Syntheses of Rotational Isomers of Substituted 9-*t*-Butyltriptycenes That Carry an Oxygen Substituent in *t*-Butyl Group and Outstanding Steric Effects Observed in the Synthesis of an Intermediate

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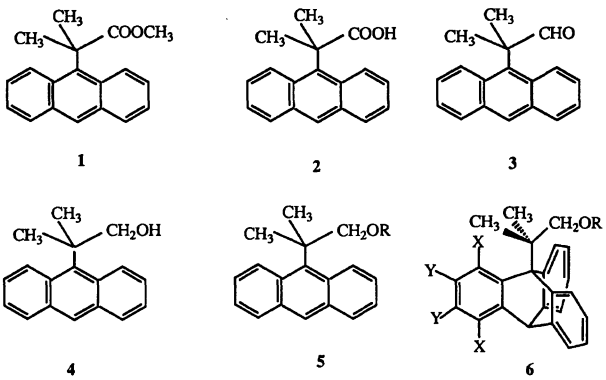
The title rotational isomers were synthesized. Reduction of methyl 2-(9-anthryl)-2-methylpropanoate caused difficulty due to severe steric effects. Thus the compound was converted to the free acid by treating it with a lithium thiolate and the resulted acid was reduced to the corresponding alcohol with borane. The alcohol was protected as either an acetate or a silyl ether and was subjected to the reaction with a benzyne. The resulted rotamers of triptycenes were separated by chromatography. Rotamers that carry an acetoxy, a hydroxy, or a *t*-butoxy substituent were prepared.

Syntheses of 9-*t*-butyltriptycenes that carry an oxygenated substituent in the *t*-butyl group are of interest. Diazotization of substituted 2-methyl-2-(9-triptycyl)-propylamine with isopentyl nitrite and acetic acid in benzene affords the corresponding acetate in a minute to a good yield.[1,2] Thermal decomposition of *t*-butyl 3-methyl-3-(substituted 9-triptycyl)peroxybutanoates affords a minute amount of the corresponding *t*-butyl ether.[3] Yet, due to paucity of the samples, characterization and use of these compounds to other reactions were limited. If these compounds were made in ample amount, they could be used for reactions that produce cations and radicals, in which we have been interested,[4] because alcohols are known to be derived to esters which would produce cations[5] and radicals.[6,7]

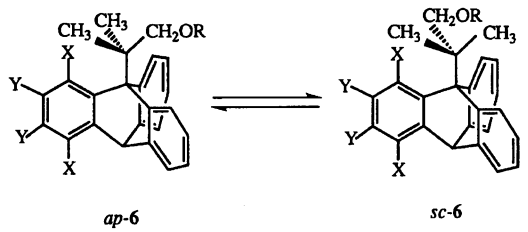
At the outset of this investigation, we expected that the synthesis of these compounds was straightforward. Since we knew that methyl 2-(9-anthryl)-2-methylpropanoate (**1**) could be prepared,[8] reduction of the compound should give 2-(9-anthryl)-2-methylpropanol (**4**), and protection of the hydroxyl group by a suitable means followed by a Diels–Alder reaction with a benzyne should give the corresponding triptycene (**6**). However, the reduction of the ester (**1**) posed difficulties due to steric effects. The ester group was never reduced to the alcohol without reducing the anthracene skeleton, the resulted 9,10-dihydro derivative being never converted back to the desired anthracene **4**. Thus we had to select a reducing reagent that was small in its size and preferred reduction of a carbonyl group more than a substituted anthracene skeleton.

The least sterically demanding reducing reagent of the carbonyl group is believed to be borane, which is applied to reduction of a free carboxylic acid.[9] Therefore, compound **1** must be converted to the free acid. Even the hydrolysis of the ester was extremely difficult under conventional conditions such as using alkali hydroxide or alkali hydroperoxide. We chose the method which should be least affected by the steric hindrance for converting compound **1** to **2**: S_N2 type removal of the methyl group by a lithium thiolate[10] was employed and we were able to obtain the acid (**2**) successfully (Scheme 1). The free acid thus produced was submitted to reduction by borane and the desired alcohol was prepared in a satisfactory yield. The extreme steric hindrance in the reaction is demonstrated by the fact that the corresponding aldehyde (**3**) was isolated from the products if the reaction was terminated after 72 h at room temperature. We believe this is a rare case in which an aldehyde can survive under lithium aluminium hydride reduction conditions for some time. However, the aldehyde could be reduced to the alcohol by subsequent reduction.

The alcohol **4** was protected as an acetate, **5**: R=$COCH_3$, or a trimethylsilyl ether, **5**: R=$Si(CH_3)_3$, the former of which was used for the reaction with a benzyne produced from an anthranilic acid and the latter of which was used for that with a benzyne produced from an *o*-halophenyllithium. The triptycenes **6** were prepared in satisfactory yields, the product being rich in *ap*-isomer as is typical in the synthesis of triptycenes of this type.[11] The product was heated either in tetralin or in 1-chloronaphthalene to isomerize (Scheme 2), except for the case of compound **6** with 1,4-dimethoxy substituents, for 12 or more hours, according to our knowledge of barriers to rotation,[12,13] and a ca. 1:1 mixture of *ap*:*sc* rotamers was obtained. This mixture as it was or a deprotected mixture was submitted to



Scheme 1. Compounds related to reduction of methyl 2-(9-anthryl)-2-methylpropanoate to alcohol and the corresponding triptycene.



Scheme 2. Preparation of rotamers of triptycenes.

HPLC on silica gel, which successfully separated the respective rotamers.

Isomerization of the rotational isomers posed difficulty in the case of 2-(1,4-dimethoxy-9-triptycyl)-2-methylpropyl acetate (**6**: X=OCH_3, Y=H, R=$COCH_3$), because some side reactions took place during the isomerization reaction. Thus we removed the acetyl group and the free alcohol (**6**: X=OCH_3, Y=R=H) was submitted to isomerization by heating for a short time to give a satisfactory result.

The protecting group of the hydroxyl group was removed in the case of acetate and the free alcohol was *t*-butylated. Since our triptycene skeleton is sensitive to strongly acidic conditions, we selected mildly acidic conditions for *t*-butylation. *t*-Butyl trichloroacetimidate and boron trifluoride method[14] gave satisfactory results for the *ap*-1,4-dimethoxy and *ap*- and *sc*-1,4-dimethyl compounds. The *sc*-1,4-dimethoxy compound was prepared by converting the free alcohol to trimethylsilyl ether[15] and then treating the product with *t*-butyl bromide and boron trifluoride by referring to the acylation procedure of silyl ethers.[16]

For the protection of the hydroxyl group in the synthesis of tetrahalotriptycenes (**6**: X=F or Cl), we first tried to introduce a methoxymethyl group to the alcohol **4** under normal conditions.[17] This treatment gave a complex mixture, from which a pure sample was never obtained. Thus we used a trimethylsilyl group for protection to obtain a satisfactory result.[15]

Treatment of the trimethylsilyl ether, **5**: R=Si(CH_3)$_3$, with tetrahalobenzynes generated from *o*-halophenyllithium derivatives afforded triptycenes, **6**: X=F or Cl, R=Si(CH_3)$_3$, in satisfactory yields. Separation of the rotational isomers as well as purification of the products was difficult as the trimethylsilyl ether. Thanks to the formation of intramolecular hydrogen bonding in the *sc*-isomers, it was possible to separate them when the protecting group was removed[18] and the products (**6**: X=F or Cl, R=H) were submitted to HPLC.

Experimental

Melting points are not corrected. ^{1}H NMR spectra were recorded on a Varian Gemini-300 machine which operated at 300 MHz. Elemental analyses were carried out on a Perkin–Elmer Analyser.

2-(9-Anthryl)-2-methylpropanoic Acid (2). A mixture of 1.20 g (0.151 mol) of powdered lithium hydride, 4.00 mL (4.40×10^{-2} mol) of 1-propanethiol, and 40 mL of DMSO was stirred for 1 h at room temperature and then excess of lithium hydride was removed by filtration. To the filtrate, was added 800 mg (2.98×10^{-3} mol) of methyl 2-(9-anthryl)-2-methylpropanoate (**1**)[8] and the solution was stirred at room temperature for 2.5 h. The mixture was poured into 600 mL of 2 mol L^{-1} hydrochloric acid and extracted with ether. The ether extract was evaporated after drying and the residue was submitted to chromatography on silica gel (1:1 hexane–dichloromethane). The desired compound was obtained in 78% yield. The analytical sample was obtained by recrystallization from dichloromethane–hexane, mp 222—223 °C. Found: C, 81.92; H, 6.18%. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10%. ^{1}H NMR ($CDCl_3$) δ=2.17 (6H, s), 7.35—7.46 (4H, m), 7.96—8.05 (2H, m), 8.22—8.31 (2H, m), 8.38 (1H, s).

Reduction of the Acid (2) with Borane. To a solution of 255 mg (1.00×10^{-3} mol) of the acid in 25 mL of THF, was added 3.00 mL (3.00×10^{-3} mol) of 1 mol L^{-1} borane THF solution at 0 °C and the mixture was stirred at room temperature for 72 h. The mixture was quenched with aqueous sodium chloride and extracted with dichloromethane. After evaporation of the solvent, the residue was submitted to chromatography on silica gel (1:1 hexane–dichloromethane) to afford the aldehyde (**3**), the alcohol (**4**), and the carboxylic acid (**2**) in this order. The alcohol was recrystallized from THF–hexane, mp 75—76 °C. The yield was 75%. Found: C, 86.08; H, 7.02%. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25%. ^{1}H NMR ($CDCl_3$) δ=1.45 (1H, t, J=6.9 Hz), 1.88 (6H, s), 4.39 (2H, d, J=6.9 Hz), 7.30—7.42 (4H, m), 7.91—7.99 (2H, m), 8.29 (1H, s), 8.49—8.59 (2H, m).

The aldehyde was obtained in 7% yield and was recrystallized from THF–hexane, mp 85—86 °C. Found: C, 86.08; H, 7.02%. Calcd for $C_{18}H_{16}O$: C, 86.35; H, 7.25%. ^{1}H NMR ($CDCl_3$) δ=1.95 (6H, s), 7.39—7.45 (4H, m), 7.98—8.03 (2H, m), 8.07—8.14 (2H, m), 8.39 (1H, s), 9.50 (1H, s).

Reduction of Aldehyde 3 to Alcohol 4. The reduction was carried out as above with borane in THF for 24 h. The alcohol, which was identical with the authentic specimen, was obtained in 85% yield.

1-(9-Anthryl)-1-methylpropyl Acetate (5: R=COCH_3). A solution of 81.4 mg (3.26×10^{-4} mol) of the alcohol and 69.4 μL (9.76×10^{-4} mol) of acetyl chloride and 131 μL (1.63×10^{-3} mol) of pyridine in 5.0 mL of THF was stirred at room temperature for 30 min and poured into dilute hydrochloric acid. The mixture was extracted with ether and the product was chromatographed on silica gel (1:1 hexane–dichloromethane eluent). It was obtained in 51% yield after recrystallization from dichloromethane–hexane, mp 61.5—62.5 °C. Found: C, 82.01; H, 6.80%. Calcd for $C_{20}H_{20}O_2$: C, 82.16; H, 6.89%. ^{1}H NMR ($CDCl_3$) δ= 1.89 (6H, s), 1.93 (3H, s), 4.89 (2H, s), 7.20—7.53 (4H, m), 7.83—8.03 (2H, s), 8.30 (1H, s), 8.40—8.70 (2H, m).

1-(9-Anthryl)-1-methylpropyl Trimethylsilyl Ether [5: R=Si(CH_3)$_3$]. To a mixture of 912 mg (3.64×10^{-3} mol) of the alcohol in 5.0 mL of THF, were added 583 μL (7.27×10^{-3} mol) of pyridine and 556 μL (4.37×10^{-3} mol) of trimethylsilyl chloride, and the whole was stirred at room temperature for 3 h. Pyridinium chloride was filtered off and the volatile materials were evaporated from the filtrate in vacuo. The residue was purified by chromatography on silica gel (hexane eluent). This product was used for the next preparation without further purification. The follow-

ing ^{1}H NMR ($CDCl_3$, δ) data were recorded: 0.00 (9H, s), 1.80 (6H, s), 4.34 (2H, s), 7.23—7.40 (4H, m), 7.88—7.98 (2H, m), 8.25 (1H, s), 8.45—8.63 (2H, m).

2-(1,4-Dimethyl-9-triptycyl)-2-methylpropyl Acetates (6: X=CH_3, Y=H, R=$COCH_3$). To a boiling solution of 222 mg (7.55×10^{-4} mol) of the acetate and 77.0 μL (7.55×10^{-4} mol) of isopentyl nitrite in 20 mL of dichloromethane, were simultaneously added a solution of 249 mg (1.51×10^{-3} mol) of 3,6-dimethylanthranilic acid[19] in 10 mL of acetone and that of 102 μL (1.51×10^{-3} mol) of isopentyl nitrite in 10 mL of dichloromethane from separate separatory funnels in 1 h. The mixture was heated under reflux for further 1 h and the solvent was evaporated. The residue was chromatographed on silica gel (1:1 dichloromethane–hexane) to afford 57% of the desired compound which contained mostly the *ap*-isomer and a small amount of the *sc*-isomer.

The product (356 mg) was dissolved in 80 mL of 1-chloronaphthalene and heated under reflux for 12 h. The solvent was evaporated and the residue was chromatographed on silica gel (10:1 hexane–ether), when the *sc* and *ap* forms were eluted in this order. The analytical samples were obtained by recrystallization from tetrahydrofuran–hexane.

ap-Isomer: Mp 299—300 °C, yield 27%. Found: C, 84.67; H, 6.92%. Calcd for $C_{28}H_{28}O_2$: C, 84.81; H, 7.12%. ^{1}H NMR ($CDCl_3$) δ=2.24 (3H, s), 2.27 (6H, s), 2.49 (3H, s), 2.66 (3H, s), 5.13 (2H, s), 5.59 (1H, s), 6.75 (2H, s), 6.98—7.01 (4H, m), 7.35—7.38 (2H, m), 7.84—7.86 (2H, m).

sc-Isomer: Mp 267—268 °C, yield 26%. Found: C, 84.67; H, 7.09%. Calcd for $C_{28}H_{28}O_2$: C, 84.81; H, 7.12%. ^{1}H NMR ($CDCl_3$) δ=2.08 (3H, s), 2.20 (3H, s), 2.25 (3H, s), 2.51 (3H, s), 2.56 (3H, s), 4.87 and 5.42 (2H, ABq, J=12.3 Hz), 5.59 (1H, s), 6.74 and 6.77 (2H, ABq, J=7.9 Hz), 6.97—7.01 (4H, m), 7.35—7.37 (2H, m), 7.84—7.90 (2H, m).

2-(1,4-Dimethyl-9-triptycyl)-2-methyl-1-propanols (6: X=CH_3, Y=R=H). To a slurry of 19.2 mg (5.05×10^{-4} mol) of lithium aluminium hydride in 20 mL of ether, was added 200 mg (5.05×10^{-4} mol) of the acetate in 40 mL of ether and the mixture was stirred for 30 min at room temperature. The excess of lithium aluminium hydride was decomposed with methanol and dilute hydrochloric acid was added. The aqueous layer was extracted with ether and the extracts were dried. After evaporation of the solvent the residue was chromatographed on silica gel (1:1 hexane–dichloromethane eluent). The product was recrystallized from THF–hexane.

ap-Isomer: Mp 194—196 °C (decomp), yield 81%. Found: C, 88.09; H, 7.39%. Calcd for $C_{26}H_{26}O$: C, 88.28; H, 7.32%. ^{1}H NMR ($CDCl_3$) δ=2.30 (6H, s), 2.49 (3H, s), 2.67 (3H, s), 4.60 (2H, s), 5.56 (1H, s), 6.75 (2H, s), 6.75—7.03 (4H, m), 7.20—7.43 (2H, m), 7.70—7.96 (2H, m). No OH proton signal was observed.

sc-Isomer: Mp 189—193 °C (decomp), yield 81%. Found: C, 87.97; H, 7.12%. Calcd for $C_{26}H_{26}O$: C, 88.28; H, 7.32%. ^{1}H NMR ($CDCl_3$) δ=2.10 (3H, s), 2.13 (3H, s), 2.50 (3H, s), 2.60 (3H, s), 4.43 and 4.85 (2H, ABq, J=12.0 Hz), 5.57 (1H, s), 6.75 (2H, s), 6.83—7.10 (4H, m), 7.13—7.45 (2H, m), 7.65—8.03 (2H, m). No OH proton signal was observed.

***t*-Butyl 2-(1,4-Dimethyl-9-triptycyl)-2-methylpropyl Ethers [6: X=CH_3, Y=H, R=$C(CH_3)_3$].** To a solution of 75.0 mg (2.12×10^{-4} mol) of the alcohol in 5 mL of hexane were added 51.0 mg (2.33×10^{-4} mol) of *t*-butyl trichloroacetimidate[14] and 4.0 μL of boron trifluoride etherate and the whole was stirred for 12 h at room temperature. In the case of the *sc*-isomer, it was necessary to stir for 20 h for completion of the reaction. Sodium hydrogencarbonate was added and the product was purified by preparative TLC (dichloromethane eluent). The analytical samples were obtained by recrystallization from THF–hexane.

ap-Isomer: Mp 230—233 °C (decomp), yield 49%. Found: C, 87.50; H, 8.46%. Calcd for $C_{30}H_{34}O$: C, 87.76; H, 8.35%. ^{1}H NMR ($CDCl_3$) δ=1.23 (9H, s), 2.22 (6H, s), 2.46 (3H, s), 2.65 (3H, s), 4.21 (2H, s), 5.55 (1H, s), 6.71 (2H, s), 6.78—7.04 (4H, m), 7.25—7.41 (2H, m), 7.70—8.00 (2H, m).

sc-Isomer: Mp 201—203 °C, yield 52%. Found: C, 87.76; H, 8.35%. Calcd for $C_{30}H_{34}O$: C, 87.76; H, 8.35%. ^{1}H NMR ($CDCl_3$) δ=1.30 (9H, s), 2.05 (3H, s), 2.10 (3H, s), 2.51 (3H, s), 2.62 (3H, s), 4.07 and 4.40 (2H, ABq, J=12.0 Hz), 5.57 (1H, s), 6.75 (2H, s), 6.83—7.10 (4H, m), 7.13—7.45 (2H, m), 7.65—8.03 (2H, m).

Addition of 3,6-Dimethoxybenzyne to the Anthracene. This reaction was carried out similarly as above with use of the acetate and 3,6-dimethoxyanthranilic acid.[20] The solvent for the reaction was DME. A mixture of *ap* and *sc* isomers (**6**: X=OCH_3, Y=H, R=$COCH_3$) was obtained in 52% yield.

2-(1,4-Dimethoxy-9-triptycyl)-2-methyl-1-propanols (6: X=OCH_3, Y=R=H). The mixture of the acetate was treated with lithium aluminium hydride as above and the alcohol was obtained in 82% yield. The alcohol mixture in 1-chloronaphthalene was heated for 2 h under reflux and the resulted isomers were separated by chromatography on silica gel (1:1 hexane–dichloromethane eluent) followed by HPLC (2:3 hexane–ether eluent), when the *sc*-isomer was first eluted and the *ap*-isomer followed. The analytical sample was obtained by recrystallization from THF–hexane.

ap-Isomer: Mp 271—272 °C (decomp), yield 38%. Found: C, 81.07; H, 6.91%. Calcd for $C_{26}H_{26}O_3$: C, 80.80; H, 6.78%. ^{1}H NMR ($CDCl_3$) δ=2.12 (6H, s), 3.74 (3H, s), 3.80 (3H, s), 4.60 (2H, s), 5.87 (1H, s), 6.58 and 6.62 (2H, ABq, J=9.0 Hz), 6.93—7.01 (4H, m), 7.39—7.42 (2H, m), 7.82—7.85 (2H, m). No OH proton signal was observed.

sc-Isomer: Mp 260—261 °C (decomp), yield 32%. Found: C, 80.67; H, 6.80%. Calcd for $C_{26}H_{26}O_3$: C, 80.80; H, 6.78%. ^{1}H NMR ($CDCl_3$) δ=2.00 (3H, s), 2.05 (3H, s), 3.79 (3H, s), 3.83 (3H, s), 4.47 and 4.55 (2H, ABq, J=11.6 Hz), 5.90 (1H, s), 6.58 and 6.63 (2H, ABq, J=7.7 Hz), 6.95—7.00 (4H, m), 7.38—7.43 (2H, m), 7.79—7.85 (1H, m), 7.90—7.96 (1H, m). No OH proton signal was detected.

2-(1,4-Dimethoxy-9-triptycyl)-2-methylpropyl Acetates (6: X=OCH_3, Y=H, R=$COCH_3$). The acetylation of the alcohols was carried out as described for the preparation of compound **6** (X=CH_3, Y=H, R=$COCH_3$). It was necessary to allow the reaction to proceed for 2 and 3 h, respectively, to complete for *ap* and *sc* isomers. The products were recrystallized from THF–hexane.

ap-Isomer: Mp 294—295 °C, yield 86%. Found: C, 78.25; H, 6.61%. Calcd for $C_{28}H_{28}O_4$: C, 78.48; H, 6.59%. ^{1}H NMR ($CDCl_3$) δ=2.08 (3H, s), 2.24 (3H, s), 3.73 (3H, s), 3.80 (3H, s), 5.12 (2H, s), 5.88 (1H, s), 6.58 and 6.62 (2H, ABq, J=9.0 Hz), 6.95—7.01 (4H, m), 7.39—7.42 (2H, m), 7.83—7.87 (2H, m).

sc-Isomer: Mp 249—259 °C (decomp), yield 80%. Found:

C, 78.45; H, 6.64%. Calcd for $C_{28}H_{28}O_4$: C, 78.48; H, 6.59%. ^{1}H NMR ($CDCl_3$) δ=2.00 (3H, s), 2.07 (3H, s), 2.25 (3H, s), 3.73 (3H, s), 3.81 (3H, s), 5.04 and 5.22 (2H, ABq, J=11.5 Hz), 5.89 (1H, s), 6.57 and 6.63 (2H, ABq, J=10.1 Hz), 6.95—7.03 (4H, m), 7.38—7.43 (2H, m), 7.83—7.90 (2H, m).

***t*-Butyl *ap*-2-(1,4-Dimethoxy-9-triptycyl)-2-methylpropyl Ether [6: X=OCH_3, Y=H, R=$C(CH_3)_3$].** This compound was prepared similarly as above. The yield was 43%. It was recrystallized from THF–hexane, mp 298—300 °C. Found: C, 81.52; H, 8.51%. Calcd for $C_{30}H_{34}O_3$: C, 81.31; H, 8.53%. ^{1}H NMR ($CDCl_3$) δ=1.26 (9H, s), 2.06 (6H, s), 3.72 (3H, s), 3.80 (3H, s), 4.20 (2H, s), 5.87 (1H, s), 6.57 and 6.61 (2H, ABq, J=10.6 Hz), 6.95—6.98 (4H, m), 7.38—7.41 (2H, m), 7.85—7.88 (2H, m).

***t*-Butyl *sc*-2-(1,4-Dimethoxy-9-triptycyl)-2-methylpropyl Ether [6: X=OCH_3, Y=H, R=$C(CH_3)_3$].** A mixture of 211 mg (5.47×10^{-4} mol) of the alcohol, 32.8 mg (8.21×10^{-4} mol) of sodium hydride (ca. 60% suspension in oil) and 40.0 mL of DMSO was stirred for 1 h at room temperature and then 104 μL (8.21×10^{-4} mol) of trimethylsilyl chloride was added. The whole was stirred for further 4 h and then 93.7 μL (8.21×10^{-4} mol) of *t*-butyl bromide and 13.4 μL of boron trifluoride–diethyl ether complex were added. The reaction was allowed to proceed for 12 h. A small amount of methanol was added and then dilute hydrochloric acid. The mixture was diluted with water and extracted with ether. The product was, after evaporation of the solvent, chromatographed on silica gel (1 : 1 hexane–dichloromethane eluent), when trimethylsilyl ether (10%), *t*-butyl ether (43%), and the starting alcohol (12%) were eluted in this order. The *t*-butyl ether was recrystallized from THF–hexane, mp 282—284 °C. Found: C, 81.60; H, 8.80%. Calcd for $C_{30}H_{34}O_3$: C, 81.31; H, 8.53%. ^{1}H NMR ($CDCl_3$) δ=1.26 (9H, s), 1.94 (3H, s), 2.03 (3H, s), 3.73 (3H, s), 3.81 (3H, s), 4.40 and 4.43 (2H, ABq, J=10.6 Hz), 5.87 (1H, s), 6.55 and 6.61 (2H, ABq, J=7.7 Hz), 6.95—6.99 (4H, m), 7.37—7.40 (2H, m), 7.92—7.94 (2H, m).

The following ^{1}H NMR data ($CDCl_3$, δ) were recorded for the trimethylsilyl ether: 0.21 (9H, s), 1.95 (3H, s), 2.04 (3H, s), 3.73 (3H, s), 3.81 (3H, s), 4.40 and 4.43 (2H, ABq, J=10.6 Hz), 5.87 (1H, s), 6.55 and 6.61 (2H, ABq, J=7.7 Hz), 6.95—6.99 (4H, m), 7.37—7.40 (2H, m), 7.92—7.94 (2H, m).

In order to test whether the alcohol was an artifact during the process of the products, the trimethyl silyl ether was treated with *t*-butyl bromide and boron trifluoride–diethyl ether complex in DMSO as above. The reaction was followed by TLC, which indicated that the reaction did not proceed further after 12 h. The reaction mixture was treated similarly and 44% *t*-butyl ether, 14% trimethylsilyl ether, and 11% starting alcohol were obtained. Thus, at least, some of the alcohol was a true product from the reaction.

2-Methyl-2-(1,2,3,4-tetrafluoro-9-triptycyl)-1-propanols (6: X=Y=F, R=H). To a solution of 2.40 mL (18.6×10^{-3} mol) of chloropentafluorobenzene in 50 mL of ether was added 11.5 mL (18.6×10^{-3} mol) of butyllithium in hexane with cooling in a Dry Ice–acetone bath. The mixture was stirred for 2 h at the temperature and 1.21 g (3.75×10^{-3} mol) of the trimethylsilyl ether [**5**: R=Si(CH_3)$_3$] in 10 mL of ether was added. Stirring was continued for further 2 h at the temperature and the temperature was allowed to rise to room temperature during the night. The mixture was heated under reflux for 2 h and was decomposed with dilute hydrochloric acid. The mixture was extracted with ether and the solvent was evaporated. The residue was chromatographed on silica gel (hexane eluent) to give a mixture of *ap* and *sc* triptycenes, which still contained some impurities.

The trimethylsilyl ether (2.71 g including impurities) was dissolved in 20 mL of THF and 5.3 mL of 1 mol L^{-1} solution of tetrabutylammonium fluoride in THF was added. The solution was stirred for 0.5 h at room temperature, diluted with water and extracted with dichloromethane. A mixture of alcohols, which contained impurities, was obtained in 796 mg yield after chromatography of the product on silica gel (1 : 1 hexane–dichloromethane), the *ap*/*sp* ratio being 2 : 1. The mixture of alcohols was dissolved in 10 mL of tetralin and the solution was heated under reflux for 12 h. Solvent was removed by vacuum distillation and the residue was chromatographed on silica gel (1 : 1 hexane–dichloromethane), when the *ap*/*sc* ratio was 4 : 3. The separation of the rotamers was accomplished by HPLC (1 : 10 hexane–dichloromethane eluent), when *sc*-isomer was eluted first and then the *ap*. The analytical samples were obtained by recrystallization from THF–hexane.

ap-Isomer: Yield 9.3%, mp 261.5—262.5 °C. Found: C, 72.11; H, 4.49%. Calcd for $C_{24}H_{18}F_4O$: C, 72.36; H, 4.55%. ^{1}H NMR ($CDCl_3$) δ=1.87 (1H, t, J=5.8 Hz), 2.07 (6H, d, J=8.3 Hz), 4.59 (2H, d, J=5.8 Hz), 5.69 (1H, s), 7.00—7.11 (4H, m), 7.38—7.48 (2H, m), 7.77—7.88 (2H, m).

sc-Isomer: Yield 6.9%, mp 272.5—273.5 °C. Found: C, 72.21; H, 4.50%. Calcd for $C_{24}H_{18}F_4O$: C, 72.36; H, 4.55%. ^{1}H NMR ($CDCl_3$) δ=1.65 (1H, d, J=8.5 Hz), 1.99 (3H, d, J=8.5 Hz), 2.10 (3H, s), 4.28 and 4.59 (2H, AB of ABX, where X=F, J_{AB}=11.5 Hz, J_{AX}=3.9 Hz, J_{BX}=3.6 Hz), 5.69 (1H, d, J=1.3 Hz), 7.01—7.12 (4H, m), 7.38—7.47 (2H, m), 7.84—7.95 (2H, m).

2-Methyl-2-(1,2,3,4-tetrafluoro-9-triptycyl)propyl Acetates (6: X=Y=F, R=$COCH_3$). Acetylation of the alcohol was similarly carried out with use of acetic anhydride and pyridine. The reaction period was 1 h for the *ap* and 2 h for the *sc* at room temperature. The analytical samples were obtained by recrystallization from THF–hexane.

ap-Isomer: Mp 173.5—175.0 °C, yield 91%. Found: C, 70.79; H, 4.51%. Calcd for $C_{26}H_{20}F_4O_2$: C, 70.90; H, 4.58%. ^{1}H NMR ($CDCl_3$) δ=2.04 (6H, d, J=8.6 Hz), 2.27 (3H, s), 5.11 (2H, s), 5.70 (1H, s), 7.03—7.12 (4H, m), 7.40—7.48 (2H, m), 7.80—7.89 (2H, m).

sc-Isomer: Mp 117.0—119.5 °C, yield 89%. Found: C, 71.11; H, 4.64%. Calcd for $C_{26}H_{20}F_4O_2$: C, 70.90; H, 4.58%. ^{1}H NMR ($CDCl_3$) δ=2.04 (3H, d, J=8.0 Hz), 2.05 (3H, s), 2.26 (3H, s), 4.71 and 5.18 (2H, AB of ABX, where X=F, J_{AB}=11.6 Hz, J_{AX}=3.8 Hz, J_{BX}=0 Hz), 5.69 (1H, s), 7.01—7.12 (4H, m), 7.38—7.47 (2H, m), 7.80—7.90 (2H, m).

***t*-Butyl 2-Methyl-2-(1,2,3,4-tetrafluoro-9-triptycyl) Ethers [6: X=Y=F, R=$C(CH_3)_3$].** These compounds were similarly prepared from the corresponding alcohols as described for the preparation of the 1,4-dimethyl compound except that some dichloromethane was added to increase the solubility of the substrate. The analytical samples were obtained by recrystallization from methanol.

ap-Isomer: Yield 69%, mp 99.5—102.0 °C. Found: C,

73.86; H, 5.67%. Calcd for $C_{28}H_{26}F_4O$: C, 73.99; H, 5.77%. ^{1}H NMR ($CDCl_3$) δ=1.27 (9H, s), 2.00 (6H, d, J=8.2 Hz), 4.18 (2H, s), 5.69 (1H, s), 7.00—7.10 (4H, m), 7.38—7.47 (2H, m), 7.81—7.90 (2H, m).

sc-Isomer: Yield 72%, mp 94.5—96.5 °C. Found: C, 73.86; H, 5.71%. Calcd for $C_{28}H_{26}F_4O$: C, 73.99; H, 5.77%. ^{1}H NMR ($CDCl_3$) δ=1.28 (9H, s), 1.99 (3H, d, J=8.0 Hz), 2.00 (3H, s), 3.94 and 4.15 (2H, AB of ABX, where X=F, J_{AB}=9.3 Hz, J_{AX}=3.8 Hz, J_{BX}=3.3 Hz), 5.68 (1H, s), 6.94—7.14 (4H, m), 7.36—7.45 (2H, m), 7.87—7.98 (1H, m), 8.00—8.10 (1H, m).

2-Methyl-2-(1,2,3,4-tetrachloro-9-triptycyl)-1-propanol (6: X=Y=Cl, R=H). To a solution of 4.36 g (15.3×10^{-3} mol) of hexachlorobenzene in 50 mL of ether was added 9.50 mL (15.3×10^{-3} mol) of butyllithium in hexane with cooling by a Dry-Ice–acetone bath. The mixture was stirred for 6 h at the temperature and 987 mg (1.36×10^{-3} mol) of the trimethylsilyl ether in 10 mL of ether was added. The mixture was stirred at −78 °C for 2 h, the temperature of the reaction mixture was allowed to rise to room temperature in 12 h, and then the mixture was heated under reflux for 2 h. After usual treatment, like the one shown in the tetrafluoro compound, the triptycene was obtained as a mixture of *ap* and *sc* in 1.82 g yield. The protective group of the trimethylsilyl ether was removed as for the fluoro compound, the *sc*-isomer was enriched to 2:3 *ap*/*sc* ratio from that of 7:2 by heating in tetralin for 12 h, and the mixture of the propanol rotamers thus obtained was purified by HPLC (1:5 hexane–dichloromethane), when *sc* isomer was more easily eluted than the *ap*. The analytical samples were obtained by recrystallization from hexane–dichloromethane.

ap-Isomer: Yield 14%, mp 266.5—268.5 °C. Found: C, 61.86; H, 3.81%. Calcd for $C_{24}H_{18}Cl_4O$: C, 62.10; H, 3.91%. ^{1}H NMR ($CDCl_3$) δ=1.86 (1H, t, J=6.0 Hz), 2.36 (6H, s), 4.52 (2H, d, J=6.0 Hz), 6.07 (1H, s), 6.99—7.13 (4H, m), 7.41—7.49 (2H, m), 7.89—7.98 (2H, m).

sc-Isomer: Yield 21%, mp 225—226 °C. Found: C, 62.29; H, 3.85%. Calcd for $C_{24}H_{18}Cl_4O$: C, 62.10; H, 3.91%. ^{1}H NMR ($CDCl_3$) δ=2.01 (1H, br s), 2.04 (3H, s), 2.24 (3H, s), 4.71 and 4.75 (2H, ABq, J=12.2 Hz), 6.08 (1H, s), 7.03—7.13 (4H, m), 7.41—7.50 (2H, m), 7.96—8.12 (2H, m).

2-Methyl-2-(1,2,3,4-tetrachloro-9-triptycyl)propyl Acetates (6: X=Y=Cl, R=COCH$_3$). These compounds were similarly prepared as for the preparation of the 1,4-dimethyl compounds except that dichloromethane–hexane was used as a solvent. Analytical samples were obtained by recrystallization from hexane–dichloromethane.

ap-Isomer: Yield 86%, mp 216.5—218.0 °C. Found: C, 61.74; H, 3.91%. Calcd for $C_{26}H_{20}Cl_4O_2$: C, 61.69; H, 3.98%. ^{1}H NMR ($CDCl_3$) δ=2.25 (3H, s), 2.33 (6H, s), 5.04 (2H, s), 6.08 (1H, s), 7.03—7.14 (4H, m), 7.42—7.50 (2H, m), 7.89—7.98 (2H, m).

sc-Isomer: Yield 82%, mp 206.0—207.0 °C. Found: C, 61.74; H, 3.91%. Calcd for $C_{26}H_{20}Cl_4O_2$: C, 61.69; H, 3.98%. ^{1}H NMR ($CDCl_3$) δ=2.01 (3H, s), 2.24 (3H, s), 2.31 (3H, s), 5.18 and 5.26 (2H, ABq, J=11.9 Hz), 6.08 (1H, s), 6.98—7.18 (4H, m), 7.42—7.50 (2H, m), 7.90—8.02 (2H, m).

***t*-Butyl 2-Methyl-2-(1,2,3,4-tetrachloro-9-triptycyl)propyl Ethers [6: X=Y=Cl, R=C(CH$_3$)$_3$].** These compounds were prepared similarly as described for the preparation of 1,4-dimethyl compound except that a hexane–dichloromethane mixture was used as a solvent to increase the solubility of the *ap*-isomer. The analytical samples were obtained by recrystallization from methanol.

ap-Isomer: Yield 66%, mp 168—170 °C. Found: C, 64.79; H, 5.11%. Calcd for $C_{28}H_{26}Cl_4O$: C, 64.63; H, 5.04%. ^{1}H NMR ($CDCl_3$) δ=1.24 (9H, s), 2.30 (6H, s), 4.14 (2H, s), 6.07 (1H, s), 6.99—7.14 (4H, m), 7.40—7.51 (2H, m), 7.91—8.02 (2H, m).

sc-Isomer: Yield 63%, mp 207—208 °C. Found: C, 64.34; H, 5.12%. Calcd for $C_{28}H_{26}Cl_4O$: C, 64.63; H, 5.04%. ^{1}H NMR ($CDCl_3$) δ=1.30 (9H, s), 1.95 (3H, s), 2.25 (3H, s), 4.27 and 4.36 (2H, ABq, J=9.5 Hz), 6.06 (1H, s), 7.00—7.14 (4H, m), 7.40—7.49 (2H, m), 7.98—8.08 (1H, m), 8.22—8.30 (1H, m).

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