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Reactivities of Stable Rotamers. XXII. Lewis Acid-Catalyzed Reactions of 3-(1,4-Disubstituted 9-Triptycyl)-3-methylbutanoyl Chloride: Isolation of Rotameric Ketones and Competition between Cyclizations to Substituted and to Unsubstituted Benzene Rings[1,2]

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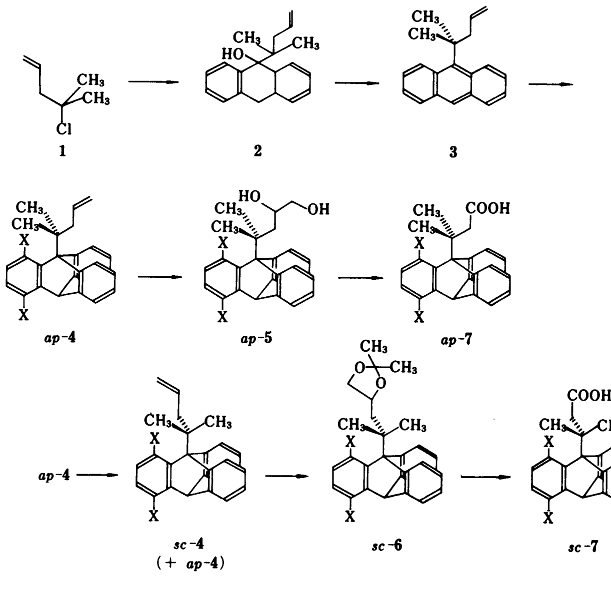
Rotational isomers of 3-(1,4-disubstituted 9-triptycyl)-3-methylbutanoic acid, where the substituent is either a methoxyl or a methyl, have been prepared, starting from 1,4-disubstituted 9-(1,1-dimethyl-3-butenyl)triptycene. Lewis acid-catalyzed reactions of the *ap*-acid chloride afforded corresponding ketones expected from the intramolecular Friedel–Crafts reaction. The *sc* form of the 1,4-dimethoxy compound gave a ketone that was formed by the reaction of the unsubstituted benzene ring and a lactone which was derived by the attack of the acylium ion on the methoxy-oxygen followed by demethylation. The *sc* form of the 1,4-dimethyl compound afforded a ketone which was expected from cyclization to the unsubstituted benzene ring and another ketone that was derived from the ipso attack of the acylium ion followed by 1,2-methide migration. In both cases, the ketone derived from the *ap* form of the acid chloride was different from that obtained from the *sc*. The barriers to isomerization of the *ap*-ketone to the *sc*-ketone was 29.6 kcal mol^{-1} at 100.5 °C and 25.6 kcal mol^{-1} at 56.0 °C for the methoxy and the methyl compounds, respectively. In both cases, the ketone derived from the *sc*-form was more stable than that from the *ap*, the *sc*/*ap* ratio at the equilibrium being 20.0 (56.0 °C) and 5.9 (100.5 °C), respectively, for the methyl and the methoxy compounds. In the reaction of the *sc* form, the competitive results between the cyclization toward the unsubstituted benzene ring and that toward the substituted vary according to the solvent and the Lewis acid used.

Since the isolation of rotational isomers in the triptycene and 9-arylfluorene series,[3] we have been interested in the study of reactivities of rotational isomers.[3] Due to the difficulty in the syntheses of the triptycene series, the examples that have been studied are rather limited: halogenation of a *t*-butyl group,[5] and some radical reactions[6] and cation-forming reactions[7] of the halogenated compounds. We now wish to report successful isolation of 3-(1,4-disubstituted 9-triptycyl)-3-methylbutanoic acid rotamers where the substituents are methyls or methoxyls and Lewis acid-catalyzed reactions of the corresponding acid chlorides.

Results

Syntheses of the compounds were carried out in the following ways. A Grignard reagent prepared from 4-chloro-4-methyl-1-pentene (**1**) was added to 9-anthrone and the adduct (**2**) was treated with phosphorus pentaoxide to form 9-(1,1-dimethyl-3-butenyl)anthracene (**3**). Addition of benzynes to the anthracene afforded the corresponding olefinic triptycenes (**4**), the *ap* isomer being the major product. Recrystallization of the product from hexane–dichloromethane afforded pure *ap*-form of **4**. The *ap*-olefins were oxidized with trimethylamine oxide in the presence of osmium tetraoxide[8] to the corresponding diols which were successively oxidized with periodic acid[9] and then with potassium permanganate to yield the desired *ap*-carboxylic acid (*ap*-**7**). Separation of the *sc*-isomers was tried at various stages of the synthesis of the carboxylic acid (**7**) but none of them was promising. Thus, although the number of steps required for the synthesis increased, we derived the corresponding diols to acetonides which were separated by chromatography. The best route to the prepartion of the *sc*-acid (*sc*-**7**) was the following. The



a: X=CH$_3$O b: X=CH$_3$

Scheme 1. Synthetic routes to 3-(1,4-disubstituted 9-triptycyl)-3-methylbutanoic acid rotamers: X is a methoxyl or a methyl. Only one form of the *sc* is shown.

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olefin (**4**) was heated in 1-chloronaphthalene to isomerize and the *sc*-enriched olefin was oxidized with trimethylamine oxide as above and the resulted diols **5** were converted to acetonides in the presence of *p*-toluenesulfonic acid. The acetonides (**6**) were separated by medium-pressure chromatography on silica gel, the *sc* form giving two diastereomers (two pairs of enantiomers) due to the fact that a new chiral center was formed in addition to the chirality due to the frozen rotation about the C_9-to-substituent bond. The separated two forms of *sc*-acetonides were hydrolyzed to regenerate the diols (*sc*-**5**) which were similarly oxidized with periodic acid and then with potassium permanganate to yield the *sc*-carboxylic acid (*sc*-**7**).

3-(1,4-Dimethoxy-9-triptycyl)-3-methylbutanoic acid (**7a**) was treated with oxalyl dichloride to produce the corresponding chloride which was then treated with titanium(IV) chloride in benzene. *ap*-**7a** gave the corresponding ketone (*ap*-**8a**) in a good yield, whereas *sc*-**7a** afforded the corresponding ketone (*sc*-**8a**) and a lactone (**9**) which was formed by the reaction of intervening acylium ion on the methoxy-oxygen followed by demethylation. The formation ratio, *sc*-**8a**/**9**, varied when the solvent and/or the catalyst was varied and the results are shown in Table 1. *ap*-**8** and *sc*-**8** were definitely different, though they melted at the same temperature and their analytical data as well as the spectral data were all consistent with the proposed structure, 8,11-dimethoxy-1,1-dimethyl-1,2-dihydro-7*H*-7,11b-*o*-benzeno-3*H*-benz[*de*]anthracen-3-one.

The similar treatment of *ap*-3-(1,4-dimethyl-9-triptycyl)-3-methylbutanoic acid (*ap*-**7b**) afforded the corresponding ketone (*ap*-**8b**) as a sole product. By contrast, *sc*-**7b** yielded under the similar conditions a ketone (*sc*-**8b**) which was conformationally isomeric with *ap*-**8b** and another ketone to which we assign structure **10** from spectroscopic evidence and from consideration of reaction mechanisms. The formation ratio, *sc*-**8b**/**10**, was affected again by the reaction conditions, solvent and Lewis acid. The results are summarized in Table 2.

Heating *ap*-**7b** with thionyl chloride afforded *ap*-**8b** and a vinyl chloride type compound (**11**) which could be independently synthesized from *ap*-**8b** and thionyl chloride. Similarly *sc*-**7b** afforded **11** and another vinyl chloride type compound(**12**) in addition to *ap*-**8b** and **10**, when it was heated with thionyl chloride. **12** was independently synthesized from **10** and thionyl chloride.

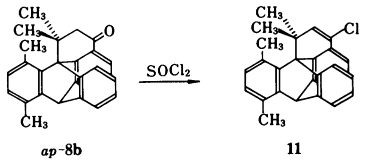


Table 1. The Effects of Solvent and Catalyst on the Formation Ratio, *sc*-**8a**/**9**, in the Reaction of *sc*-**7a** in the Presence of 2 Equivalents of the Lewis Acid

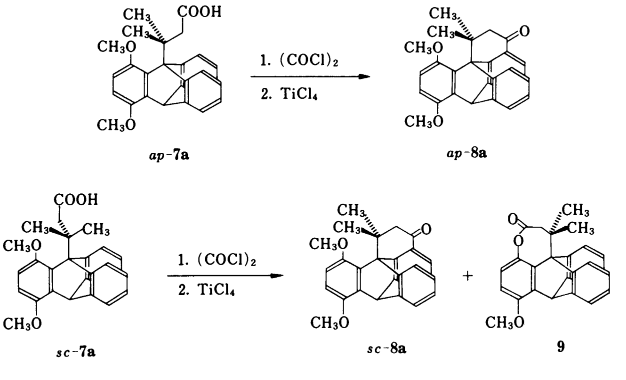
Solvent	Lewis acid	*sc*-**8a**/**9**
CH_2Cl_2	$TiCl_4$	42
C_6H_6	$TiCl_4$	6.0
C_6H_{12}[a]	$TiCl_4$	1.3
CH_2Cl_2	$SnCl_4$	1.7
C_6H_6	$SnCl_4$	0.42
C_6H_{12}[a]	$SnCl_4$	0.18
C_6H_6	$AlCl_3$	0.84
C_6H_{12}[a]	$AlCl_3$	0.49

a) Cyclohexane.

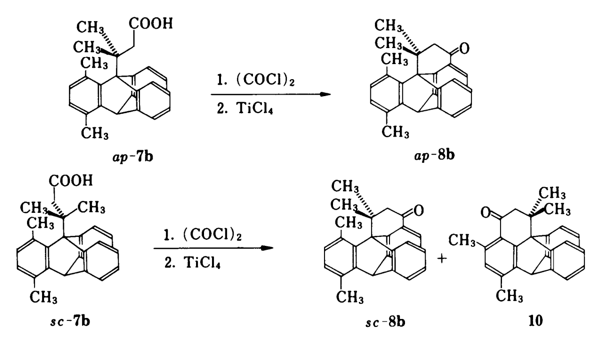
Table 2. The Effects of Solvent and Catalyst on the Formation Ratio, *sc*-**8b**/**10**, in the Reaction of *sc*-**7b** in the Presence of 2 Equivalents of the Lewis Acid

Solvent	Lewis acid	*sc*-**8b**/**10**
CH_2Cl_2	$TiCl_4$	0.96
C_6H_6	$TiCl_4$	0.89
C_6H_{12}[a]	$TiCl_4$	1.2
C_6H_6	$SnCl_4$	1.4

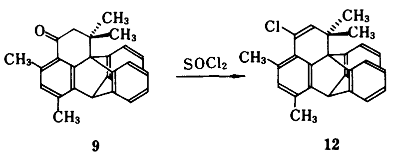
a) Cyclohexane.



Scheme 2. Reaction of *ap*-**7a** and *sc*-**7a** under the Friedel–Crafts reaction conditions. Only one form of enantiomers is given.

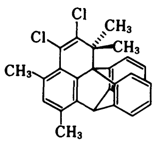


Scheme 3. Reaction of *ap*-**7b** and *sc*-**7b** under the Friedel–Crafts conditions. Only one enantiomeric form is shown.



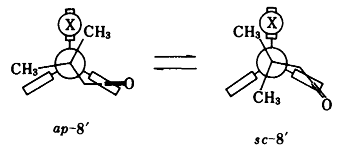
9 **12**

Further heating of the chloro compound (**12**) with thionyl chloride afforded further-chlorinated compounds, the main product being a dichloro compound to which we assign the structure of 2,3-dichloro-1,1,4,6-tetramethyl-7*H*-7,11b-*o*-benzeno-1*H*-benz[*de*]-anthracene (**13**). The reason for the assignment is the loss of the olefinic proton signal in its ^{1}H NMR spectra. However, the compound could not be purified to give the correct elemental analyses. Mass spectra of the enriched dichloro compound **13** showed that there were even trichlorinated and tetrachlorinated compounds as contaminants. Interestingly **11** did not give further-chlorinated compound on the same treatment as above.



13

The ketone **8** obtained from the *ap*-form and the *sc* of the acids could be isomerized by heating. The rate constants for isomerization, thermodynamic parameters, and activation parameters are shown in Tables 3 and 4. Apparently, the barrier to rotation in the methyl series was lower than that of the methoxyl series and at the equilibrium the *sc*-ketone was favored over the *ap*, the preference being greater in the methyl series than in the methoxyl series.



Scheme 4. Isomerization of ketones (**8**): X is either a methoxyl or a methyl.

Table 3. Rate Constants for Isomerization, *ap*-**8a**$\rightarrow$*sc*-**8a**, Equilibrium Constants, Thermodynamic Parameters and Activation Parameters

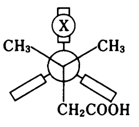
Temperature/°C	$k\times10^5$/s^{-1}	K(*sc*-**8a**/*ap*-**8a**)
77.5	0.31±0.01	6.2
90.0	1.24±0.04	6.0
100.5	3.8 ±0.1	5.9
111.5	11.1 ±0.4	5.6

$\Delta H^{\ne}$=27.6±0.6 kcal mol^{-1}; $\Delta S^{\ne}$=−5±2 cal mol^{-1} K^{-1}; $\Delta H°$=−0.8±0.6 kcal mol^{-1}; $\Delta S°$=1±2 cal mol^{-1} K^{-1}.

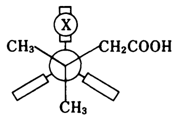
The gem-dimethyl groups in **9**, **10**, and **12** were found to be diastereotopic in ^{1}H NMR spectra, suggesting that there are enantiomers. The barriers to racemization were investigated but are apparently higher than 26 kcal mol^{-1} (1 cal=4.184 J), because their ^{1}H NMR spectra did not change up to 130 °C.

Discussion

When one looks at the Newman-type projections of the *ap*-acid and the *sc*, it is clear why the *ap*-acid gives a ketone as a sole product, because the cyclization to one benzeno bridge gives an enantiomer of the one that is obtained by cyclization to another benzeno bridge. The carboxyl group in the *ap* is too far to have any significant interactions with the substituted benzeno bridge. By contrast,the carboxymethyl group in the *sc* isomer is flanked by an unsubstituted and a substituted benzeno bridge. If cyclization takes place to the unsubstituted benzeno bridge, the ketone (**8**) is formed, whereas the acid gives another product if it reacts with the other substituted benzeno bridge.



ap



sc

The structures of the products other than the normal ketones were elucidated in the following ways. Compound **9** showed in its ^{1}H NMR spectra the loss of one methoxy-methyl group: that is consistent with the high resolution MS. Infrared spectrum showed an absorption at 1750 cm^{-1} to indicate the presence of an ester group. This is confirmed by ^{13}C NMR spectra. To accommodate these spectral information together with consideration of reaction mechanisms described below, we are compelled to assume the structure of the lactone (**9**). Although the IR absorption at 1750 cm^{-1} is a little low for phenolic esters,[10)] we believe this is due to abnormal bond angles and conformations that are needed because of the congestedness of the molecular structure. The ketone other than that which can be isomerized to the ketone **8b**, both of which were obtained by the reaction of *sc*-**7b**, showed the presence of four methyl groups, two aromatic and two

Table 4. Rate Constants for Isomerization, *ap*-**8b**$\rightarrow$*sc*-**8b**, Equilibrium Constants, Thermodynamic Parameters and Activation Parameters

Temperature/°C	$k\times10^5$/s^{-1}	K(*sc*-**8b**/*ap*-**8b**)
56.0	7.0±0.2	20.0
61.0	11.5±0.1	19.9
70.0	28.7±0.8	19.6
80.0	76 ±2	18.6

$\Delta H^{\ne}$=22.4±0.9 kcal mol^{-1}; $\Delta S^{\ne}$=−10±3 cal mol^{-1} K^{-1}; $\Delta H°$=−0.7±0.7 kcal mol^{-1}; $\Delta S°$=4±2 cal mol^{-1} K^{-1}.

aliphatic, and loss of an aromatic proton that shows absorption at high magnetic fields in its ^{1}H NMR spectra. It is most reasonable to assume that a proton on the dimethylbeneno bridge is lost, because these give absorptions at a high field among aromatic protons. The IR spectrum indicates the presence of a carbonyl group by the absorption at 1673 cm^{-1}. Although this absorption seems to be at a too low frequency for the normal noncoplanar aromatic carbonyl group,[11] this anomaly may again be attributed to abnormal molecular structure of this kind of congested molecules. Thus we assign structure **10** to this compound that accommodates all of spectroscopic, analytical, and mechanistic implications.

Formation of a lactone (**9**) from *sc*-**7a** is interesting because it is a reaction of an ether with an acyl chloride to form an ester in the presence of a Lewis acid. However, there are some literatures that reported this type of reactions.[12] The mechanism of the reaction must be the attack of the acylium ion produced from the acyl chloride in the presence of the Lewis acid on the 1-methoxy-oxygen atom followed by demethylation by a nucleophile. In *sc*-**7b**, the basicity of the methyl group at 1-position is too low to be attacked by the acylium ion, instead the π-system at the 1-position is attacked (ipso attack).[13] The benzenonium ion thus produced undergoes 1,2-methide shift to afford the product.

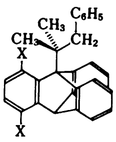
The results in Tables 1 and 2 reveal that, whereas the ratio of *sc*-**8b**/**10** is not much affected by the reaction conditions, that of *sc*-**8a**/**9** changes dramatically by the conditions. Therefore, we should like to discuss the results of *sc*-**7a** first.

The results in Table 1 indicate that the *sc*-**8a**/**9** ratio is generally small if the solvent is nonpolar: in dichloromethane with titanium(IV) chloride catalyst *sc*-**8a** is practically the sole product, whereas in cyclohexane *sc*-**8a** and **9** are almost equally produced. This tendency is again observed when tin(IV) chloride is used as a catalyst: this time, the lactone becomes an overwhelming product when cyclohexane is used as a solvent. The reaction rates, though it was not possible to determine exactly, were large in dichloromethane and small in benzene and further smaller in cyclohexane. Since titanium(IV) chloride is known to be a stronger Lewis acid than tin(IV) chloride,[14] we should like to propose the following mechanisms for the explanation of the results.

The acid chloride and the Lewis acid form a complex and then an ion pair, $RCO^+MCl_5^-$. The ion pair must be tighter, when the acidity of the Lewis acid is low and when the solvent polarity is low. When the ion pair is loose, the steric effects on the approach of the acylium ion to the reaction site will be small, whereas the steric effects will be great, when the ion pair is tight, because the acylium cation as well as the MCl_5^- anion must approach the reaction site. Thus the reaction with less steric hindrance will be favored when the ion pair is tight. In the Lewis acid-catalyzed reaction of *sc*-**7a**, there are two sites of reaction: though in principle it is possible to consider the ipso attack of the acylium ion to the 1-position where the methoxyl group is borne, the electron density at this position is too low[15] for the reaction. The reaction that occurs at the methoxy-oxygen suffers less steric hindrance than that occurring at the benzeno bridge, because the acylium cation must approach the peri-carbon, penetrating into the triptycene skeleton, if it reacts at the 8-position. The results with aluminium chloride are confusing in that aluminium chloride is a stronger Lewis acid than others. However, there is a possibility that the reaction with aluminium chloride is very complex and may even be taking place under heterogeneous conditions. We defer the discussion of the results until further information becomes available.

Examination of Table 2 reveals that, firstly, the ratio *sc*-**8b**/**10** is relatively insensitive to the conditions and, secondly, the attack to the 1-position is slightly favored in dichloromethane but, in cyclohexane, cyclization to the 8-position is slightly favored. We should like to attribute this difference between the methoxy compound and the methyl compound to the difference in the reaction sites. Namely, in the methyl compound, both reactions are occurring to the π-system of the triptycene skeleton. The steric effects given at the 1-position may not be much different from that given at the 8-position, although the methyl group at the 1-position gives additional steric effects on the attack. These steric effects together with the fact that the π-electron density at the 1-position must be slightly higher than at the 8-position where no substituent is present are reflected in the product ratio. However, the tendency seen in the methoxy compound, that is a less crowded site is more favorably attacked in nonpolar solvents and in the presence of less acidic Lewis acid is again reproduced.

As to the barriers to isomerization of the ketones **8**, we may compare them with those in similarly substituted 9-(1,1-dimethyl-2-phenylethyl)triptycenes (**14**),[16] because they are structurally similar and the substituent at the β-position of the 9-substituent is known to affect the barrier to rotation little, if any.[5] Table 5 compiles free energies of activation, calculated by using the reported activation parameters and the equilibrium constants, at 150 °C that is an interim point for the two series. The barriers are strikingly



14

reduced in the ketones (**8**) relative to the open chain analogs (**14**). This must reflect the instability of the ground state of the ketone. However, the order of the height of barriers is the same: in both series, the methyl compound gives a lower barrier to isomerization than the methoxy compound. According to our discussion previously made,[16] this is a reflection of the fact that the ground state of the methyl compound is more congested than the methoxy compound because of the steric size of the methyl and the methoxyl groups.

The congestedness of the methyl compound seems to be reflected as well in the population ratio: the *sc*-**8b**/*ap*-**8b** is 18.6 at 80 °C, whereas the *sc*-**8a**/*ap*-**8a** is 6.0 at 90 °C. As the first approximation, we would assume that the ketones are planar with the benzeno bridge to which it is attached and the gem-dimethyl groups would eclipse the benzeno bridges. However, it is not the case, because a pair of isomers is isolated for each compound, **8a** and **8b**. To the next approximation, one would think that the ketone moiety avoids coplanarity with the benzeno bridge and the carbonyl moiety taking the planar structure, as is seen in the Newman type projections (*ap*-**8′** and *sc*-**8′**). However, the dihedral angle made by the benzeno bridge and the carbonyl cannot be very large if one considers the carbonyl absorption in the IR spectra. This model also fails to show why *ap*-**8b** and *sc*-**8b** are so much different in their stabilities. Since good crystals of these compounds have not been obtained so far, we decided to carry out molecular mechanics calculations to find possible answers to these questions.

Since MM2 calculations with the parameters originally given gave far larger differences in the total energies of the *ap*- and *sc*-ketones than the observed,[2] we have modified some parameters which are concerned with the carbonyl-to-aromatic ring bond for the calculation here. The results are compiled in Table 6.

Table 5. Comparison of Free Energies of Activation for Rotation at 423 K in **8** and **14** (kcal mol^{-1})

X	Process	Compound **8**	Compound **14**
CH_3O	*ap* → *sc*	29.9	42.5
	sc → *ap*	31.2	42.0
CH_3	*ap* → *sc*	26.5	37.7
	sc → *ap*	28.8	36.1

The calculations predict that *sc*-**8a** is more stable than *ap*-**8a** by 2.74 kcal mol^{-1} and *sc*-**8b** more stable than *ap*-**8b** by 3.27 kcal mol^{-1}. Thus the calculations still overestimate the energy difference of the rotamers but the difference is smaller than the results using the standard parameters and the tendency is correctly predicted. Of particular interest in the calculated structures of the ketones is the large distorsion of the triptycene skeleton. The geometries are far different from those expected from molecular models. The dihedral angles about the bridgehead to substituent bond are about 45° at the smallest. The difference in the stabilities between *ap*-**8** and *sc*-**8** is mainly ascribed to the difference in the torsion term, suggesting that the distorsion of the triptycene skeleton is severer in *ap*-**8** than in *sc*-**8**.

This predicted distorsion of the triptycene skeleton by the calculation is supported by the ^{1}H NMR spectra. The most interesting feature in the ^{1}H NMR spectra of these ketones is that one of the aliphatic methyl groups gives its signal at a considerably high field of δ ca. 1.65, compared with the other methyl, as a doublet because of the long range coupling of ca. 1.5 Hz with one of the methylene protons. The molecular mechanics calculations show that the relevant methyl group (-*sc*-methyl in *ap*-**8′** and *ap*-methyl in *sc*-**8′** in Scheme 4) and one of the methylene hydrogens are exactly antiperiplanar, ideally located for the W-letter coupling. It further indicates that the methyl group is located in the shielding region of the highly distorted benzene ring and also in the shielding region of the carbonyl moiety, in conformity with the ^{1}H NMR spectra.

Although cyclization of the acid (**7b**) on heating with thionyl chloride might seem odd, there is a precedence of this type of reactions. Namely, 3-(9-triptycyl)propionic acid is known to cyclize when it is heated with thionyl chloride.[17] The proximity of the carbonyl

Table 6. Steric Energies and Their Components Calculated by MM2 Method

	8a		**8b**	
	ap	*sc*	*ap*	*sc*
Total steric energy	28.08	25.34	25.61	22.34
Compression	5.48	4.97	6.01	5.72
Bending	17.69	18.16	18.00	17.69
Stretch-Bend	−0.03	−0.07	−0.01	−0.07
van der Waals, 1,4-	26.20	26.03	22.62	22.76
other	−1.49	−1.82	−0.29	−1.01
Torsional	−19.50	−21.47	−21.14	−23.21
Dipole	−0.28	−0.46	0.42	0.45

Table 7. Modified Parameters for MM2 Calculations

Atom type[a)]	Stretching l_0/Å	k/mdyn Å^{-1}
2-2	1.3925	8.0667
2-3	1.4950	4.40

Atom type[a)]	Torsional/kcal mol^{-1} V_1	V_2	V_3
2-2-2-5	−0.93	9.0	−1.06
n-2-2-m[b)]	−0.93	9.0	0.0
2-2-3-1	0.0	0.9	0.0
2-2-3-7	0.0	0.9	0.0

a) Atom type: 1=sp^3 carbon, 2=aromatic carbon, 3=carbonyl carbon, 5=hydrogen, 7=carbonyl oxygen.
b) Any combination other than 2-2-2-5.

moiety to the triptycene skeleton must be the cause for this reaction. Easily enolizable ketones are known to afford vinyl chloride type compounds, when they are heated with thionyl chloride.[18,19] The formation of **11** and **12** can be rationalized by the analogies of this reaction, because acetophenone is known to undergo this reaction.[19]

Experimental

Spectral Measurements. The ^{1}H NMR spectra were recorded on a JEOL GX270 spectrometer which operates at 270 MHz. The infrared spectra were obtained on a Hitachi IR-260-30 spectrophotometer with KBr discs.

9-(1,1-Dimethyl-3-butenyl)-9,10-dihydro-9-anthracenol (2). A solution of 6.2 g (56.6 mmol) of 4-chloro-4-methyl-1-pentene (**1**)[20] and 5.15 mL (56.6 mmol) of 1,2-dibromoethane in 60 mL of tetrahydrofuran was added to 2.75 g (113 mmol) of magnesium covered with 10 mL of tetrahydrofuran in 2 h under a nitrogen atmosphere. After the formation of the Grignard reagent was completed, the mixture was diluted with 50 mL of tetrahydrofuran and 5.0 g (26 mmol) of 9-anthrone was added. The mixture was stirred for 1 h at room temperature and then heated under reflux for 1 h. After cooling, the mixture was decomposed with aqueous ammonium chloride. The mixture was extracted with benzene and the solvent was evaporated from the combined extract. After removal of the unreacted anthrone that deposited from the mixture, the products were submitted to medium-pressure chromatography on silica gel (hexane eluent) to give the desired material in 10% yield. The pure sample was obtained by recrystallization from hexane, mp 76.0 °C. Found: C, 86.01; H, 7.94%. Calcd for $C_{20}H_{22}O$: C, 86.29; H, 7.97%. ^{1}H NMR (CDCl$_3$) δ=0.83 (6H, s), 2.01 (1H, s), 2.11 (2H, d, J=7.3 Hz), 3.87 and 4.16 (2H, ABq, J=20 Hz), 4.86—4.98 (2H, m), 5.66—5.79 (1H, m), 7.23—7.34 (6H, m), 7.80—7.84 (2H, m).

9-(1,1-Dimethyl-3-butenyl)anthracene (3). A solution of 1.45 g (5.2 mmol) of the preceding alcohol (**2**) in 40 mL of carbon tetrachloride was heated under reflux with 11 g of phophorus pentaoxide for 15—20 min. The carbon tetrachloride solution was decanted and the residue was extracted several times with hot carbon tetrachloride. The solvent was evaporated from the carbon tetrachloride solution and the residue was chromatographed on silica gel (7:1 hexane–dichloromethane eluent) to give the desired product in 90% yield. The pure sample was obtained by recrystallization from hexane, mp 57.5—59.5 °C. Found: C, 92.11; H, 7.71%. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74%. ^{1}H NMR (CDCl$_3$) δ=1.82 (6H, s), 3.13 (2H, d, J=7.3 Hz), 4.88—5.07 (2H, m), 5.54—5.67 (1H, m), 7.26—7.35 (4H, m), 7.88—7.92 (2H, m), 8.23 (1H, s), 8.48—8.52 (2H, m).

1,4-Dimethoxy-9-(1,1-dimethyl-3-butenyl)triptycene (4a). To a solution of 4.5 g (17 mmol) of **3** and 3.5 mL (26 mmol) of isopentyl nitrite in 300 mL of dichloromethane, were simultaneously added from two dropping funnels 7.0 g (34 mmol) of 3,6-dimethoxyanthranilic acid[21] in 130 mL of acetone and 5 mL (37 mmol) of isopentyl nitrite in 40 mL of dichloromethane in 6 h, with stirring and refluxing under a nitrogen atmosphere. After the addtion was over, the whole was refluxed for another hour and cooled. The solvents were evaporated and the residue was submitted to chromatography on silica gel (5:1 hexane–dichloromethane eluent) to afford 35% of the desired material as a ca. 5.5:1 mixture of *ap* and *sc* isomers. The pure *ap*-**4a** was obtained by recrystallization of the product from dichloromethane–hexane, mp 245.5—246.5 °C. Found: C, 84.64; H, 6.91%. Calcd for $C_{28}H_{28}O_2$: C, 84.81; H, 7.12%. ^{1}H NMR (CDCl$_3$) δ=2.04 (6H, s), 3.29 (2H, d, J=6.9 Hz), 3.71 (3H, s), 3.80 (3H, s), 5.20—5.29 (2H, m), 5.87 (1H, s), 6.22—6.38 (1H, m), 6.57 and 6.60 (2H, ABq, J=8.8 Hz), 6.92—7.00 (4H, m), 7.37—7.41 (2H, m), 7.83—7.87 (2H, m).

1,4-Dimethyl-9-(1,1-dimethyl-3-butenyl)triptycene (4b). This compound was similarly prepared as described above, starting from **3** and 3,6-dimethylanthranilic acid.[22] The yield of the crude product (ca. 5.5:1 mixture of *ap*-**4b** and *sc*-**4b**) was 96%. Recrystallization of the product from hexane–dichloromethane afforded pure *ap*-**4b**, mp 208.5—209.0 °C. Found: C, 92.10; H, 7.62%. Calcd for $C_{28}H_{28}$: C, 92.26; 7.74%. ^{1}H NMR (CDCl$_3$) δ=2.22 (6H, s), 2.49 (3H, s), 2.64 (3H, s), 3.31 (2H, d, J=7.0 Hz), 5.23—5.57 (2H, m), 5.58 (1H, s), 6.19—6.34 (1H, m), 6.73 (2H, s), 6.93—7.02 (4H, m), 7.24—7.38 (2H, m), 7.83—7.88 (2H, m).

***ap*-3-(1,4-Dimethoxy-9-triptycyl)-3-methylbutanoic Acid (*ap*-7a).** A solution of 20 mg of osmium tetraoxide in 1 mL of *t*-butyl alcohol was added to a solution of 1.0 g (2.5 mmol) of the olefin (*ap*-**4a**), 3.7 g (49 mmol) of trimethylamine oxide dihydrate and 2 mL of pyridine in 15 mL of water and 50 mL of *t*-butyl alcohol and the whole was refluxed for 12 h. The mixture was cooled and treated with 20 mL of 20% aqueous sodium sulfite. Most of the *t*-butyl alcohol was evaporated and the aqueous layer was extracted with dichloromethane after being saturated with sodium chloride. The extract was washed with dilute hydrochloric acid to remove pyridine. Evaporation of the solvent afforded practically pure *ap*-4-(1,4-dimethoxy-9-triptycyl)-4-methyl-1,2-pentanediol (*ap*-**5a**) in almost quantitative yield. ^{1}H NMR (CDCl$_3$) δ=2.10 (3H, s), 2.23 (3H, s), 2.55 (1H, dd, J=15 and 2.6 Hz), 2.68 (1H, dd, J=15 and 7.3 Hz), 3.52 (1H, m), 3.73 (3H, s), 3.75—3.80 (1H, m), 3.80 (3H, s), 4.30—4.47 (1H, m), 5.87 (1H, s), 6.58 and 6.61 (2H, ABq, J=9.2 Hz), 6.90—7.02 (4H, m), 7.38—7.42 (2H, m), 7.66—7.70 (1H, m), 7.98—8.01 (1H, m).

Periodic acid (750 mg or 3.5 mmol) was added to a solution of 400 mg (0.93 mmol) of the diol (*ap*-**5a**) in 15 mL of tetrahydrofuran and 3 mL of water and the whole was stirred for 1 h at room temprature. The mixture was poured into water and extracted with dichloromethane. Evaporation of the solvent afforded *ap*-3-(1,4-dimethoxy-9-triptycyl)-3-methylbutanal in 75% yield. ^{1}H NMR ($CDCl_3$) δ=2.26 (6H, s), 3.65 (2H, d, J=2.6 Hz), 3.74 (3H, s), 3.80 (3H, s), 5.88 (1H, s), 6.58 and 6.62 (2H, ABq, J=9.1 Hz), 6.97—7.00 (4H, m), 7.40—7.44 (2H, m), 7.76—7.82 (2H, m), 10.25 (1H, t, J=2.6 Hz).

To a solution of 100 mg (0.25 mmol) of the *ap*-aldehyde in 4 mL of acetone were added 4 mg of sodium hydrogencarbonate and 40 mg (0.25 mmol) of potassium permanganate with ice-cooling and the mixture was stirred for 50 min. The mixture was treated with an aqueous solution of sodium hydrogensulfite to destroy the excess of potassium permanganate, acidified with hydrochloric acid, and extracted with dichloromethane. After evaporation of the solvent the residue was recrystallized from tetrahydrofuran-pentane to give pure *ap*-**7a**, mp 198.5 °C (decomp). The yield was 60%. Found: C, 77.98; H, 6.49%. Calcd for $C_{27}H_{26}O_4$: C, 78.24; H, 6.32%. ^{1}H NMR ($CDCl_3$) δ=2.25 (6H, s), 3.62 (2H, s), 3.73 (3H, s), 3.81 (3H, s), 5.89 (1H, s), 6.59 and 6.62 (2H, ABq, J=8.1 Hz), 6.99—7.03 (4H, m), 7.41—7.44 (2H, m), 7.86—7.90 (2H, m).

***ap*-3-(1,4-Dimethyl-9-triptycyl)-3-methylbutanoic Acid (*ap*-7b).** This compound was prepared similarly as described above from *ap*-**4b**. The NMR data and yield, where appropriate, are given. *ap*-4-(1,4-Dimethyl-9-triptycyl)-4-methyl-1,2-pentanediol (*ap*-**5b**): ^{1}H NMR ($CDCl_3$) δ=2.27 (3H, s), 2.42 (3H, s), 2.49 (3H, s), 2.67 (3H, s), 2.45—2.84 (2H, m), 3.48 (1H, dd, J=11 and 2.1 Hz), 3.69 (1H, dd, J=11 and 2.1 Hz), 4.3—4.5 (1H, m), 5.58 (1H, s), 6.74 (2H, s), 6.85—7.10 (4H, m), 7.29—7.41 (2H, m), 7.60—8.22 (2H, m); yield>95%. *ap*-3-(1,4-Dimethyl-9-triptycyl)-3-methylbutanal: ^{1}H NMR ($CDCl_3$) δ=2.43 (6H, s), 2.49 (3H, s), 2.67 (3H, s), 3.74 (2H, d, J=2.2 Hz), 5.60 (1H, s), 6.76 (2H, s), 6.90—7.01 (4H, m), 7.36—7.42 (2H, m), 7.78—7.81 (2H, m), 10.19 (1H, t, J=1.9 Hz); yield>95%. *ap*-**7b**: ^{1}H NMR ($CDCl_3$) δ=2.43 (6H, s), 2.50 (3H, s), 2.68 (3H, s), 3.67 (2H, s), 5.60 (1H, s), 6.76 (2H, s), 7.01—7.13 (4H, m), 7.37—7.40 (2H, m), 7.85—7.87 (2H, m); yield 95%. This compound did not give correct analyses of elements, the phenomenon being often observed in the compounds in triptycene series probably because of inclusion of solvent or other molecules. The methyl ester, mp 204—205 °C, however, gave correct analytical results. Found: C, 84.70; H, 7.00%. Calcd for $C_{28}H_{28}O_2$: C, 84.81; H, 7.12%. ^{1}H NMR ($CDCl_3$) δ=2.36 (6H, s), 2.48 (3H, s), 2.65 (3H, s), 3.59 (2H, s), 3.80 (3H, s), 5.58 (1H, s), 6.73 (2H, s), 6.97—7.00 (4H, m), 7.35—7.38 (2H, m), 7.84—7.88 (2H, m).

***sc*-3-(1,4-Dimethoxy-9-triptycyl)-3-methylbutanoic Acid (*sc*-7a).** Thermal isomerization of *ap*-**4** was accomplished by heating a solution of *ap*-**4** in 1-chloronaphthalene at 250 °C for 12 h under a nitrogen atmosphere. The solvent was removed by chromatography on silica gel. The residue showed the presence of isomers in *sc*/*ap*=1.4 ratio. It was possible to enrich the *sc*-isomer up to 95% by recrystallization from dichloromethane-hexane. ^{1}H NMR ($CDCl_3$) δ=1.97 (3H, s), 2.02 (3H, s), 3.31 and 3.54 (2H, AB of ABX, J=6.2 and 7.3 Hz), 3.74 (3H, s), 3.82 (3H, s), 5.17—5.24 (2H, m), 6.23—6.38 (1H, m), 6.55 and 6.63 (2H, ABq, J=8.8 Hz), 6.90—7.02 (4H, m), 7.38—7.42 (2H, m), 7.66—7.70 (1H, m), 7.98—8.01 (1H, m).

Dihydroxylation of the olefin mixture with osmium tetraoxide and trimethylamine oxide was carried out similarly as described for the *ap*-isomer. The *sc*-olefin gave two isomers (I and II) due to the fact that a new chiral center was formed, the ratio, I/II, being ca. 1.0. The yield was quantitative. ^{1}H NMR data ($CDCl_3$, δ) of *sc*-diols which were separated from the *ap* at the acetonide stage (see below): *sc*-**5a**(I) 2.09 (3H, s), 2.13 (3H, s), 2.67 (1H, dd, J=15 and 2.6 Hz), 2.68 (1H, dd, J=15 and 7.3 Hz), 3.52 (1H, m), 3.73 (3H, s), 3.75—3.87 (1H, m), 3.78 (3H, s), 3.82 (3H, s), 4.30—4.47 (1H, m), 5.87 (1H, s), 6.58 and 6.61 (2H, ABq, J=8.8 Hz), 6.90—7.02 (4H, m), 7.38—7.42 (2H, m), 7.66—7.70 (1H, m), 7.98—8.01 (1H, m); *sc*-**5a**(II) 2.06 (3H, s), 2.21 (3H, s), 2.64 (1H, dd, J=15 and 8.1 Hz), 2.69 (1H, dd, J=15 and 2.9 Hz), 3.49—3.56 (1H, m), 3.64—3.75 (1H, m), 3.70 (3H, s), 3.82 (3H, s), 4.37—4.45 (1H, m), 5.88 (1H, s), 6.57 and 6.64 (2H, ABq, J=9.2 Hz), 6.92—7.03 (4H, m), 7.35—7.42 (2H, m), 7.88—7.91 (1H, m), 8.01—8.04 (1H, m).

A solution of 300 mg of the mixture of diols **5a** in 15 mL of acetone was heated under reflux for 4 h with a catalytic amount of *p*-toluenesulfonic acid, the formed water being trapped by Molecular Sieves 5A. After cooling, the mixture was poured into aqueous sodium hydrogencarbonate and extracted with dichloromethane. After evaporation of the solvent, the residue was submitted to flash column or medium-pressure column chromatography on silica gel (9 : 1 hexane–ether eluent). The order of elution was *ap*-**6a**, *sc*-**6a**(I), and *sc*-**6a**(II). The separation of the two *sc* forms was not complete. The following ^{1}H NMR data ($CDCl_3$, δ) were recorded. *ap*-**6a**: 1.45 (3H, s), 1.49 (3H, s), 2.07 (3H, s), 2.18 (3H, s), 2.68 (1H, dd, J=15 and 6.8 Hz), 2.92 (1H, dd, J=15 and 3.6 Hz), 3.59 (1H, t, J=8.1 Hz), 3.72 (3H, s), 3.79 (3H, s), 4.26 (1H, dd, J=8.1 and 5.9 Hz), 4.64—4.74 (1H, m), 5.88 (1H, s), 6.57 and 6.60 (2H, ABq, J=9.2 Hz), 6.93—6.99 (4H, m), 7.38—7.41 (2H, m), 7.70—7.73 (1H, m), 8.00—8.03 (1H, m). *sc*-**6a**(I): 1.55 (6H, s), 2.04 (3H, s), 2.10 (3H, s), 2.70 (1H, dd, J=15 and 4.8 Hz), 3.24 (1H, dd, J=15 and 6.6 Hz), 3.64 (1H, dd, J=8.4 and 7.7 Hz), 3.77 (3H, s), 3.82 (3H, s), 4.27 (1H, dd, J=7.7 and 5.5 Hz), 4.67—4.73 (1H, m), 5.88 (1H, s), 6.59 and 6.64 (2H, ABq, J=8.8 Hz), 6.92—7.00 (4H, m), 7.35—7.41 (2H, m), 7.71—7.75 (1H, m), 7.84—7.87 (1H, m). *sc*-**6a**(II): 1.50 (3H, s), 1.51 (3H, s), 2.04 (3H, s), 2.16 (3H, s), 2.82 (1H, dd, J=11 and 8.1 Hz), 2.88 (1H, dd, J=11 and 2.6 Hz), 3.56 (1H, t, J=7.7 Hz), 3.70 (3H, s), 3.81 (3H, s), 4.16 (1H, dd, J=7.7 and 5.9 Hz), 4.68—4.72 (1H, m), 5.88 (1H, s), 6.63 and 6.65 (2H, ABq, J=8.8 Hz), 6.94—7.00 (4H, m), 7.36—7.40 (2H, m), 7.88—7.91 (1H, m) 8.06—8.10 (1H, m).

The mixture of *sc*-**6a**(I) and *sc*-**6a**(II) (1.0 g) in 25 mL of tetrahydrofuran was added to 25 mL of 1 M hydrochloric acid (1 M=1 mol L^{-1}) and the mixture was stirred at room temperature for 2.5 h. The mixture was poured into water and extracted with dichloromethane. Evaporation of the solvent afforded a mixture of two forms of *sc*-**5a**.

The oxidation of the mixture of *sc*-**5a** was carried out as described for the *ap*-form to afford the *sc*-aldehyde. ^{1}H NMR ($CDCl_3$) δ=2.19 (3H, s), 2.25 (3H, s), 3.57 and 3.97 (2H, ABdq, J=16 and 2.6 Hz), 3.72 (3H, s), 3.82 (3H, s), 5.90 (1H, s), 6.59 and 6.65 (2H, ABq, J=9.2 Hz), 6.94—7.02 (4H, m), 7.38—7.43 (2H, m), 7.74—7.82 (2H, m), 10.19 (1H, t, J=2.6 Hz).

The oxidation of the *sc*-aldehyde was caried out similarly as described for the *ap* form to afford 60% *sc*-**7a**, mp 270 °C (decomp). ^{1}H NMR ($CDCl_3$) δ=2.22 (3H, s), 2.24 (3H, s), 3.50 and 4.28 (2H, ABq, J=15 Hz), 3.79 (3H, s), 3.83 (3H, s), 5.90 (1H, s), 6.59 and 6.69 (2H, ABq, J=9.2 Hz), 6.96—7.03

(4H, m), 7.38—7.44 (2H, m), 7.81—7.85 (1H, m), 7.91—7.94 (1H, m). This compound did not give correct analyses but its methyl ester, mp 231—232 °C, did the correct data. Found: C, 78.38; H, 6.47%. Calcd for $C_{28}H_{28}O_4$: C, 78.48; H, 6.39%. ^{1}H NMR ($CDCl_3$) δ=2.14 (3H, s), 2.15 (3H, s), 3.60 (2H, ABq, *J*=15 Hz), 3.73 (3H, s), 3.79 (3H, s), 3.81 (3H, s), 5.89 (1H s), 6.56 and 6.62 (2H, ABq, *J*=9.2 Hz), 6.93—7.00 (4H, m), 7.36—7.42 (2H, m), 7.80—7.83 (1H, m), 7.90—7.94 (1H, m).

sc*-3-(1,4-Dimethyl-9-triptycyl)-3-methylbutanoic Acid (*sc*-7b).** This compound was prepared as described for the preparation of *sc*-**7a**. The ^{1}H NMR data ($CDCl_3$, δ) and yield, where appropriate, are given. *sc*-**4b**: 2.07 (3H, s), 2.13 (3H, s), 2.52 (3H, s), 2.63 (3H, s), 3.21—3.70 (2H, m), 5.28 (2H, d, *J*=5.1 Hz), 5.68 (1H, s), 6.14—6.36 (1H, m), 6.78 (2H, s), 6.92—7.02 (4H, m), 7.32—7.41 (2H, m), 7.82—7.90 (2H, m); *sc*/*ap* ratio 0.69. *sc*-**5b** (**I**): 2.12 (3H, s), 2.36 (3H, s), 2.52 (3H, s), 2.55 (3H, s), 2.65—2.97 (2H, m), 3.47—3.86 (2H, m), 4.3—4.4 (1H, m), 5.57 (1H, s), 6.73 and 6.77 (2H, ABq, *J*=6.1 Hz), 6.85—7.10 (4H, m), 7.29—7.41 (2H, m), 7.60—8.22 (2H, m). *sc*-**5b**(II): 2.12 (3H, s), 2.34 (3H, s), 2.52 (3H, s), 2.77 (3H, s), 2.65—2.97 (2H, m), 3.47—3.86 (2H, m), 4.3—4.4 (1H, m), 5.57 (1H, s), 6.73 and 6.77 (2H, ABq, *J*=6.1 Hz), 6.85—7.10 (4H, m), 7.29—7.41 (2H, m), 7.60—8.22 (2H, m). The ratio *sc*-**5*b(I)/*sc*-**5b**(II) was ca. 2:1. *ap*-**6b**: 1.45 (3H, s), 1.48 (3H, s), 2.25 (3H, s), 2.38 (3H, s), 2.48 (3H, s), 2.66 (3H, s), 2.60—3.01 (2H, m), 3.55 (1H, dd, *J*=10.0 and 7.1 Hz), 4.24 (1H, dd, *J*=10.0 and 7.1 Hz), 4.63—4.75 (1H, m), 5.55 (1H, s), 6.74 (2H, s), 6.91—7.20 (4H, m), 7.32—7.40 (2H, m), 7.68—7.75 (1H, m), 7.98—8.06 (1H, m). *sc*-**6b**(I): 1.53 (6H, s), 2.20 (6H, s), 2.51 (3H, s), 2.56 (3H, s), 2.65—3.16 (2H, m), 3.60 (1H, dd, *J*=7.9 and 5.9 Hz), 4.19 (1H, dd, *J*=7.9 and 5.9 Hz), 4.68—4.82 (1H, m), 5.58 (1H, s), 6.73 and 6.76 (2H, ABq, *J*=7.9 Hz), 6.90—7.10 (4H, m), 7.28—7.42 (2H, m), 7.76—8.20 (2H, m). *sc*-**6b**(II): 1.46 (3H, s), 1.48 (3H, s), 2.09 (3H, s), 2.31 (3H, s), 2.52 (3H, s), 2.77 (3H, s), 2.63—3.15 (2H, m), 3.58 (1H, dd, *J*=8.0 and 5.9 Hz), 4.19 (1H, dd, *J*=8.0 and 5.9 Hz), 4.68—4.82 (1H, m), 5.58 (1H, s), 6.60—6.70 (2H, m), 6.85—7.05 (4H, m), 7.30—7.42 (2H, m), 7.65—8.08 (2H, m). *sc*-Aldehyde: 2.31 (3H, s), 2.36 (3H, s), 2.53 (3H, s), 2.62 (3H, s), 3.79 (2H, m), 5.60 (1H, s), 6.78—6.79 (2H, m), 6.97—7.02 (4H, m), 7.35—7.40 (2H, m), 7.78—7.84 (2H, m), 10.24 (1H, m). *sc*-**7b**: mp 149—160 °C, yield>95%. Found: C, 84.51; H, 6.61%. Calcd for $C_{27}H_{26}O_2$: C, 84.78; H, 6.85%. ^{1}H NMR ($CDCl_3$) δ=2.30 (3H, s), 2.37 (3H, s), 2.53 (3H, s), 2.75 (3H, s), 3.75 and 3.94 (2H, ABq, *J*=16 Hz), 5.60 (1H, s), 6.80 (2H, s), 6.98—7.05 (4H, m), 7.35—7.41 (2H, m), 7.84—7.87 (1H, m), 7.91—7.94 (1H, m). *sc*-**7b** methyl ester: mp 210—211 °C. Found: C, 85.02; H, 7.00%. Calcd for $C_{28}H_{28}O_2$: C, 84.81; H, 7.12%. ^{1}H NMR ($CDCl_3$) δ=2.21 (3H, s), 2.28 (3H, s), 2.50 (3H, s), 2.70 (3H, s), 3.7—3.8 (2H, m), 3.81 (3H, s), 5.56 (1H, s), 6.75 (2H, s), 6.9—7.1 (4H, m), 7.2—7.5 (2H, m), 7.75—7.95 (2H, m) at 90 MHz.

Lewis Acid-Catalyzed Reaction of 3-(1,4-Dimethoxy-9-triptycyl)-3-methylbutanoic Acid (7a). The carboxylic acid (100 mg or 0.24 mmol) in 7.5 mL of benzene was stirred with 0.3 mL (3.5 mmol) of oxalyl dichloride at room temperature for 2 h and the solvent and the excess of oxalyl dichloride were evaporated in vacuo. The residue showed the following ^{1}H NMR spectra ($CDCl_3$, δ). *ap*: 2.22 (6H, s), 3.73 (3H, s), 3.80 (3H, s), 4.29 (2H, s), 5.89 (1H, s), 6.55 and 6.65 (2H, ABq, *J*=9.1 Hz), 6.98—7.05 (4H, m), 7.36—7.44 (2H, m), 7.73—7.77 (2H, m). *sc*: 2.17 (3H, s), 2.22 (3H, s), 3.79 (3H, s), 3.83 (3H, s), 4.32 and 4.82 (2H, ABq, *J*=19 Hz), 5.90 (1H, s), 6.60 and 6.70 (2H, ABq, *J*=10 Hz), 6.96—7.05 (4H, m), 7.35—7.46 (2H, m), 7.72—7.88 (2H, m).

The acid chloride produced in the above reaction was dissolved in 10 mL of benzene and 0.050 mL (2 equiv) of titanium(IV) chloride was added. The mixture was stirred for 4 h at room temperature and decomposed with water. The aqueous layer was extracted with dichlomethane and the solvents were evaporated from the combined organic layers.

The *ap*-acid afforded, after purification by recrystallization from tetrahydrofuran–pentane, 8,11-dimethoxy-1,1-dimethyl-1,2-dihydro-7*H*-7,11b-*o*-benzeno-3*H*-benz[*de*]anthracen-3-one (*ap*-**8a**), mp 283.0—284.0 °C, in 70% yield. Found: C, 81.52; H, 5.85%. Calcd for $C_{27}H_{24}O_3$: C, 81.79; H, 6.10%. ^{1}H NMR ($CDCl_3$) δ=1.67 (3H, d, *J*=1.4 Hz), 2.10 (3H, s), 2.71 (1H, d, *J*=15 Hz), 3.37 (1H, app dd, *J*=15 and 1.4 Hz), 3.75 (3H, s), 3.87 (3H, s), 5.93 (1H, s), 6.62 and 6.71 (2H, ABq, *J*=9.0 Hz), 6.88—7.00 (2H, m), 7.06—7.13 (1H, m), 7.32—7.35 (1H, m), 7.56—7.62 (2H, m), 7.79—7.82 (1H, m), IR (KBr disc): 1690 cm^{-1}.

The *sc*-acid afforded a ketone (*sc*-**8a**) and a lactone (**9**) which were not easily separated. The pure ketone was obtained by recrystallization of the product, obtained with the use of dichloromethane or benzene as a solvent, from tetrahydrofuran–pentane. The pure lactone was obtained by chromatography on silica gel (1:2 hexane–dichloromethane) after conversion of the ketone into its oxime. The combined yields of the lactone and the ketone were ca. 70%.

sc-**8a**: mp 283.0—284.0 °C. Found: C, 81.54; H, 6.34%. Calcd for $C_{27}H_{24}O_3$: C, 81.79; H, 6.10%. ^{1}H NMR ($CDCl_3$) δ=1.63 (3H, d, *J*=1.5 Hz), 2.07 (3H, s), 2.62 (1H, d, *J*=16 Hz), 3.91 (1H, app dd, *J*=16 and 1.5 Hz), 3.75 (3H, s), 3.76 (3H, s), 5.94 (1H, s), 6.51 and 6.55 (2H, ABq, *J*=8.1 Hz), 7.09—7.25 (3H, m), 7.47—7.64 (3H, m), 7.86—7.89 (1H, m). IR (KBr disc): 1690 cm^{-1}.

9: mp 238.5—240.0 °C. This compound failed to give correct analysis, the phenomenon being often observed in the triptycene series as mentioned in the analysis of *ap*-**7b**. High resolution MS: M$^+$ 382.1549 (82.9%) and 383.1590 (25.6%) in accordance with the calculated values 382.1567 for $C_{26}H_{22}O_3$ and 383.1601 for $C_{25}{}^{13}CH_{22}O_3$. ^{1}H NMR ($CDCl_3$) δ=1.97 (3H, s), 2.19 (3H, s), 3.13 and 3.90 (2H, ABq, *J*=15 Hz), 3.87 (3H, s), 5.93 (1H, s), 6.69 and 6.82 (2H, ABq, *J*=9.2 Hz), 6.98—7.10 (4H, m), 7.39—7.58 (3H, m), 7.82—7.85 (1H, m). IR (KBr disc): 1750 cm^{-1}. ^{13}C NMR ($CDCl_3$): 170.6 ppm from TMS.

Lewis Acid-Catalyzed Reaction of 3-(1,4-Dimethyl-9-triptycyl)-3-methylbutanoic Acid (7b). The reaction was carried out as described for **7a**. The following ^{1}H NMR data ($CDCl_3$, δ) were recorded at 90 MHz.

***ap*-Acid Chloride:** 2.41 (6H, s), 2.47 (3H, s), 2.61 (3H, s), 4.30 (2H, s), 5.56 (1H, s), 6.72 (2H, s), 6.8—7.1 (4H, m), 7.2—7.5 (2H, m), 7.5—7.8 (2H, m).

***sc*-Acid Chloride:** 2.27 (3H, s), 2.34 (3H, s), 2.61 (3H, s), 2.70 (3H, s), 4.37 and 4.52 (2H, ABq, *J*=19.8 Hz), 5.56 (1H, s), 6.78 (2H, s), 6.8—7.2 (4H, m), 7.3—7.4 (2H, m), 7.6—7.9 (2H, m).

The *ap*-acid chloride afforded 1,1,8,11-tetramethyl-1,2-dihydro-7*H*-7,11b-*o*-benzeno-3*H*-benz[*de*]anthracen-3-one (**8b**), mp 192.0—192.5 °C, in 70% yield. Found: C, 88.64; H, 6.55%. Calcd for $C_{27}H_{24}O$: C, 88.97; H, 6.64%. ^{1}H NMR ($CDCl_3$) δ=1.70 (3H, d, *J*=1.8 Hz), 2.18 (3H, s), 2.52 (3H, s), 2.61 (3H, s), 2.72 (1H, d, J=15 Hz), 3.31 (1H, dd, J=15 and 1.8 Hz), 5.56 (1H, s), 6.76 and 6.81 (2H, ABq, J=8.1 Hz), 6.85—6.96 (2H, m), 7.02—7.08 (1H, m), 7.23—7.29 (1H, m), 7.46—7.57 (2H, m), 7.72—7.75 (1H, m). IR (KBr disc): 1678 cm^{-1}.

The *sc*-acid chloride gave two ketones which were separated by preparative TLC on silica gel (1:2 hexane–dichloromethane eluent).

1,1,8,11-Tetramethyl-1,2-dihydro-7*H*-7,11b-*o*-benzeno-3*H*-benz[*de*]anthracen-3-one (*sc*-8b): mp 247.0—248.0 °C. Yield 33%. Found: C, 88.75; H, 6.57%. Calcd for $C_{27}H_{24}O$: C, 88.97; H, 6.64%. ^{1}H NMR ($CDCl_3$) δ=1.65 (3H, d, J=1.5 Hz), 2.21 (3H, s), 2.43 (3H, s), 2.65 (3H, s), 2.73 (1H, d, J=15 Hz), 3.74 (1H, dd, J=15 and 1.5 Hz), 5.66 (1H, s), 6.66 and 6.67 (2H, ABq, J=8.1 Hz), 7.04—7.14 (3H, m), 7.43—7.46 (1H, m), 7.52—7.55 (1H, m), 7.63—7.67 (1H, m), 7.79—7.83 (1H, m). IR (KBr disc): 1692 cm^{-1}.

1,1,4,6-Tetramethyl-1,2-dihydro-7*H*-7,11b-*o*-benzeno-3*H*-benz[*de*]anthracen-3-one (10): mp 262.5—263.0 °C, yield 37%. Found: C, 88.85; H, 6.52%. Calcd for $C_{27}H_{24}O$: C, 88.97; H, 6.64%. ^{1}H NMR ($CDCl_3$) δ=1.69 (3H, s), 2.09 (3H, s), 2.51 (3H, s), 2.53 (3H, s), 2.60 and 3.55 (2H, ABq, J=16 Hz), 5.51 (1H, s), 6.75 (1H, s), 6.91—6.96 (2H, m), 7.04—7.08 (2H, m), 7.30 and 7.46 (2H, ABq, J=6.8 Hz), 7.75 and 7.83 (2H, ABq, J=7.3 Hz). IR (KBr disc): 1673 cm^{-1}.

Effects of Solvent and Catalyst. The reactions were carried out in essentially the same manner as described in the reaction of **7a**. Although the results were irregular when the amount of the catalyst was less than 1.0 equivalent to the acid chloride, they were essentially the same when the catalyst was 1.0—10 equivalents. When the solvent was cyclohexane, the reaction was slow. The results are given in Tables 1 and 2. The analysis of the products were caried out by ^{1}H NMR spectra using the signals due to the methyl or methoxyl protons.

3-Chloro-1,1,8,11-tetramethyl-7*H*-7,11b-*o*-benzeno-1*H*-benz[*de*]anthracene (11). A mixture of 100 mg of *sc*-**8b** and 5 mL of thionyl chloride, which was distilled over triphenylphospine, was heated under reflux for 2 h under a nitrogen atmosphere. The excessive thionyl chloride was evaporated in vacuo and the residue was treated with water. The mixture was extracted with dichloromethane, and the extract was washed with aqueous sodium hydrogencarbonate and dried over magnesium sulfate. After evaporation of the solvent, the residue was submitted to preparative TLC on silica gel with 2:1 hexane–dichloromethane as an eluent. **11** was obtained as crystals, mp 264.0—266.0 °C, in 50% yield. High resolution MS: M$^+$ 382.1480 and 384.1468. Calcd for $C_{27}H_{23}{}^{35}Cl$ and $C_{27}H_{23}{}^{37}Cl$: 382.1486 and 384.1458. ^{1}H NMR ($CDCl_3$) δ=1.72 (3H, s), 2.21 (3H, s), 2.34 (3H, s), 2.54 (3H, s), 5.54 (1H, s), 6.40 (1H, s), 6.49 and 6.62 (2H, ABq, J=8.1 Hz), 6.99—7.28 (5H, m), 7.47—7.50 (1H, m), 7.80—7.83 (1H, m).

3-Chloro-1,1,4,6-tetramethyl-7*H*-7,11b-*o*-benzeno-1*H*-benz[*de*]anthracene (12): mp 223.0—225.0 °C, was similarly obtained in ca. 50% yield from **10**. High resolution MS: M$^+$ 382.1468 and 384.1443. Calcd for $C_{27}H_{23}{}^{35}Cl$ and $C_{27}H_{23}{}^{37}Cl$: 382.1468 and 384.1458. ^{1}H NMR ($CDCl_3$) δ=1.74 (3H, s), 2.12 (3H, s), 2.44 (3H, s), 2.46 (3H, s), 5.43 (1H, s), 6.41 (1H, s), 6.64 (1H, s), 6.80—6.88 (2H, m), 7.02—7.24 (3H, m), 7.47—7.54 (2H, m), 7.76—7.82 (1H, m).

Further Heating of 11 and 12 with Thionyl Chloride. **12** and thionyl chloride for 12 h afforded a product which was almost pure on the ^{1}H NMR spectral ground. The structure of the product was assigned as 2,3-dichloro-1,1,4,6-tetramethyl-7*H*-7,11b-*o*-benzeno-1*H*-benz[*de*]anthracene (**13**). ^{1}H NMR ($CDCl_3$) δ=1.85 (3H, s), 2.28 (3H, s), 2.43 (3H, s), 2.46 (3H, s), 5.44 (1H, s), 6.65 (1H, s), 6.84—6.93 (2H, m), 7.05—7.25 (3H, m), 7.38—7.53 (2H, m), 7.84—7.87 (1H, m). High resolution MS: M$^+$ 416.1072 and 418.1049. Calcd for $C_{27}H_{22}{}^{35}Cl_2$ and $C_{27}H_{22}{}^{35}Cl{}^{37}Cl$: 416.1097 and 418.1067. The mass spectrum also showed the presence of peaks which indicated the contamination of **13** by trichloro and tetrachloro compounds.

11 did not react with thionyl chloride any more under the conditions.

Heating *ap*-7b and *sc*-7b with Thionyl Chloride. The *ap*-acid (100 mg) was heated with 5 mL of thionyl chloride similarly as mentioned above. The reaction afforded *sc*-**8b**, **11**, and *ap*-**8b** in 70, 11, and 3% yields, respectively.

sc-**7b**, on a similar treatment, afforded **10**, *sc*-**8b**, **12**, and **11** in 21, 42, 20, and 5% yields, respectively. In addition, **13** and *ap*-**8b** were detected by ^{1}H NMR spectra, the yields being ca. 1 and 2%, respectively.

Thermal Equilibration of Ketones 8. The *ap*-ketone was dissolved in toluene-d_8 to make up a ca. 25 mmol L^{-1} solution. The sample solution was heated in an appropriate boiling solvent bath except for the cases at 70 and 90 °C, when a thermostatted bath was used. The solvents used for the bath were toluene (111.5 °C), water (100.5 °C), and acetone (56.0 °C). The rates of isomerization were followed by ^{1}H NMR spectra by observing methyl signals. The rate constants were obtained by assuming the first order reaction which is reversible. The error limit in Tables 3 and 4 are given at the 95% confidence.

Calculation of the Data in Table 5. It was assumed that the thermodynamic parameters obtained at about or below 100 °C could be extrapolated to 150 °C for the ketones (**8**) and those obtained at 200 °C or higher temperatures for **14** could as well be extrapolated to 150 °C. Then the equilibrium contants at 150 °C could be calculated and were used for the calculation of the reverse reaction rates. Free energies of activation for the forward and backward reactions were thus calculated and listed.

Molecular Mechanics Calculations. Calculations were performed on Hitachi M-680H computer system at the Computer Center of the University of Tokyo (CCUT) using a modified version[23] of the MM2 program.[24] Some of the force field parameters were modified in order to properly reproduce deformations about the bond which connects a benzene ring with a carbonyl function attached to it and are listed in Table 7.

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