Restricted Rotation Involving the Tetrahedral Carbon. XVI. Isolation of Stable Rotamers about an sp^3-sp^3 Carbon Bond[1,2]

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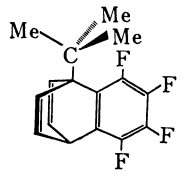
Both antiperiplanar and synclinal rotamers resulted from the restricted rotation about a C–C single bond between the bridgehead *t*-alkyl group and the skeleton of 9-(1,1-dimethyl-2-phenylethyl)-11-methoxycarbonyl-9,10-dihydro-9,10-ethenoanthracene-12-carboxylic acid are isolated. Optical resolution of the synclinal rotamer is successfully performed by way of the mono-(−)-menthyl esters and a pair of enantiomers of the acid, $[\alpha]_D^{32}$ ±24.7°, are isolated as stable entities. Activation energy for the interconversion between the rotamers of dimethyl esters is found to be 33.2 kcal/mol with a frequency factor of $10^{13.3}$ s^{-1}.

Isolation of stereoisomers originated from the restricted rotation about a single bond, *i.e.*, atropisomerism,*[3] has been one of the challenging problems for organic chemists. In substituted biphenyl and styrene derivatives, in which both of the two carbon atoms constructing the bond in quenstion is sp^2 hybridized, plenty of examples of realization of atropisomerism have been reported[4] with the first example of optical resolution of 6,6′-dinitrodiphenic acid as far back as 1922.[5]

As for the bond between two sp^3 hybridized carbon atoms, the situation is quite different. It had long been believed that the rotation about a saturated carbon bond is completely free, and it was not until 1949 that the concept of the energy barrier to rotation about the C–C bond in ethane with the staggered forms as the most stable conformations was definitely established.[6] Since then many investigations have been performed on the internal rotation in ethane derivatives making use of infrared and microwave spectroscopies as well as thermodynamic methods. Toward the end of 1950s nuclear magnetic resonance spectroscopy, especially so-called dynamic NMR, became available to this area of investigation and a vast number of reports have appeared since then. Several review articles have been published.[7]

At the outset of this investigation, all the compounds yet examined by DNMR had an energy barrier to rotation of less than 20 kcal/mol and no example had been recorded in which the rotation was still slow on the NMR time scale at the highest temperature attained. In order that the atropisomerism is realized at room temperature, the energy barrier to rotation about the bond in question should be higher than 23 kcal/mol assuming the mean lifetime of 1 hr at 25 °C and the frequency factor of 10^{13} s^{-1}.**

The energy barrier to internal rotation of a *t*-butyl group attached to a flexible residue could not exceed 12 kcal/mol,[10] but when a *t*-butyl group is attached to the bridgehead position of a rigid framework, the barrier rises considerably. First of such cases was reported by Brewer *et al.* in an ethenonaphthalene derivative **1**.[11] Although the authors did not give the



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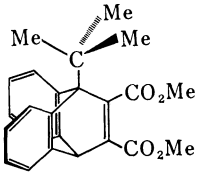
definite value, the energy barrier of about 20 kcal/mol is estimated, based on the chemical shift (*ca.* 0.2 ppm) and the coalescence temperature (between 120 °C and 180 °C). In one of the preceding papers of this series, a 9-*t*-butyl-9,10-dihydroethenoanthracene derivative **2** has been shown to exist in a staggered conformation shown by the Newman projection **3** and to have an extraordinarily high barrier to rotation about the axis bond (more than 25 kcal/mol), from the observation that the methyl signals of the *t*-butyl group remained 2:1 doublet even at 180 °C without any indication of line broadening.[12]



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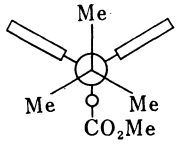

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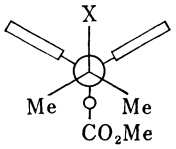
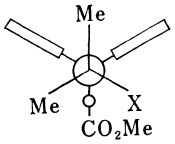
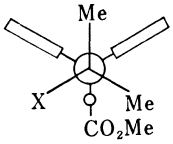
If one of the methyls of the *t*-butyl group of **2** is replaced by a suitable group X of similar bulkiness, the resulting three staggered conformations **4**, **5a**, and **5b** should exist as atropisomers, which are stable at room temperature.



4: *ap*



5a: *P-sc*



5b: *M-sc*

* We confine the discussion in this article only to carbon-carbon single bonds.

** Realization of atropisomerism at low temperatures does not necessarily require the high barrier to rotation. Certain compounds are known to be conformationally pure in the crystalline state. Crystals of *gauche* and *trans* conformations of 1,1,2,2-tetrabromoethane were independently obtained depending on the way of crystallization.[8] The equatorial conformer of chlorocyclohexane was purely isolated not only in the crystalline state but also in solution at −150 °C.[9] In these compounds the energy barrier is lower than 15 kcal/mol and naturally the conformational equilibrium is immediately attained in solution at room temperature.

Table 1. PMR data of the atropisomers **7** and **8**[a]

Protons	*ap*-Isomer (**7**)		*sc*-Isomer (**8**)	
	$CDCl_3$	C_6D_6	$CDCl_3$	C_6D_6
C–Me	1.78 (6H, s)	1.90 (6H, s)	1.83 (6H, br, s)[b]	1.83 (3H, s) 1.97 (3H, s)
O–Me	3.65 (3H, s) 3.72 (3H, s)	3.25 (3H, s) 3.39 (3H, s)	3.72 (3H, s) 3.75 (3H, s)	3.28 (3H, s) 3.43 (3H, s)
CH_2	3.75 (2H, s)	3.70 (2H, s)	3.64 (2H, q: J_{AB}=13.8 Hz, δ_{AB}=18.1 Hz)	3.90 (2H, q: J_{AB}=14.4 Hz, δ_{AB}=4.9 Hz)
10-H	5.57 (1H, s)	5.70 (1H, s)	5.56 (1H, s)	5.69 (1H, s)
aromatic[c]	6.9—7.6(11H, m)	6.7—7.5(11H, m)	6.7—7.6(11H, m)	6.6—7.6(11H, m)
peri	8.0 (2H, m)	8.0 (2H, m)	7.7 (1H, m) 8.0 (1H, m)	7.7 (1H, m) 8.0 (1H, m)

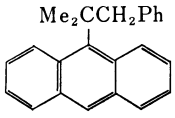
a) Obtained for *ca.* 10% (w/v) solution at 34 °C and 60 MHz, and given in ppm relative to internal tetramethylsilane. b) Appearent singlet with a half width of 2.1 Hz, suggesting the overlap of two slightly shifted singlets. c) Excluding the *peri*-protons.

We report here the successful manifestation of this prediction in a case where X is a benzyl group in the following sequence of procedures***: stereoselective synthesis of the antiperiplanar or meso form (**4**), isomerization of **4** to the equilibrium mixture of the atropisomers, isolation of the racemic synclinal form (**5a** and **5b**), and optical resolution of the *sc*-form† through mono-(−)-menthyl ester of the acid.

Enantiomeric atropisomerism, or optical activity due to the restricted rotation, involving an sp^3-sp^3 carbon bond is completely unprecedented, although realization of diastereomeric atropisomerism has been claimed by several groups of investigators without "convincing" evidence.[14]

Results and Discussion

Stereoselective Synthesis of the Antiperiplanar Isomer. 9-(1,1-Dimethyl-2-phenylethyl)anthracene (**6**) was synthesized by treatment of 1,1-dimethyl-2-phenylethylmagnesium chloride with anthrone followed by dehydration with phosphorus pentoxide.



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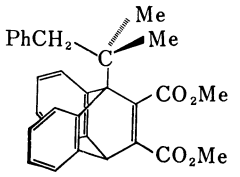
Heating **6** with dimethyl acetylenedicarboxylate in toluene under reflux for 5 hr gave colorless needles, mp 200—201 °C, in a spectral yield of *ca.* 85%. PMR data (Table 1) as well as those of MS and elemental analysis of the product clearly showed that it was a 1:1 Diels-Alder adduct with 9,10-dihydro-9,10-ethenoanthracene skeleton. The benzylic methylene as well as the geminal dimethyl groups appeared as a singlet and the *peri*-protons (protons at 1- and 8-positions of the skeleton), which appeared at δ *ca.* 8.0 separated from the other aromatic protons (δ 6.9—7.6), showed a two-proton multiplet indicating the magnetic equivalence of the two *peri*-protons. Although these NMR features could be understood assuming that the internal rotation of the bridgehead *t*-alkyl group were fast on the NMR time scale, such an interpretation is not consistent with the slow rotation of the *t*-butyl group in compound **2**. The most reasonable interpretation will be that the product has the antiperiplanar conformation (**7**) and the rotation about the axis bond is hindered at room temperature.



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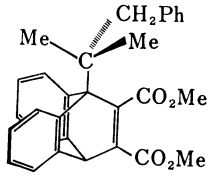

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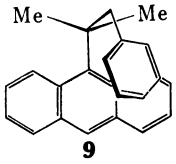
Careful inspection of the reaction mixture by PMR revealed the existence of *ca.* 15% of another product, spectral properties of which were consistent with the other atropisomer of the synclinal conformation (**8**).†† Separation of **8** from the reaction mixture seemed laborious and time consuming because of the small quantity and the similar chromatographic behavior as that of **7**. Thus the isolation and characterization of **8** was performed by another way described in the next section. No other products than these two were identified in the reaction mixture. The selective formation of the *ap*-isomer (**7**) in the Diels-Alder reaction is not the result of thermodynamic control as is shown later and therefore must be the result of kinetic origin. This means that the approach of the dienophile from the opposite direction to the benzyl group is favored. Since the *peri*-protons to the *t*-alkyl group in **6** give PMR signals at δ 8.0 in contrast to those in 9-*t*-butylanthracene (δ 8.4), the *peri*-protons in **6** are considered to be within the shielding cone of the benzyl-phenyl group. Although this does not necessarily mean that the conformation is fixed in such a form, the population of the folded conformation (**9**)

*** The benzyl group was chosen because of the synthetic convenience.

† Nomenclature of conformations used here is in accord with that proposed by Cahn, Ingold and Prelog.[13]

†† One of the enantiomers, the *P*-*sc* form, is illustrated.

must, at least, be significant. In conformation **9**, the attack of the dienophile from the benzyl side may effectively be blocked. This type of stereoselectivity has been observed in the Diels-Alder reaction between 9-*t*-alkylanthracenes and dienophiles such as dimethyl acetylenedicarboxylate[15] and benzynes.[16]



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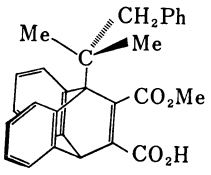
Equilibration of the Rotamers and Isolation of the Synclinal Isomer. The *ap*-isomer (**7**) was thermally quite stable at room temperature both in solution and in the crystalline state. Upon heating in chlorobenzene at 150 °C, however, **7** gradually isomerized to give an equilibrium mixture in which **7** and an isomerization product existed in a ratio of 1 : 3. The major component was isolated as colorless granules, mp 149—151 °C, upon chromatography on silica gel and was concluded to be the *sc*-atropisomer (**8**) from the data of PMR (Table 1) together with those of MS and elemental analysis. Two singlets for *gem*-methyls, an AB quartet for the methylene and the nonequivalent *peri*-protons suggested the chiral structure of the compound and are consistent with **8**. And these spectral features of **8** are the same as those of the minor product in the Diels-Alder reaction.

Reversible nature of the interconversion of these two atropisomers was confirmed by the equilibration experiment starting from the *sc*-isomer: upon heating in chlorobenzene at 150 °C, **8** afforded the same equilibrium mixture as that attained from the *ap*-isomer (**7**).

Kinetics of the equilibration and thermodynamics of the equilibrium are described in later section in some detail.

Optical Resolution of the Synclinal Isomer. Treatment of the synclinal dimethyl ester **8** with alcoholic potassium hydroxide afforded an isoluble crystalline mass which upon acidification gave a monocarboxylic acid. The acid was shown by PMR to have retained the synclinal conformation regarding the axis bond. Although no definite conclusion has yet been available as to which of the two methoxycarbonyl groups was hydrolyzed, structure **10** was tentatively assigned from the consideration of steric effects on hydrolysis.†††



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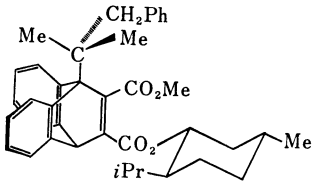
Attempts to obtain crystalline salts of **10** with alkaloid bases such as strychnine, quinine, cinchonine, and brucine gave no successful results. Thus resolution of **10** by way of the ester with a chiral alcohol was attempted. The racemic carboxylic acid **10** was converted to the corresponding acid chloride and treated with (−)-menthol to afford *ca.* 1 : 1 mixture of two diastereomeric (−)-menthyl esters **11** and **12** as an oil. Upon dissolution of the oil in hexane, one of the diastereomers (tentatively named as **A**) selectively crystallized out, leaving *ca.* 1 : 5 mixture of **A** and the other diastereomer (named as **B**) in the mother liquor. The glass obtained



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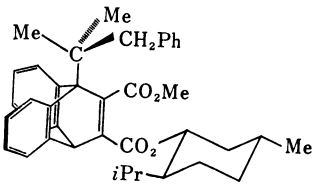

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upon evaporation of the mother liquor resisted crystallization, andvarious attempts to isolate pure **B** were unsuccessful.

Alkaline hydrolysis of the distereomerically pure **A** gave a crystalline monocarboxylic acid, $[\alpha]_D^{32}$ −24.6°, whose PMR spectrum was identical with that of the racemic acid. The obtained acid ((−)-**10**) showed poorer solubility (for example in benzene) than (±)-**10**, and the IR spectrum of (−)-**10** in Nujol mull was essentially the same as that of the racemic acid. These observations suggested that (±)-**10** formed a conglomerate rather than a racemate or a racemic solid solution. The fact that the specific rotation of (−)-**10** did not change by further recrystallization together with the observations mentioned above suggested that (−)-**10** was obtained optically pure.

Similar saponification of the glassy mixture (1 : 5) of **A** and **B** afforded another crystalline carboxylic acid, $[\alpha]_D^{32}$ +24.8°, which showed the same PMR and IR spectra as those of (±)-**10**. The poorer solubility of (+)-**10** compared to the racemic acid seemed to help to isolate the pure dextrorotatory form.

Equilibration and Its Kinetics. Interconversion of the atropisomers is most reasonably assumed to occur through the rotation about the axis bond, although possibility of alternative mechanisms such as retro-Diels-Alder reaction and bond fission-recombination mechanisms involving biradical or zwitterionic intermediates could not be definitely eliminated. Thus kinetics of equilibration of the *ap*-isomer (**7**) was studied using PMR in order to obtain the energy barrier to interconversion between the atropisomers (**7** and **8**).

TABLE 2. KINETIC DATA OF EQUILIBRATION OF THE *ap*-ISOMER (**7**)[a]

$ap \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} sc$: $K = k_1/k_{-1}$

Temperature (°C)	k_1 (s^{-1})	τ (hr)	K
111	2.5×10^{-6}	114	3.0
126	1.1×10^{-5}	24	3.0
138	3.7×10^{-5}	7.5	3.0
152	1.6×10^{-4}	1.7	3.0

a) Measured in *ca.* 10% solution in chlorobenzene.

††† The remaining methoxycarbonyl group severely resisted hydrolysis.

Detailed method is described in the experimental section. First order rate constants k_1 (*ap*→*sc*) and equilibrium constants K were obtained at four temperatures in the range of 111—152 °C and shown in Table 2 along with the mean lifetime τ.

Arrhenius and Eyring plots of k_1's gave the good linear relationship and thermodynamic parameters were obtained as shown in Table 3.‡ Extrapolation of the data gives the mean lifetime of 18 days at 100 °C, 7 months at 80 °C, and 2600 years at 25 °C.

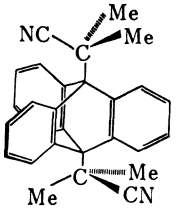
Table 3. Thermodynamic parameters of equilibration of the *ap*-isomer (**7**)

$E_a=33.2$ kcal/mol	$\Delta H^{\ddagger}=32.4$ kcal/mol
$\log A=13.3$	$\Delta S^{\ddagger}=-0.4$ eu

Kinetics of the equilibration starting from the *sc*-isomer (**8**) was studied at 138 °C, and gave the rate constant k^{-1} of 1.1×10^{-5} s^{-1} and hence k_1 ($=K\times k^{-1}$) of 3.3×10^{-5} s^{-1} which agreed well with $k_1=3.7\times10^{-5}$ s^{-1} obtained from the forward reaction.

Ratio of *sc*- to *ap*-isomers at equilibrium remained constant at 3.0 throughout the temperature range examined. This means that there is little enthalpy difference between the isomers and the entropy term is in favor of the *sc*-isomer by 2.2 eu due to entropy of mixing and some other factors.

The barrier obtained here represents the third highest barrier to rotation about an sp^3-sp^3 carbon bond yet reported, following 37.7 kcal/mol for 9,10-bis(1-cyano-1-methylethyl)triptycene (**13**)[17] and 33.6 kcal/mol for 2,3-dichloro-9-(1,1-dimethyl-2-phenylethyl)-triptycene (**14**).[16]



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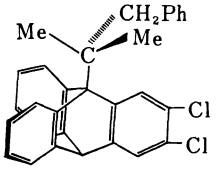

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Experimental

Melting points were uncorrected. PMR spectra were recorded on a Hitachi R-20B spectrometer at 60 MHz and 34 °C, and tetramethylsilane was used as an internal reference. Mass spectra were measured on a Hitachi RMU-6L mass spectrometer, IR spectra on a Hitachi EPI-G2 grating spectrophotometer, and optical rotations on a JASCO DIP-SL automatic polarimeter using a 10 mm quartz cell.

9-(1,1-Dimethyl-2-phneylethyl)anthracene (6). To a chilled Grignard reagent prepared from 67.5 g (0.4 mol) of 1,1-dimethyl-2-phenylethyl chloride according to the procedure of Brown *et al.*[19] was added 19.4 g (0.1 mol) of anthrone powder in small portions during the course of 1 hr. The reaction mixture was allowed to stand overnight at room temperature and decomposed with a saturated aqueous solution of ammonium chloride. The ethereal solution was evaporated and heated *in vacuo* at 100 °C to remove low boiling substances. The residual oil, mainly composed of 9-(1,1-dimethyl-2-phenylethyl)-9-hydroxy-9,10-dihydroanthracene‡‡ and anthrone, was dissolved in 200 ml of carbon tetrachloride and heated under reflux for 5 hr in the presence of 30 g of phosphorus pentoxide. The carbon tetrachloride solution was filtered and evaporated. The residue was chromatographed through alumina column with the use of hexane containing 5% of benzene as an eluent to give **6** as pale yellow fluorescent crystals, mp 125—127 °C, in 15% yield. (Found: C, 93.04; H, 7.32%. Calcd for $C_{24}H_{22}$: C, 92.86; H, 7.14%). PMR (CCl_4): δ 1.74 (6H, s), 3.68 (2H, s), 7.01 (5H, s), and 6.9—8.2 (9H, m). The presence of mineral acids easily induced the decomposition of **6** into anthracene and (2-methyl-1-propenyl)benzene.‡‡‡

ap-*9-(1,1-Dimethyl-2-phenylethyl)-11,12-bis(methoxycarbonyl)-9,10-dihydro-9,10-ethenoanthracene (7).* A mixture of 2.80 g (9 mmol) of the anthracene **6** and 2 ml of dimethyl acetylenedicarboxylate in 30 ml of toluene was heated under reflux for 5 hr. Recrystallization of the product from chloroform–methanol gave 2.79 g (70%) of colorless needles, mp 200—201 °C. (Found: C, 79.78; H, 6.18%. Calcd for $C_{30}H_{28}O_4$: C, 79.62; H, 6.24%). MS (*m/e*): 452 (M^+, 1.5), 361 (61), 301 (44), 273 (68), 260 (33), 243 (50), 242 (48), 241 (33), 203 (33), 202 (39), and 91 (100).* IR (Nujol): 1735 and 1715 cm^{-1}.

(±)-sc-9-(1,1-Dimethyl-2-phenylethyl)-11,12-bis(methoxycarbonyl)-9,10-dihydro-9,10-ethenoanthracene (8). The *ap*-isomer **7** was heated at 150 °C for 10 hr in *o*-dichlorobenzene. After evaporation of the solvent, the equilibrated mixture was chromatographed on silica gel (Wakogel C-200) and eluted with benzene. Although the separation was poor, the *sc*-isomer was eluted slightly faster than the *ap*-isomer and repeated chromatographic operation of the fractions containing both of the two isomer enabled us to isolate **8**. Recrystallization of **8** from methanol gave colorless granules, mp 149—151 °C. (Found: C, 79.54; H, 6.42%. Calcd for $C_{30}H_{28}O_4$: C, 79.62; H, 6.24%). MS (*m/e*): 452 (M^+) (Essentially the same fragmentation pattern as that of the *ap*-isomer was obtained). IR (Nujol): 1742 and 1725 cm^{-1}. Recrystallization of **8** from solvents containing benzene or chloroform resulted in the inclusion of the solvent into the crystals.

(±)-sc-9-(1,1-Dimethyl-2-phenylethyl)-11-methoxycarbonyl-9,10-dihydro-9,10-ethenoanthracene-12-carboxylic acid (10). A solution of 420 mg (0.93 mmol) of the dimethyl ester **8** in 20 ml of ethanol was mixed with a solution of 200 mg of potassium hydroxide in 10 ml of ethanol and allowed to stand overnight at room temperature. The resulted crystalline mass was collected by filtration, acidified with dilute hydrochloric acid, and extracted with ether. The ethereal solution, upon evaporation of the solvent followed by recrystallization from chloroform–carbon tetrachloride, afforded 298 mg (73%) of white crystals, mp 188—190 °C (dec.). Found: C, 79.13; H, 5.69%. Calcd for $C_{29}H_{26}O_4$: C, 79.43; H, 5.98%. PMR ($CDCl_3$): δ 1.84 (6H, br s), 3.63 (2H, q, $J_{AB}=14.8$,

‡ The parameters obtained here correspond to the pathway through the anticlinal transition state. Information on the synperiplanar transition state would be obtained by the study of racemization behavior of the optically active *sc*-isomer, which is left for future study.

‡‡ This alcohol was not isolated but its formation was recognized by the PMR spectrum (CCl_4) of the reaction mixture: δ 0.62 (6H, s), 2.60 (2H, s), and 3.82 (2H, q: $J_{AB}=19$, $\delta_{AB}=24$ Hz).

‡‡‡ The acid-catalyzed decomposition of 9-*t*-butylanthracene to anthracene and isobutylene was reported.[19]

* Fragmentation peaks with the intensity of more than 30% are cited.

δ_{AB}=16.7 Hz), 3.72 (3H, s), 5.55 (1H, s), 6.8—8.1 (13H, m), and 11.7 (1H, br s); (C_6H_6): δ 1.82 (3H, s), 1.97 (3H, s), 3.39 (3H, s), 3.90 (2H, br s), and 5.68 (1H, s). IR (Nujol): 1735 and 1685 cm^{-1}.

ap-9-(1, 1-Dimethyl-2-phenylethyl)-11-methoxycarbonyl-9, 10-dihydro-9,10-ethenoanthracene-12-carboxylic acid, mp 223—225 °C (dec.), was similarly prepared from the *ap* diester (**7**). Found: C, 79.77; H, 6.32%. Calcd for $C_{29}H_{26}O_4$: C, 79.43; H, 5.98%. PMR ($CDCl_3$): δ 1.76 (6H, s), 3.63 (3H, s), 3.72 (2H, s), 5.52 (1H, s), 6.9—8.1 (13H, m), *ca.* 8.1 (1H, br s). IR (Nujol): 1735 and 1675 cm^{-1}.

(−)-Menthyl esters of the carboxylic acid ***10***. A solution of 710 mg (1.6 mmol) of the carboxylic acid **10** and 0.5 ml of thionyl chloride in 50 ml of benzene was heated under reflux for 1 hr in the presence of a catalytic amount of pyridine. Complete convertion of **10** to the corresponding acid chloride was checked by PMR of the reaction mixture: δ 1.77 and 1.88 (*gem*-Me_2), 3.30 (OMe), 3.78 (q, J_{AB}=14, δ_{AB}=8.5 Hz, CH_2Ph), and 5.69 (bridgehead). The reaction mixture was evaporated and the residual oil, without purification, was heated with 500 mg of (−)-menthol in 50 ml of pyridine at 100 °C for 2 hr. Evaporation of the solvent followed by chromatography on silica gel with benzene afforded a glass, which was shown to be *ca.* 1: 1 mixture of two diastereomeric esters by PMR. One of the diastereomers (Diastereomer **A**) crystallized out upon dissolution of the glass in hexane. Recrystallization from tetrahydrofuran–methanol gave 133 mg (15%) of colorless granules, mp 199—200 °C. $[\alpha]_D^{25}$ −77.0° (c=5.7, $CHCl_3$). PMR (C_6H_6): δ 1.84 and 2.02 (*gem*-Me_2), 3.51 (OMe), 3.87 (q, J_{AB}=14.1, δ_{AB}=9.1 Hz, CH_2Ph), and 5.87 (bridgehead). MS (*m/e*): 576 (M^+). IR (Nujol): 1735 and 1715 cm^{-1}.

Evaporation of the mother liquor gave a glass which was found by PMR to be *ca.* 1: 5 mixture of **A** and the other diastereomer (**B**). The latter showed the following PMR signals (C_6H_6): δ 1.87 and 1.96 (*gem*-Me_2), 3.51 (OMe), 3.98 (br s, CH_2Ph), and 5.87 (bridgehead).

(−)-sc-9-(1,1-Dimethyl-2-phenylethyl)-11-methoxycarbonyl-9,10-dihydro-9,10-ethenoanthracene-12-carboxylic acid. A solution of 330 mg (0.57 mmol) of Diastereomer **A** in 20 ml of ethanol containing 200 mg of potassium hydroxide was heated at 60 °C for 3 hr and allowed to stand overnight at room temperature. The solution was evaporated *in vacuo* and the residue was acidified with dilute hydrochloric acid and extracted with chloroform. The chloroform solution was dried over magnesium sulfate and evaporated. The resulting solid mass was washed twice with small amounts of benzene to remove (−)-menthol. Recrystallization from chloroform–benzene gave 210 mg (84%) of colorless crystals, mp 188—190 °C (dec.). $[\alpha]_D^{32}$ −24.6 ° (c=2.4, $CHCl_3$). Found: C, 79.25; H, 6.08%. Calcd for $C_{29}H_{26}O_4$: C, 79.43; H, 5.98%.

(+)sc-(1, 1-Dimethyl-2-phenylethyl)-11-methoxycarbonyl-9, 10-dihydro-9,10-ethenoanthracene-12-carboxylic acid. Similar treatment of 182 mg of the glassy mixture (1: 5) of **A** and **B** with potassium hydroxide followed by recrystallization from chloroform–benzene afforded 58 mg of colorless crystals, $[\alpha]_D^{32}$ +24.8° (c=1.2, $CHCl_3$).

Kinetics. A solution of the *ap*-isomer (**7**) in chlorobenzene (*ca.* 10% (w/v)) was sealed in a PMR sample tube and dipped in a boiling solvent bath. At appropriate intervals the sample tube was taken out from the bath and rapidly cooled to room temperature. The PMR spectrum was measured at 34 °C. Careful integration of methyl signals of the methoxycarbonyl groups of the *ap*- and *sc*-isomers afforded the relative population of both isomers.

The rate law for a first order reversible reaction is given[20] by

$$\log\left[1-\left(1+\frac{1}{K}\right)\frac{x}{a}\right] = -\frac{k_1}{2.303}\left(1+\frac{1}{K}\right)t$$

where a is the initial concentration of the *ap*-isomer, x the quantity of the *sc*-isomer formed at time t, and K the equilibrium constant [*sc*]/[*ap*]. The left side of the equation was calculated from the PMR integration data and the plot against t gave a good straight line, the slope of which afforded the rate constant k_1. This procedure was performed at four temperatures using the following solvents as a bath: toluene (111 °C), diethyl carbonate (126 °C), *p*-xylene (138 °C), and cumene (152 °C).

Thermodynamic parameters were obtained from the least square analysis of the following equations:

$$\log k_1 = \log A - \frac{E_a}{4.576}\cdot\frac{1}{T} \quad \text{(Arrhenius plot)}$$

$$\log\frac{k_1}{T} = \left(\frac{\Delta S^{\ddagger}}{4.576}+10.319\right) - \frac{\Delta H^{\ddagger}}{4.576}\cdot\frac{1}{T} \quad \text{(Eyring plot)}$$

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