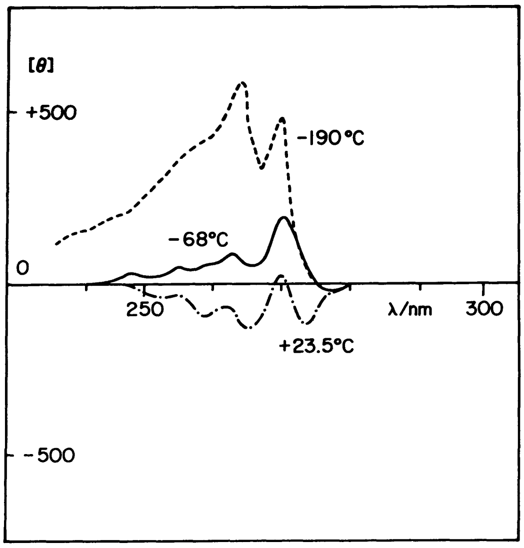


Fig. 2. Temperature-dependent CD spectra of (+)-**9**.

TABLE 3. CONTRIBUTION $\delta\Delta\varepsilon$ AND δR OF A METHYL GROUP TO TETRALIN

	^1L_b			^1L_a		
	λ/nm	$\delta\Delta\varepsilon$	$R\times10^{42}$ c.g.s.	λ/nm	$\delta\Delta\varepsilon$	$R\times10^{42}$ c.g.s.
1-Quasiaxial	272 265	-0.014 $+0.117$	$+10.5$	215	$+0.18^{a)}$	$-22.2^{a)}$
1-Quasiequatorial	272 265	≤ -0.325 ≤ -0.321	<-55.1	215	—	—
2-Equatorial	272 265	$+0.030$ $+0.042$	$+11.3$	215	$+0.882$	$+107.4$
2-Axial	272 265	$+0.036$ $+0.042$	$+6.0$	215	$+0.112$	$+13.4$
Ring B	272 265	$+0.131$ $+0.104$	$+22.6$	215	-0.334	-29.1

a) These contributions were differences between the values of (+)-**8** and (+)-**34**.

considered to be fixed in the 1-*quasiaxial*-methyl form, which is a stable conformer, since the sign of the Cotton effect of (−)-**35** was the same as that of (+)-**8** in the region of the ^1L_b benzenoid transition. On the other hand, Cotton effects of (+)-**9** depended on the temperature and changed from negative at room temperature to positive at lower temperature as shown in Fig. 2. The analysis[12] showed that the conformational free-energy difference (ΔG°) was 2.3 kJ/mol, assuming that (+)-**9** was composed of two conformers.

Since the introduction of the 2-*axial*- or the 2-*equatorial*-methyl group did not deform the half-chair conformation, we could obtain the contributions $\delta\Delta\varepsilon$ and δR of the 2-*axial*- and 2-*equatorial*-methyl groups and ring B, as mentioned above.

The contribution of the 1-*quasiaxial*-methyl group may be estimated either by subtracting the Cotton effects of (+)-**34** from those of (+)-**8** or by subtracting the contribution of ring B from the Cotton effect of (−)-**35**. The contribution obtained from both estimations had the same sign in δR in both regions of the benzenoid transitions, but the magnitudes differed and the $\delta\Delta\varepsilon$ values were ambiguous in sign. The chemical shift of the methyl group of (−)-**35** was lower than that of (+)-**8** and almost the same as that of (+)-**9**. This may suggest that compound (−)-**35** is composed of two conformers. But the Force Field Theory suggested that the more stable *quasiaxial*-methyl form **35a** showed less deformation from a half-chair form than that of **8a**. The proton at the C-1 position of (+)-**8** would cause more deformation of ring B owing to the *peri*-effect. Although the rotational strength of (−)-**35** was not influenced much by temperature, we adopted the difference of the Cotton effect of (−)-**35** at −190 °C from the contribution of ring B as the contribution of the 1-*quasiaxial*-methyl group.

As mentioned before, the Cotton effect of (+)-**9** depended on temperature. We estimated the stable conformer to be a twist-boat form from the Force Field Theory. Also, to estimate the conformation of (+)-**9**, we measured the CD spectra of 1,3,5(10)-estratriene,*** which was regarded as the 1-*quasiequatorial*-2-*equatorial*-dimethylene derivative with a half-chair conformation. The half-chair form of (+)-**9** can be regarded as the derivative with one 1-*quasiequatorial*-methyl and two 2-2-*equatorial*-methylene groups, in other words, it has one 2-*equatorial*-methylene group more than the steroid, if the methyl and the methylene groups in the 1-*quasiequatorial*-position make the same contribution to the Cotton effect. We estimated the contribution of the 2-*equatorial*-methylene group from the CD spectra of (+)-**34** to be small. We then compared the CD spectra of the steroid and (+)-**9**. The CD spectra of the steroid resembled that of (+)-**9** at room temperature rather than that at low temperature. This means that (+)-**9** is in equilibrium between the twist-boat and the half-chair forms, and the twist-boat form is the stable one. Therefore, we could not estimate the contribution of the 1-*quasiequatorial* group by direct comparison, but the negative Cotton effect was deduced for the unstable conformer from the Cotton effect at room temperature. The contributions of the 1-*quasiequatorial*-methyl group were larger than those obtained by subtracting the Cotton effects of (+)-**34** from those of (+)-**9** at room temperature. These results are summarized in Table 3. The sign of the contribution agreed well with Snatzke's sector rule except for ring B in the ^1L_a region, although the contribution of the 1-*quasiequatoria*-methyl group was not clear.

In the ^1L_b benzenoid transition, the 1-*quasiaxial*-, 2-*axial*- and 2-*equatorial*-methyl groups showed smaller contributions than the 1-*quasiequatorial* group. In the ^1L_a benzenoid transition, the 2-*equatorial*-methyl group contributed more than the 1-*quasiaxial* and 2-*axial*-methyl groups. Since ring B is not always in the complete half-chair conformation, the contribution is not directly attributable to the methyl group but contains the contribution of the deformation of ring B by the substituent. These apparent contributions should be useful for predicting the position and orientation of the substituent of the tetralin derivatives.****

*** In cyclohexane, 274 nm ($\Delta\varepsilon$ −0.124), 271 (+0.028), 266.5 (−0.085), 260 (−0.042).

**** We tried to analyze the contribution using the CNDO/S molecular orbital model[13] and the dipole velocity method[14] but have some doubt about the reliability and accuracy of the calculation owing to the quantitative instability with a number of configurations.

Experimental

Melting points are uncorrected. Optical rotations were determined with a Perkin-Elmer Model 141 polarimeter, using a 1.0-dm microcell. CD curves were obtained using a JASCO Model J-40 spectropolarimeter. Infrared spectra were recorded on a JASCO-DS-402G spectrophotometer. ^1H NMR spectra were measured with Varian A56/60D spectrometer using tetramethylsilane as the internal standard. UV spectra were obtained on a Hitachi Model 323 spectrometer.

*(4a*S, *9a*R*)-(+)-9-Methylene-1, 2, 3, 4, 4a, 9, 9a, 10-octahydroanthracene, (+)-**2**.* Methyltriphenylphosphonium bromide (31 g) was added to a suspension of potassium *t*-butoxide (15 g) and the (+)-ketone (**1**, 5.8 g) in dry ether (400 ml) under a nitrogen atmosphere. The mixture was stirred overnight and poured onto ice water. The organic phase was separated and the aqueous phase was extracted with ether. The combined organic phases were washed with dimethyl sulfoxide–water (1 : 1) and then water, dried (Na_2SO_4) and concentrated *in vacuo*. The residue was crystallized from ether and the crystals were removed by filtration. The filtrate was chromatographed on thick silica gel plate (Merck Co., precoated, 2 mm) in hexane and then distilled at 121 °C at 0.9 mm Hg, 5.4 g (94.0%); $[\alpha]_D^{24\ 5}$ +140.3 ±1.7° (*c* 1.047, $CHCl_3$); IR (film) 888 cm^{-1}; NMR ($CDCl_3$) δ=0.9—2.5 (m, 10H), 2.5—3.1 (m, 2H), 4.97 (s,1H),5.49 (s, 1H), 7.0—7.3 (m, 3H), 7.4—7.8 (m, 1H); UV_{max} (hexane) 298^{sh} nm (ε 758), 288 (864), 281 (843), 250 (11300), 222^{sh} (10500), 211 (21700); CD (hexane) 283 nm (Δε +0.933), 243 (+4.88), 211.5 (+11.3), 190! (−7.24). Found: C, 91.00; H, 9.06%. Calcd for $C_{15}H_{18}$: C, 90.85; H, 9.15%.

*Hydroboration of (+)-**2**.* A solution of diborane in tetrahydrofuran, which was prepared from $NaBH_4$ (5.3 g), boron trifluoride etherate (44 g) and diglyme (130 ml), was added to a solution of the (+)-olefin (**2**, 5.40 g) in tetrahydrofuran (100 ml) with ice-cooling. The mixture was stirred at 0 °C for 2 h. Water was added dropwise carefully with ice-cooling. 3 mol dm^{-3} NaOH (22 ml) and then 30% hydrogen peroxide (25 ml) were added. The mixture was stirred for 4 h and allowed to stand for 2 d. Water (200 ml) was added. The mixture was extracted with ether. The solution was washed with water, dried (Na_2SO_4) and concentrated *in vacuo*. The small portion of residue was distilled at 160 °C (bath temperature) at 0.2 mmHg through a short-path distillation apparatus, $[\alpha]_D^{23.5}$ +73.0 ±0.8° (*c* 0.958, MeOH). Found: C, 83.69; H, 9.49%. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32%.

*(4a*S, *9*R, *9a*R*)-(+)-1,2,3,4,4a,9,9a,10-Octahydro-9-anthracenylmethyl* p-*Nitrobenzoate, (+)-**6**.* *p*-Nitrobenzoyl chloride (18 g) was added to a cold solution of the above (+)-alcohols (**3**, **4** and **5**, 5.6 g) in pyridine (80 ml). The mixture was allowed to stand at room temperature overnight, poured into water and extracted with ethyl acetate. The solution was washed with dilute HCl, aqueous $NaHCO_3$ and water, dried (Na_2SO_4) and concentrated *in vacuo*. The residue was crystallized from ether and recrystallized from ethyl acetate–ethanol, 0.432 g, mp 126—128 °C; $[\alpha]_D^{24}$ +136.1 ±2.1° (*c* 0.867, $CHCl_3$); IR ($CHCl_3$) 1724, 1530 cm^{-1}; UV_{max} (dioxan) 340^{sh} nm (ε 280), 261 (13300), 218^{sh} (12100), 207.5 (17100); CD (MeOH) 325 nm (Δε +0.018), 264.5 (+2.75), 259 (+2.58), 210 (+6.30). Found: C, 72.20; H, 6.39; N, 3.78%. Calcd for $C_{22}H_{23}NO_4$: C, 72.31; H, 6.34; N, 3.83%.

*(4a*S, *9*R, *9a*R*)-(+)-9-Hydroxymethyl-1,2,3,4,4a,9,9a,10-octahydroanthracene, (+)-**3**.* The (+)-ester (**6**, 2.6 g) was hydrolyzed with KOH (2 g) in water (10 ml) and methanol (20 ml) by heating under reflux for 2 h and treated as usual. The alcohol was crystallized from hexane, 1.5 g, mp 85—86 °C, $[\alpha]_D^{24}$ +105.5 ±1.4° (*c* 1.071, MeOH); IR (nujol) 3300, 1056 cm^{-1}; NMR ($CDCl_3$) δ=0.7—2.2 (m, 11H), 2.3—3.2 (m; 3H), 3.62 (dd, *J*=5, 11 Hz, 1H), 7.11 (s, 4H). Found: C, 83.28; H, 9.49%. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32%.

*(4a*S, *9*R, *9a*S*)-(+)-9-Hydroxymethyl-1,2,3,4,4a,9,9a,10-octahydroanthracene, (+)-**5**.* The mother liquor of the *p*-nitrobenzoate **6** was hydrolyzed as above. The oily residue (1.5 g) was chromatographed on thin silica gel plate (Merck Co., precoated, 0.5 mm) in hexane–ether (3 : 1). The fraction of the smaller R_f value was distilled at 160 °C at 0.2 mmHg through a short-path distillation apparatus, 300 mg; $[\alpha]_D^{24}$ +30.9 ±0.6° (*c* 0.941, MeOH); IR (film) 3350 cm^{-1}; NMR ($CDCl_3$) δ=0.8—2.4 (m, 10H), 2.6—3.3 (m, 3H), 3.87 (dd, *J*=7, 11 Hz, 1H), 4.22 (dd, *J*=6, 11 Hz, 1H), 6.9—7.5 (m, 4H); UV_{max} (MeOH) 274 nm (ε 600), 266 (566), 261^{sh} (405), 255^{sh} (278), 217^{sh} (8020), 213 (9140), 197.5 (44400), 195^{sh} (43000); CD (MeOH) 272.5 nm (Δε −0.215), 265.5 (−0.212), 259.5 (−0.136), 210 (−1.61). Found: C, 83.22; H, 9.40%. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32%.

*(−)-Camphanyl Ester of (4a*S, *9*S, *9a*R*)-(+)-9-Hydroxymethyl-1,2,3,4,4a,9,9a,10-octahydroanthracene, (−)-**7**.* A solution of the fraction with the larger R_f value (0.18 g) in pyridine (3 ml) was added to (−)-ω-camphanoyl chloride (0.362 g) in pyridine (3 ml). The mixture was allowed to stand at room temperature overnight, poured into water and extracted with ether. The solution was washed with ice-cold dilute HCl, aqueous $NaHCO_3$ and water, dried (Na_2SO_4) and concentrated *in vacuo*. The residue was chromatographed on thin silica gel plate (Merck Co., precoated, 0.5 mm) in hexane–ether (5 : 1). The development was repeated three times. The fraction of the smaller R_f value (−)-**7** was recrystallized from hexane, 181 mg, $[\alpha]_D^{22}$ 0°, $[\alpha]_{365}^{22}$ −5.9 ±0.3° (*c* 1.107, $CHCl_3$); mp 129.0—130.0; IR (Nujol) 1790, 1744 cm^{-1}; NMR ($CDCl_3$) δ=0.63 (s, 3H), 0.71 (s, 3H), 1.03 (s, 3H), 0.7—2.9 (m, 17H), 4.32 (dd, *J*=12, 3 Hz, 1H), 4.77 (dd, *J*=12, 4 Hz, 1H), 6.9—7.4 (m, 4H). Found: C, 75.33; H, 8.04%. Calcd for $C_{25}H_{32}O_4$: C, 75.73; H, 8.13%.

The fraction with the larger R_f value, the ω-camphanic ester of (+)-**3**, was recrystallized from hexane, 57.7 mg, mp 154 °C; $[\alpha]_D^{22}$ +76.9 ±1.0° (*c* 0.844, $CHCl_3$); IR (nujol) 1789, 1722 cm^{-1}; NMR ($CDCl_3$) δ=0.76 (s, 3H), 0.96 (s, 3H), 1.07 (s, 3H), 0.6—2.6 (m, 15H), 2.7—3.2 (m, 2H), 4.23 (dd, *J*=6, 12 Hz, 1H), 4.52 (dd, *J*=6, 12 Hz, 1H), 6.9—7.3 (m, 4H). Found: C, 74.90; H, 7.99%. Calcd for $C_{25}H_{32}O_4$: C, 75.73; H, 8.13%.

*(4a*S, *9*S, *9a*R*)-(+)-9-Hydroxymethyl-1,2,3,4,4a,9,9a,10-ocatahydroanthracene, (+)-**4**.* The ester [(−)-**7**, 400 mg] was hydrolyzed with 5% KOH in methanol (10 ml) by heating under reflux for 2 h. The residue was distilled at 160 °C (bath temperature) at 0.2 mmHg through a short-path distillation apparatus, 157 mg; $[\alpha]_D^{21}$ +76.4 ±0.8° (*c* 1.017, MeOH) IR (film) 3370, 1046 cm^{-1}; NMR ($CDCl_3$) δ=0.7—2.2 (m, 10H), 2.3—2.8 (m, 3H), 3.73 (dd, *J*=11, 3 Hz, 1H), 4.01 (dd, *J*=11, 3 Hz, 1H), 6.9—7.4 (m, 4H). Found: C, 82.63; H, 9.24%. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32%.

*(4a*S,*9*R,*9a*R*)-(+)-9-Methyl-1,2,3,4,4a,9,9a,10-octahydroanthracene, (+)-**8**.* A solution of *p*-toluenesulfonyl chloride (1.3 g) in pyridine (10 ml) was added to a solution of the (+)-alcohol (**3**, 30)1 mg in pyridine (3 ml) at −5—−10 °C over a period of 1 h. The solution was allowed to stand at 4 °C overnight, poured into ice-cold dilute HCl and extracted with ether. The solution was washed with cold dilute HCl, aqueous $NaHCO_3$ and water, dried (Na_2SO_4) and concentrated *in vacuo*, 402 mg. The crystalline tosylate was used for the next preparation without further purification.

A solution of the optically active tosylate (400 mg) in dry tetrahydrofuran (15 ml) was added to a slurry of $LiAlH_4$ (0.4 g) in tetrahydrofuran (5 ml) with ice-cooling. The mixture was then heated under reflux for 5 h. Excess $LiAlH_4$ was decomposed with a solution of methanol in ether and then dilute HCl. The mixture was chromatographed on thin silica gel plate (Merck Co., precoated, 0.5 mm) in hexane and distilled at 110 °C (bath temperature) at 0.2 mmHg giving a colorless oil, 141.5 mg; $[\alpha]_D^{23}$ +90.2 ±1.1° (*c* 1.282, hexane); IR (film) 755 cm^{-1}; NMR ($CDCl_3$) δ=1.08 (d, *J*=7 Hz, 3H), 0.9—3.2 (m, 10H), 7.05 (m, 4H). Found: C, 89.65; H, 10.15%. Calcd for $C_{15}H_{20}$: C, 89.94; H, 10.06%.

*(4a*S*,9*R*,9a*S*)-(+)-9-Methyl-1,2,3,4,4a,9,9a,10-octahydroanthracene, (+)-**10**.* The *cis*-alcohol [(+)-**5**] was treated as above. The oily residue was chromatographed on thin silica gel plate (Merck Co., precoated, 0.5 mm) in hexane and distilled at 110 °C at 0.2 mmHg; $[\alpha]_D^{22}$ +43.0 ±0.6° (*c* 1.146, hexane); CD 273.5 nm ($\Delta\varepsilon$ −0.158), 266.5 (−0.133), 260 (−0.064), 217 (+0.621); IR (film) 755 cm^{-1}; NMR ($CDCl_3$) δ=0.5—3.3 (m, 13H), 1.31 (d, *J*=7 Hz, 3H), 6.9—7.4 (m, 4H). Found: C, 89.13; H, 9.90%. Calcd for $C_{15}H_{20}$: C, 89.94; H, 10.06%.

*(4a*S*, 9*S*, 9a*R*)-(+)-9-Methyl-1,2,3,4,5a,9,9a,10-octahydroanthracene, (+)-**9**.* The *trans*-alcohol [(+)-**4**] was treated as above. The residue was chromatographed on thin silica gel plate (Merck Co., precoated, 0.5 mm) in hexane and distilled at 120 °C (bath temperature) at 0.2 mmHg through a short-path distillation apparatus. The distillate crystallized quickly, mp 65—68 °C; $[\alpha]_D^{22}$ +99.1 ±0.9° (*c* 1.018, hexane); IR (nujol) 763, 744 cm^{-1}; NMR ($CDCl_3$) δ=0.5—2.8 (m, 3H), 1.28 (d, *J*=7 Hz, 3H), 6.9—7.4 (m, 4H). Found: C, 89.66; H, 10.47%. Calcd for $C_{15}H_{20}$: C, 89.94; H, 10.06%.

*Oxidation of Alcohols (+)-**3**, (+)-**4**, and (+)-**5**.* *1)*: A solution of the (+)-*cis*-alcohol[(+)-**5**, 199 mg] in dichloromethane (6 ml) was added to a mixture of anhydrous sodium acetate (26 mg) and pyridinium chlorochromate (311 mg) in dichloromethane (5 ml) in one portion. The mixture was stirred at room temperature for 2 h. Ether was added. The mixture was chromatographed on florisil (20 g) in ether. The residue was chromatographed on thin silica gel plate (Merck Co., pre-coated plate) in benzene.

The fraction of the larger R_f value; oil (44.4 mg); IR (film) 1723 cm^{-1}; NMR ($CDCl_3$) δ=1.0—3.1 (m, 12H), 3.41 (dd, *J*=6, 2 Hz, 1H), 6.9—7.4 (m, 4H), 9.59 (d, *J*=2 Hz, 1H); This fraction was the aldehyde derivative **13**.

The fraction of smaller R_f value (42.4 mg) was recrystallized from pentane; mp 79—81 °C; $[\alpha]_D^{25}$ +40.8 ±0.6 (*c* 1.046, $CHCl_3$); IR (Nujol) 1677, 749, 738 cm^{-1}; NMR ($CDCl_3$) δ=1.2—2.9 (m, 10H), 2.99 (d, *J*=5 Hz, 1H), 7.1—7.6 (m, 3H), 8.15 (dd, *J*=8, 1 Hz, 1H); UV_{max} (heptane) 355 nm^{sh} (ε 118), 342 (174), 330 (192), 316 (209), 298 (1580), 288 (1650), 278^{sh} (1110), 251^{sh} (9620), 245 (12500), 204 (30400); CD (heptane) 374 nm ($\Delta\varepsilon$ +0.115), 357 (+0.348), 343.5 (+0.494), 330.5 (+0.424), 318 (+0.227), 307.5 (+0.064), 296 (−0.082), 286 (−0.109), 243 (+1.42), 222 (+0.594), 210.5 (−4.30), 193 (+7.79). Found: C, 83.70; H, 8.14%. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05%. This was the *cis*-ketone (+)-**14**.

2): The (+)-alcohol [(+)-**3**, 105 mg] was treated as above. The fraction of the larger R_f value (49.8 mg) could not be crystallized and was contaminated with other compounds but the following band and signal were observed; IR (film) 1720 cm^{-1}; NMR ($CDCl_3$) δ=9.61 (d, *J*=6 Hz). The fraction of the smaller R_f value (25.7 mg) was recrystallized from pentane and was identical with the authentic sample, (+)-**1**.

3): The alcohol [(+)-**4**, 117 mg] was treated as above. The fraction of the larger R_f value (64.3 mg) was recrystallized from pentane; mp 79—81 °C; $[\alpha]_D^{25}$ +15.2 ±0.4 (*c* 1.246, $CHCl_3$); IR (Nujol) 1728, 751 cm^{-1}; NMR ($CDCl_3$) δ=0.8—2.9 (m, 12H), 3.28 (dd, *J*=9, 6 Hz, 1H), 6.8—7.3 (m, 4H), 9.38 (d, *J*=5 Hz, 1H); UV_{max} (heptane) 296 nm (ε 103), 273 (400), 266 (408), 262^{sh} (325), 253 (266), 218^{sh} (8390); CD (heptane) 325 nm^{sh} ($\Delta\varepsilon$ −0.524), 313^{sh} (−1.15), 305 (−1.43), 296.5 (−1.38), 271.5 (−1.02), 265 (−0.709), 260 (−0.412), 225.5 (−1.02), 201.5 (+9.30). Found: C, 84.01; H, 8.54%. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47%.

The fraction of the smaller R_f value (9.5 mg) was recrystallized from pentane and was identical with the authentic sample, (+)-**1**.

*Reduction of (+)-**1**.* *a)*: $NaBH_4$ (0.3 g) was added in small portions to a suspension of (+)-**1** (0.317 g) in methanol (10 ml) at −10 °C. The mixture was stirred for 2 h. Dilute HCl was added. The crystals were collected by filtration, washed with water, dried and recrystallized from methanol, 0.212 g, mp 142—143 °C; $[\alpha]_D^{25}$ +119.4 ±1.0° (*c* 1.016, $CHCl_3$); IR (Nujol) 3380, 3350 cm^{-1}; NMR ($CDCl_3$) δ=0.8—3.2 (m, 12H), 4.26 (d, *J*=6 Hz, 1H), 6.8—7.3 (m, 3H), 7.3—7.7 (m, 1H); UV_{max} (MeOH) 273 nm (ε 407), 266 (395), 260^{sh} (294), 217^{sh} (7410), 212 (8530), 197.5 (36400); CD (MeOH) 274 nm ($\Delta\varepsilon$ +0.138), 268 (+0.155), 263 (+0.146), 215 (+2.88). Found: C, 82.80; H, 9.13%. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97%.

b): A mixture of (+)-**1** (0.570 g) and aluminum isopropoxide (0.60 g) in isopropyl alcohol (15 ml, freshly distilled over aluminum isopropoxide) was heated at refluxing 4 h. The rate of the distillation was about 5 to 10 drops a minute. Finally the solvent was distilled off *in vacuo*. Dilute HCl was added. The mixture was extracted with ether. The solution was washed with water, dried (Na_2SO_4) and concentrated *in vacuo*. The residue was chromatographed on thin silica gel plate (Merck Co., precoated) in benzene and recrystallized from methanol. This was identical with the above product.

From the mother liquor of procedures *a*) and *b*), the other isomer could not be isolated but a singlet was detected at δ=4.35 in $CDCl_3$.

*(4a*S*, 9*R*, 9a*R*)-(+)-1,2,3,4,4a,9,9a,10-Octahydroanthracene-9-carboxylic Acid, (+)-**15**.* Jones' reagent (0.5 ml) was added to a solution of the (+)-alcohol [(+)-**3**, 226 mg] in acetone (5 ml) with ice-cooling. Water was added. The mixture was extracted with ethyl acetate. The solution was washed with water, dried (Na_2SO_4), concentrated *in vacuo* and recrystallized from hexane; 112.4 mg, mp 182—183 °C; $[\alpha]_D^{24}$ +209.1 ±2.2° (*c* 0.657, MeOH); IR (Nujol) 1690 cm^{-1}; NMR ($CDCl_3$) δ=0.8—3.1 (m, 12H), 3.73 (d, *J*=5 Hz, 1H), 7.15 (s, 4H), 10.90 (s, 1H). Found: C, 77.56; H, 7.98%. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88%.

The mother liquor was chromatographed on thin silica gel plate (Merck Co., pre-coated plate) in benzene. The elute was recrystallized from hexane and was identical with the authentic sample, (+)-**1**.

*(4a*S*, 9*R*, 9a*R*)-(+)-9-Amino-1,2,3,4,4a,9,9a,9,10-octahydroanthracene, (+)-**17**.* A mixture of the (+)-carboxylic acid [(+)-**15**, 140 mg] and oxalyl chloride (1 ml) was stirred at room temperature for 3 h. The volatile materials were removed by distillation *in vacuo*.

A solution of the acid chloride in dry tetrahydrofuran (3 ml) was added to a cold solution of NaN_3 (0.25 g) in water (5 ml). The mixture was stirred at 0 °C for 3 h and extracted with ether. The solution was washed with water, dried (Na_2SO_4) and concentrated *in vacuo*.

Dry benzene (5 ml) was added. The solution was heated under reflux for 3 h and concentrated *in vacuo*.

A solution of the isocyanate in *t*-butanol and triethylamine (1 ml) was heated under reflux for 12 h and the volatile materials were removed by distillation *in vacuo*.

Concentrated HCl (5 ml) was added. The mixture was heated at 100 °C for 18 h. After cooling, the mixture was washed with ether, treated with charcoal and concentrated *in vacuo*. The residue (57.5 mg) was recrystallized from ethyl acetate, mp 270—271 °C.

Dilute NH_4OH was added. The mixture was extracted with dichloromethane. The solution was washed with water, dried (Na_2SO_4) and concentrated *in vacuo*. The residue was distilled at 100 °C at 0.2 mmHg giving a colorless oil (28.7 mg). $[\alpha]_D^{23}$ +82.1 ±0.8° (*c* 1.092, $CHCl_3$); IR (film) 3370, 3290 cm^{-1}; NMR ($CDCl_3$) δ=0.7—2.3 (m, 12H), 2.6—3.2 (m, 2H), 3.76 (s, 1H), 7.0—7.4 (m, 4H); UV_{max} (MeOH) 272 nm (ε 411), 265 (424), 261^{sh} (347), 211^{sh} (9100), 195 (42200); CD (MeOH) 271.5 nm ($\Delta\varepsilon$ +0.409), 264 (+0.458), 216 (+2.45). Found: C, 83.20; H, 9.71; N, 6.69%. Calcd for $C_{14}H_{19}N$: C, 83.53; H, 9.51; N, 6.96%.

*(4a*S, *9*S, *9a*R*)-(+)-9-Amino-1,2,3,4,4a,9,9a,10-octahydroanthracene, (+)-**18**.* A mixture of the (+)-ketone [(+)-**1**, 507 mg], NH_2OH–HCl (411 mg), pyridine (4 ml) and ethanol (6 ml) was heated under reflux for 16 h, poured into water and extracted with ether. The solution was washed with water, dried (Na_2SO_4) and concentrated *in vacuo*.

A small amount of raney-Ni was added to a solution of the oxime in methanol (20 ml), a solution of Na_2HPO_2 (0.85 g) in water (5 ml), and 2 mol dm^{-3} NaOH (5 ml). After the bubbling had settled, the mixture was shaken under hydrogen atmosphere. The catalyst was filtered and washed with methanol. Dilute HCl was added. The crystals were collected by filtration, shaken with aqueous K_2CO_3 and extracted with dichloromethane. The solution was dried (Na_2SO_4) and concentrated *in vacuo*. The residue was recrystallized from hexane, 57.1 mg, mp 48—50 °C; $[\alpha]_D^{24}$ −96.3 ±0.9° (*c* 1.019, MeOH); IR (Nujol) 3390, 3300 cm^{-1}; NMR ($CDCl_3$) δ=0.7—2.8 (m, 12H), 3.49 (s, broad, 1H), 6.9—7.3 (m, 3H), 7.4—7.8 (m, 1H); CD (MeOH) 272 nm ($\Delta\varepsilon$ +0.199) 265 (+0.199), 217 (+2.41). Found: C, 83.52; H, 9.22; N, 6.87%. Calcd for $C_{14}H_{19}N$: C, 83.53; H, 9.51; N, 6.96%.

*Friedel-Crafts Reaction of (+)-**19** with Benzene.* Anhydrous $AlCl_3$ (8.5 g) was added in one portion to a solution of the anhydride[8] [(+)-**19**, 2.16 g] in benzene (20 ml). The mixture was heated under reflux with vigorous stirring for 3 h and poured into ice-cold HCl. The organic phase was separated and the aqueous phase was extracted with benzene. The combined organic phases were washed with water, dried (Na_2SO_4) and concentrated. The residue was chromatographed on silica gel (Merck Co., grade 1, 50 g) in ethyl acetate. The NMR spectrum showed it to be a mixture of *ca.* 10 : 1 of (−)-**20** and **21**. They could not be separated from each other by fractional recrystallization or TLC.

Racemic **20** was isolated by recrystallization twice from benzene–hexane; mp 138—139 °C; IR (Nujol) 1694, 1680 cm^{-1}; NMR ($CDCl_3$) δ=1.40 (s, 3H), 1.3—2.1 (m, 8H), 3.82 (m, 1H), 7.3—7.6 (m, 3H), 7.7—8.0 (m, 2H). Found: C, 72.22; H, 7.33%. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37%.

*(1*R, *2*S*)-(−)-2-Benzyl-2-methyl-1-cyclohexanecarboxylic Acid, (−)-**18**.* The (−)-ketone [(−)-**20**, 378 mg] was hydrogenolyzed by the same procedure cited for 2-benzoyl-1-cyclohexanecarboxylic acid.[1] The oily residue was distilled at 150 °C (bath temperature) at 0.2 mmHg through a short-path distillation apparatus. The NMR spectrum showed contamination by a small amount of **23**.

Racemic **22**: mp 133—135 °C; IR (Nujol) 1692 cm^{-1}; NMR ($CDCl_3$) δ=1.24 (s, 3H), 0.9—1.9 (m, 8H), 2.0—2.8 (m, 3H), 7.20 (s, 5H). Found: C, 77.54; H, 8.79%. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68%.

*(4a*R, *9a*S*)-(+)-4a-Methyl-1,2,3,4,4a,9,9a,10-octahydro-10-anthracenone, (+)-**24**.* The ring-forming reaction was carried out according to the procedure cited for 2-benzyl-1-cyclohexanecarboxylic acid.[1] The oily product, quantitative yield, was distilled at 140 °C at 0.5 mmHg through a short-path distillation apparatus and was contaminated with a small amount of **26**.

Racemic **24**: oil; IR (film) 1688 cm^{-1}; NMR ($CDCl_3$) δ= 1.07 (s, 3H), 1.1—2.4 (m, 1H), 2.68 (s, 1H), 2.80 (d, *J*=5 Hz, 1H), 7.0—7.7 (m, 3H), 7.9—8.2 (m, 1H). Found: C, 83.62; H, 8.45%. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47%.

*(4a*S, *9a*S*)-(+)-4a-Methyl-1,2,3,4,4a,9,9a,10-octahydroanthracene, (+)-**25**.* The (+)-ketone [(+)-**24**] was hydrogenolyzed as above. The crude oily residue was chromatographed on thin silica gel plate (Merck Co., precoated, 0.5 mm) in hexane and distilled at 80 °C (bath temperature) at 0.2 mmHg through a short-path distillation apparatus, and crystallized then recrystallized from hexane mp 52—53 °C; $[\alpha]_D^{22}$ +81.5 ±0.4° (*c* 1.277, hexane); IR (film) 743 cm^{-1}; NMR ($CDCl_3$) δ=0.81 (s, 3H), 1.0—1.9 (m, 10H), 2.51 (br, s, 3H), 7.05 (s, 4H). Found: C, 89.99; H, 10.02%. Calcd for $C_{15}H_{20}$: C, 89.94; H, 10.06%.

*(2*R, *3*R*)-(−)-2,3-Dimethyl-4-phenyl-4-oxobutanoic Acid, (−)-**27**.* Mp 88—89 °C; $[\alpha]_D^{25}$ −1.22 ±0.20°, $[\alpha]_{365}^{25}$ −107.2 ±0.5° (*c* 2.035, MeOH).

*(2*R, *3*S*)-(−)-2,3-Dimethyl-4-phenylbutanoic Acid, (−)-**28**.* Bp 145 °C at 1.5 mmHg. $[\alpha]^{25}$ −28.8 ±0.4° (*c* 1.510, MeOH).

*(2*S, *3*S*)-(+)-2,3-Dimethyl-1,2,3,4-tetrahydro-1-naphthalenone, (+)-**29**.* Mp 34—36 °C; $[\alpha]^{25}$ +49.6 ±0.3° (*c* 2.353, hexane).

*(2*S, *3*S*)-(+)-2,3-Dimethyl-1,2,3,4-tetrahydronaphthalene, (+)-**30**.* The product was crystallized from hexane with cooling in a Dry Ice–acetone bath. The crystals were collected at that temperature. The crystals were recrystallized by the same method and then distilled, $[\alpha]_D^{25}$ +103.9 ±0.9° (*c* 1.139, hexane). The NMR spectrum did not show the signal attributable to *meso*-2,3-dimethyl-1,2,3,4-tetrahydronaphthalene.

*(+)-ω-Camphanic Ester of (1*R, *2*S*)-2-Methyl-1,2,3,4-tetrahydro-1-naphthol, (+)-**31**.* The (+)-alcohol (**32**) was treated according to the procedure cited for **4**. The ester was recrystallized five times from methanol; mp 128.5—129.5 °C; $[\alpha]_D^{25}$ +31.0 ±0.6° (*c* 1.020, $CHCl_3$); IR (Nujol) 1789, 1737 cm^{-1}; NMR ($CDCl_3$) δ=0.95 (s, 3H), 1.04 (d, *J*=6 Hz, 3H), 1.06 (s, 3H), 1.09 (s, 3H), 1.5—3.0 (m, 9H), 5.94 (d, *J*=6 Hz, 1H), 7.18 (s, 4H). Found: C, 73.40; H, 7.65%. Calcd for $C_{21}H_{26}O_4$: C, 73.66; H, 7.65%.

*(1*R, *2*S*)-(−)-2-Methyl-1,2,3,4-tetrahydro-1-naphthol, (−)-**32**.* Mp 55—56 °C; $[\alpha]_D^{24}$ −92.9 ±0.7° (*c* 1.375, benzene); (lit,[7] −91.6); CD 274.5 nm ($\Delta\varepsilon$ −0.030), 269 (−0.055), 261.5 (−0.045), 205! (−2.85).

*(2*S*)-(−)-2-Methyl-1,2,3,4-tetrahydronaphthalene, (−)-**33**.* $[\alpha]_D^{25}$ −103.4 ±1.3° (*c* 1.281, dioxan).

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