room temperature, and opened. Unreacted thiol was evaporated in a stream of nitrogen and the residue diluted to 50 mL with 95% alcohol. The UV spectrum of the solution was recorded, and the absorbance at 260 nm was used to monitor the reaction rate. First-order kinetics were observed, and rate constants were obtained from the equation $1 + \log (A - A_\infty) = kt$, where A = absorbance at 260 nm and A_∞ is the absorbance at the infinity titer; the latter was obtained from a sample heated for 4 hours at 200 °C (10 half-lives). A least-squares analysis of the data gave rate constant precisions of approximately 7%.

Acknowledgment. The author would like to thank Professor Martin Stiles for helpful discussions of this work.

Registry No.—**1**, 33416-97-6; **2**, 67761-47-1; **6**, 67784-51-4; **7**, 67761-48-2; benzenediazonium 2-carboxylate, 1608-42-0; phenyl disulfide, 882-33-7; amyl nitrite, 463-04-7; anthranilic acid, 118-92-3; benzenethiol, 108-98-5; 1-butanethiol, 109-79-5.

References and Notes

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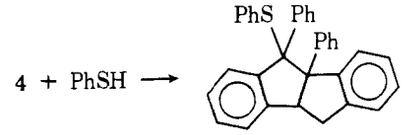
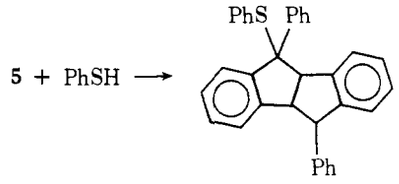
(9) Although these oils were not characterized, material balance data suggest that they, and those found in the reaction of **2** with benzenethiol, are products resulting from the *addition* of benzenethiol to the COT substrate. An addition product such as that derived from the following reaction seems plausible.



Support for this speculation is found in the work of Simonson,[4] who isolated this addition product (along with other compounds) from the photolytic reaction of **1** in benzenethiol.
(10) If our speculation regarding the structure of the oils obtained in the reaction of **1** with benzenethiol is correct (vide supra), the corresponding addition product from **2** follows from the parallel reaction.



(11) It is clear from the NMR comparison that the reaction of **1** with thiol produces none of the trapping product from **2**. One may infer then that thiol completely suppresses the rearrangement. The author would like to thank a reviewer for calling attention to this point.
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Kinetic Study of the Relationship of Rearrangement to Racemization in Certain Dibenzo[a,e]cyclooctatetraenes

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The optically active compound (+)-**16**, when heated, gave the racemic form of the expected rearrangement isomer, (±)-**17**. The rate of optical activity loss was approximately 25% greater than the rate of rearrangement. The optically active acid (−)-**23**, when heated, underwent racemization at a rate much greater than the aforementioned rates. These results led to the conclusion that loss of optical activity in (+)-**16** occurs by way of two competing mechanisms. The predominant mode is that of the biradical rearrangement pathway, and the less important mode is that of simple ring inversion. On the other hand, (−)-**23**, presumed to be incapable of racemizing via a reverse rearrangement mechanism, must utilize the more generally recognized ring inversion mode. The extent of this mechanistic dichotomy and its controlling factors are discussed.

Cyclooctatetraene (COT), as the next higher vinylogue of benzene, has been the subject of intensive inquiry since its preparation by Willstatter[1] in 1911. Unlike benzene, its reactions are more typically those of a polyene, reflecting little resonance stabilization or aromatic character. On the other hand, unlike the lower member of the $4n$ cyclopolyene series, cyclobutadiene, COT exhibits none of the characteristic instability or greatly enhanced reactivity which has come to be associated with that series of the $(CH)_n$ hydrocarbons.[2] The absence of so-called antiaromatic properties in COT undoubtedly arises from its nonplanar geometry, in which its "tub" conformation, well-established by the results of electron diffraction measurements,[3] precludes or sharply limits interaction between its π bonds.

Bond angle requirements early suggested that COT might be nonplanar, and before diffraction results became available the question of its geometry was investigated by chemical means, particularly by Cope and co-workers.[4] The substitution of any hydrogen on the COT ring renders the derivative dissymmetric. Cope attempted to resolve such derivatives, as for example, cyclooctatetraenecarboxylic acid, into the optical antipodes. Such attempts were unsuccessful, and this result suggested that the barrier to inversion, if indeed COT was nonplanar, is probably low, less than 20 kcal/mol.

Although the subsequent diffraction experiments provided an unequivocal answer to the question of geometry, there remained the still interesting problem of the energy barrier to inversion in COT. The magnitude of this barrier has been established recently as 14 kcal/mol by means of NMR spectroscopy,[5] but prior to this spectroscopic analysis Mislow and

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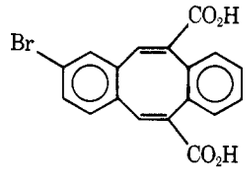
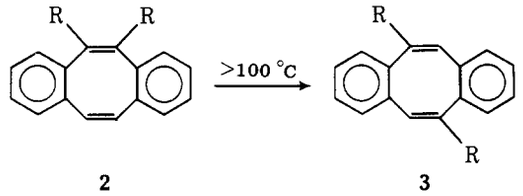
Perlmutter had pursued the energy barrier problem using a well-precedented chemical probe.[6] These workers succeeded in obtaining the first example of an optically active COT derivative by resolving the bromo diacid **1.**



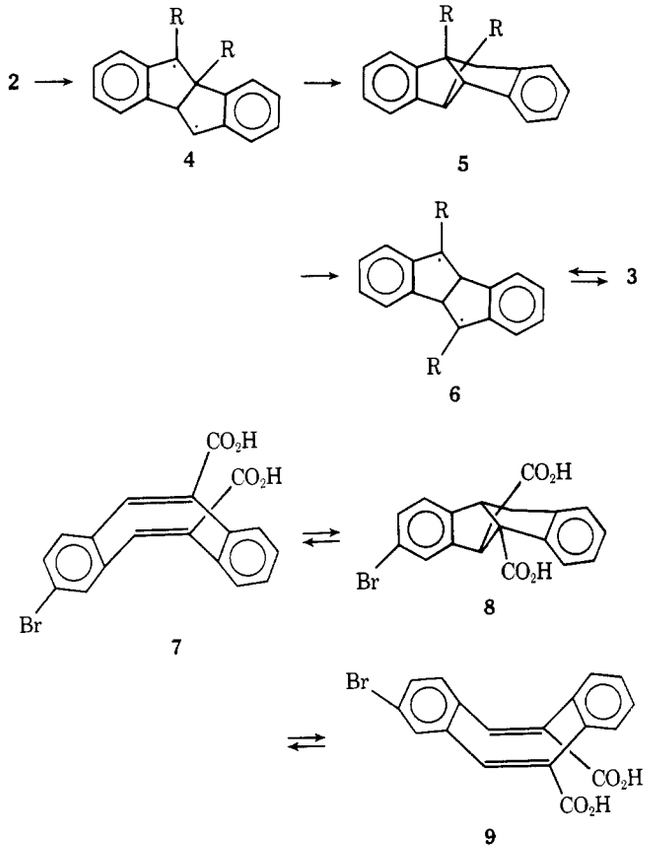
1

This compound was found to undergo racemization when heated, and a kinetic analysis suggested an inversion barrier with an upper limit of approximately 27 kcal/mol. It was assumed that the racemization pathway involved inversion of the central ring, possibly via a flattened transition state. This interpretation of the mode of racemization, straightforward and consistent with the information available at the time, would have gone unremarked if it had not been for the subsequent discovery of a novel rearrangement in closely related systems. Stiles and Burckhardt reported that 5,6-disubstituted-dibenzo[*a*,*e*]cyclooctatetraenes, when heated, are smoothly rearranged to the 5,11-isomers.[7]



2 **3**

The mechanism of this rearrangement has been established in considerable detail.[8] Trapping experiments have shown it to include the biradical intermediates **4** and **6** and, by inference, the tricyclic intermediate **5.** Note that the final step is reversible, although earlier work[9] had shown that the overall rearrangement was irreversible.



4 **5** **6** **7** **8** **9**

The relevance of the rearrangement to the racemization of Mislow and Perlmutter's acid arises from the fact that this racemization can be explained by the rearrangement mechanism.[7] Without including the associated biradical formulas, which are unnecessary to the argument, the potential relationship between these two phenomena, racemization and rearrangement, may be seen with reference to appropriate stereochemical formulas, **7, 8,** and **9.**

In this case, the symmetry of the tricyclic intermediate must lead to racemization, but nondegenerate rearrangement is precluded because of the substitution pattern of the acid. It was now apparent that simple inversion of the central ring was not necessarily the only pathway by which the racemization could be explained, so an investigation of the relationship of this phenomenon to the rearrangement was undertaken.

Results and Discussion

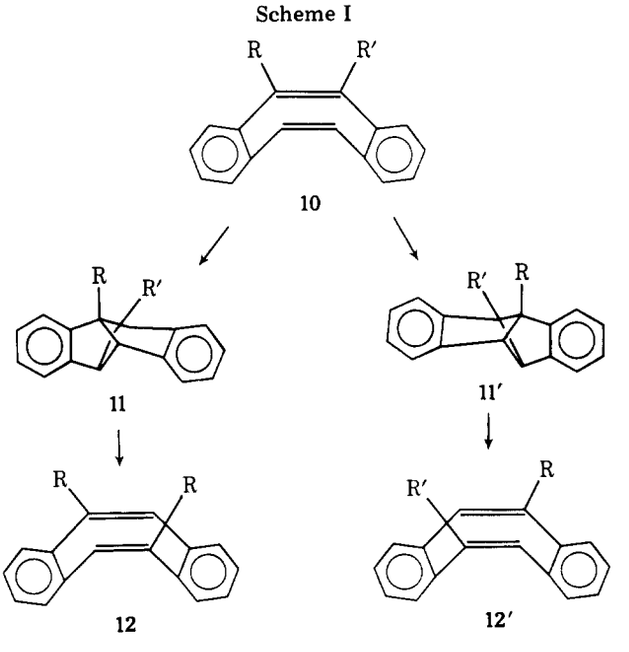
The possibility of a common mechanism was tested using classical chemical methodology. A kinetic analysis of the changes which occurred when optically active derivatives of the 5,6- and 5,11-isomers were heated was made, and the results provided detailed insight into the relationship of the rearrangement to racemization.

The initial argument, which is clarified by reference to Scheme I, was that if an optically active 5,6-disubstituted-dibenzo[*a*,*e*]cyclooctatetraene is heated, (1) the racemic 5,11-isomer should be produced, and (2) if rearrangement provides the exclusive route to racemization, e.g., prior or concurrent inversion does not occur, the rate of rearrangement should equal the rate of optical activity loss.

Counterarguments to the preceding lead to different predictions, and it is especially important to point out that if in fact the starting material was to undergo inversion prior to or concurrent with its rearrangement, the racemization rate would exceed the rearrangement rate. A proviso which must be attached to these kinetic arguments is that R and R′ must be sufficiently similar so that they will not affect the identity of the rates in the formation of the tricyclic enantiomers. In the actual experiment these substituents were phenyl and *p*-carbomethoxyphenyl, which meant that synthesis of a new compound, 5-phenyl-6-(*p*-carbomethoxyphenyl)dibenzo[*a*,*e*]cyclooctatetraene (**16**), and its resolution into the optical antipodes were required for the rate comparison.

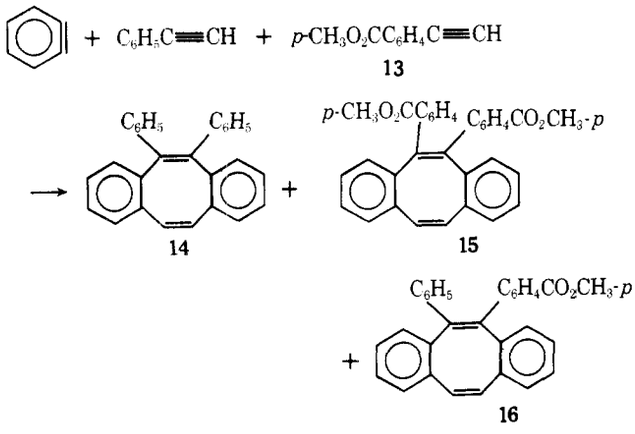
A. Synthesis and Resolution of 5-Phenyl-6-(*p*-carbomethoxyphenyl)dibenzo[*a*,*e*]cyclooctatetraene (16).

Scheme I

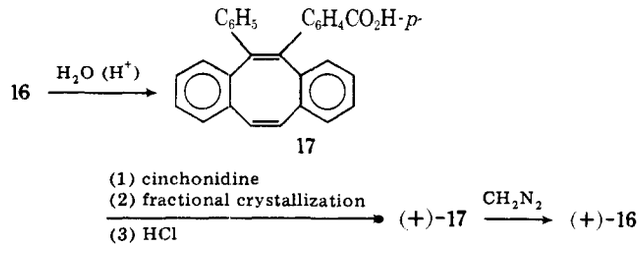


10 **11** **11′** **12** **12′**

Since the reaction of benzyne, generated by thermal fragmentation of benzenediazonium 2-carboxylate, with acetylene derivatives is a convenient route to 5,6-disubstituted-dibenzo[a,e]cyclooctatetraenes,[10] this method was applied to the synthesis of **16** by a cross reaction.



The products of this reaction were readily separated by column chromatography, and resolution of the monoester **16** was accomplished by hydrolysis to the acid **17**, fractional



crystallization of the cinchonidine salts, and reesterification with diazomethane. The dextrorotatory form of the ester was obtained in quantities sufficient for the kinetic experiments.

The key intermediate to the synthesis of the optically active monoester was (*p*-carbomethoxyphenyl)acetylene (**13**). A previous report of the preparation of this compound was found, but yields were too low for the quantities required. An efficient synthesis of **13**, summarized by Scheme II, was worked out. The dicarboxylic acid **18** and *p*-ethynylbenzoic acid (**19**) are new compounds.

B. Comparison of the Rate of Rearrangement of (±)-16 with Its Rate of Optical Activity Loss. With the requisite optically active compound in hand, it was now possible to test the possibility of the common mechanism. When (+)-**16** was heated for a period representing several rearrangement half-lives, workup of the reaction mixture provided the racemic 5,11-isomer, 5-phenyl-11-(*p*-carbomethoxyphenyl)dibenzo[a,e]cyclooctatetraene [(±)-**20**]. The product exhibited no rotation, and subsequent resolution of the parent carboxylic acid of **20** (vide infra) supported the conclusion that complete loss of optical activity attended rearrangement.

Scheme II

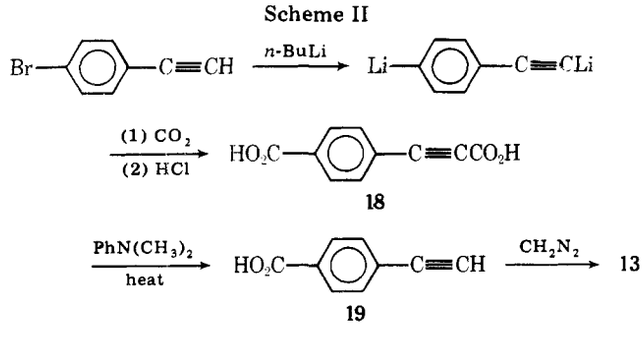
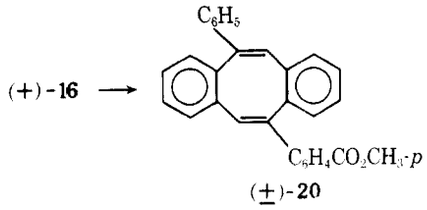


Table I. Rearrangement and Optical Activity Loss of (+)-16

temp, °C	rate of optical activity loss (k_α), s^{-1}	rearrangement rate (k_r), s^{-1}	k_α/k_r
156.5	1.80×10^{-5}	1.41×10^{-5}	1.28
164.4	3.72×10^{-5}	2.92×10^{-5}	1.27
176.9	9.52×10^{-5}	7.65×10^{-5}	1.24

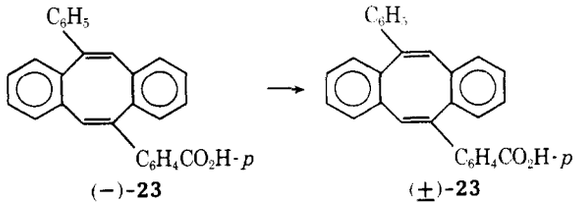
The rate of optical activity loss was measured by conventional polarimetric techniques, and the rate of rearrangement was monitored using ultraviolet spectroscopy; 5,11-diaryl isomers such as **20** absorb strongly compared to the 5,6-isomers. Standard mathematical treatment of data obtained at three temperatures showed that both optical activity loss and rearrangement obeyed first-order rate laws. Rate constants are summarized in Table I.



It can be seen from the data that at each temperature the rate of optical activity loss is approximately 25% greater than the rearrangement rate. Calculation of probable errors suggested that this difference in the two rates was real, and consideration of the measurement techniques gave no hint of any experimental artifice. At least two conclusions could be drawn from the rate comparison. (1) Concurrent racemization via ring inversion adds to the racemization rate derived from the rearrangement pathway, or (2) some reversible step in the rearrangement leads to racemization of the starting material [(+)-**16**], e.g., reversion of the tricyclic enantiomers to racemic **16** (refer to Scheme I). Since the data provided no clear choice between these alternatives, further experiments were undertaken.

C. Rate of Racemization of (−)-5-Phenyl-11-(*p*-carboxyphenyl)dibenzo[*a*,*e*]cyclooctatetraene [(−)-23]. If one assumes that reversibility is limited to the final step of the rearrangement, an informative experiment would be to examine the polarimetric behavior of an optically active 5,11-isomer. Such a compound would resist racemization unless a nonrearrangement pathway to racemization, such as ring inversion, was available to it.

Hydrolysis of **20** gave the corresponding carboxylic acid, the dissymmetric 5-phenyl-11-(*p*-carboxyphenyl)dibenzo[a,e]-cyclooctatetraene [(±)-**23**]. Fractional crystallization of its brucine salts, followed by acid hydrolysis, provided the levorotatory acid, (−)-**23**, in quantities sufficient for polarimetric studies.



When a solution of (−)-**23** was heated, rapid loss of optical activity was observed, and workup of the reaction mixture provided racemic starting material.

The racemization obeyed a first-order rate law, and the rate

Table II

compd	process	temp, °C	rate constant, s^{-1}
(+)-16	rearrangement	164.4	2.91×10^{-5}
(+)-16	optical activity loss	164.4	3.72×10^{-5}
(−)-23	racemization	110.3	2.26×10^{-5}
1	racemization	110.0	3.47×10^{-5} [a]

[a] Calculated from the data of Mislow and Perlmutter.[6]

Table III. Comparison of Activation Parameters

compd	process	E_a, kcal/mol	$H^{\ddagger}$, kcal/mol	$S^{\ddagger}$, eu/mol
(+)-16	rearrangement	31.5	30.6	−10.1
(+)-16	optical activity loss	31.0	30.5	−12.7
(−)-23	racemization	25.3	24.5	−18.5
1	racemization	27.5	26.7	−10.0

was much greater than that of rearrangement or loss of optical activity of the 5,6-compound, (+)-**16**. Rate comparisons, including data derived from the racemization of Mislow and Perlmutter's compound (**1**), are shown in Table II.

On the basis of these rate comparisons, it seems very unlikely that racemization of the 5,11-compound (−)-**23** proceeds by way of a reverse rearrangement mechanism. Such a racemization pathway is available only if reversal proceeds as far as the tricyclic intermediate stage. The tricyclic intermediate, because of its highly strained structure, should lie close to the transition state of the rearrangement. The activation energy of a racemization via reverse rearrangement should therefore be greater than that of the rearrangement. That this is not the case is shown by comparison of the activation parameters in Table III.

The results of our work resolve the question of whether or not the racemization of **1** proceeds by way of simple ring inversion or by way of the biradical rearrangement pathway. Until now the racemization mechanism for **1** and related compounds was in doubt.[11] It seems clear from our rate comparison studies that simple ring inversion is the more usual racemization pathway, while compounds such as (+)-**16** lose optical activity principally by way of the biradical rearrangement route. The unusual behavior of (+)-**16** in this regard can be explained by assuming that the bulky aryl groups in the 5 and 6 positions buttress one another during ring flattening, so that rearrangement becomes the less energetic pathway to optical activity loss.

Experimental Section

Melting points are uncorrected. Microanalyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich. IR spectra were recorded with a Perkin-Elmer Infracord Model 137, UV spectra with a Cary Model 11 recording spectrophotometer, and NMR spectra with a Varian A-60 spectrometer using deuteriochloroform as solvent and tetramethylsilane as an internal standard. Optical rotations were measured at room temperature with a Bendix Ericsson polarimeter, Type 143A, at the sodium D line wavelength.

(*p*-Carboxyphenyl)propiolic Acid (18). A 5-L, three-necked flask equipped with a mechanical stirrer, drying tube, and addition funnel was charged with a mixture of anhydrous ether (500 mL) and tetrahydrofuran (800 mL). The flask was immersed in a dry ice–acetone bath. The stirrer was started, and a solution of 1.9 M *n*-butyllithium in hexane (500 mL) was added dropwise over a 50-min period. To the resulting solution was added dropwise a solution of (*p*-bromophenyl)acetylene (45 g, 0.248 mol) in anhydrous ether (500 mL) over a 55-min period. To the resulting solution of lithium (*p*-lithiophenyl)acetylide was added powdered dry ice (2 L). A slurry was obtained which was stirred for 2.5 h and then allowed to stand overnight. To this mixture was added water (2.5 L) and sodium chloride (600 g). The mixture was stirred briefly, and the aqueous layer was separated, washed with ether, chilled with ice, and acidified to Congo Red with 5% HCl. The product separated as a copious white fluffy precipitate which was dissolved by extracting it once with tetrahydrofuran (1 L) and then twice with ether (1-L portions). The combined extracts were washed with brine, dried over $MgSO_4$, and filtered. Evaporation of the filtrate provided a solid residue which was triturated with petroleum ether and then collected on a Büchner funnel. The crude product (25.4 g, 53.5%) could be used without purification. Recrystallization of the product from methanol provided colorless platelets which decomposed without melting at 300 °C.

Anal. Calcd for $C_{10}H_6O_4$: C, 63.16; H, 3.18. Found: C, 63.30; H, 3.37.

Methyl (*p*-Carbomethoxyphenyl)propiolate. Esterification of (*p*-carboxyphenyl)propiolic acid with diazomethane provided crystalline material which was purified by sublimation at 0.1 torr and 90 °C to give colorless needles, mp 100.5–101.5 °C.

Anal. Calcd for $C_{12}H_{10}O_4$: C, 66.05; H, 4.62. Found: C, 66.22; H, 4.50.

***p*-Ethynylbenzoic Acid (19).** In a 250-mL, round-bottom flask equipped with a reflux condenser and magnetic stirrer were combined (*p*-carboxyphenyl)propiolic acid (8.55 g, 0.045 mol) and *N,N*-dimethylaniline (85 mL). The stirrer was started and the mixture heated at 150–160 °C for 2 h, after which time the evolution of CO_2 was negligible. The reaction mixture was cooled to room temperature, diluted with ether (300 mL), and extracted with 5% KOH. The alkaline extract was acidified to Congo Red with 10% HCl. The product separated as a white fluffy precipitate which was removed by extraction with ether. The extract was washed with water, dried ($MgSO_4$), and filtered. Evaporation of the filtrate provided crude product which was recrystallized from methanol to give colorless platelets (73%) which darken at 200 °C and melt with decomposition at 208 °C.

Anal. Calcd for $C_9H_6O_2$: C, 73.96; H, 4.14. Found: C, 74.02; H, 4.13.

Methyl *p*-Ethynylbenzoate (13). Esterification of *p*-ethynylbenzoic acid with diazomethane provided crystalline material which was purified by sublimation at 70 °C and 0.1 torr to give colorless needles, mp 93.0–95.0 °C (identical with literature[12] melting point).

5-Phenyl-6-(*p*-methoxycarbonylphenyl)dibenzo[*a,e*]cyclooctatetraene (16) and 5,6-Bis(*p*-methoxycarbonylphenyl)dibenzo[*a,e*]cyclooctatetraene (15). In a 500-mL, round-bottom flask equipped with a magnetic stirrer and reflux condenser were combined benzenediazonium 2-carboxylate (2.0 g, 0.0135 mol), phenylacetylene (7.6 g, 0.075 mol), methyl *p*-ethynylbenzoate (12.0 g, 0.075 mol), and dichloromethane (20 mL). The stirred suspension was refluxed for 12 h. Dichloromethane was removed by means of a rotary evaporator and unreacted acetylene in a stream of nitrogen. Unreacted methyl *p*-ethynylbenzoate was recovered by sublimation in vacuo at 70 °C. The residue was dissolved in 20 mL of 50% benzene in cyclohexane and applied to a 30 × 600 mm column of Florisil contained in the same solvent mixture. Elution with 500 mL of the solvent mixture gave 5,6-diphenyldibenzo[*a,e*]cyclooctatetraene (140 mg, 15.8%). Elution with 3 L of benzene provided the title monoester contaminated with unreacted methyl *p*-ethynylbenzoate. The latter was removed by sublimation at 70 °C and 0.1 torr. The unsublimed material was washed with methanol and recrystallized from cyclohexane. The title monoester (1.75 g, 24.8%) was obtained as colorless prisms, from five duplicate runs, mp 184.0–185.0 °C. The UV spectrum (EtOH) gradually increased in intensity between 360 and 220 nm with slight flattening between 235 and 245 nm; ϵ for 240 nm was 32 800. NMR ($CDCl_3$) δ 3.8 (s, 3, OCH_3), 7.48–7.00 (m, 17, vinyl and aromatic protons), 7.79 (dd, J_1 = 9.5 Hz, J_2 = 1.0 Hz, protons ortho to the methoxycarbonyl group).

Anal. Calcd for $C_{30}H_{22}O_2$: C, 86.92; H, 5.35. Found: C, 87.06; H, 5.29.

Further elution of the column with 1 L of 20% ether in benzene provided the title diester (140 mg, 17.5%) which was recrystallized from ether to give colorless prisms, mp 194–195 °C.

Anal. Calcd for $C_{32}H_{24}O_4$: C, 81.34; H, 5.12. Found: C, 81.31; H, 5.14.

5-Phenyl-11-(*p*-methoxycarbonylphenyl)dibenzo[*a,e*]cyclooctatetraene (20). In a small test tube was placed 5-phenyl-6-(*p*-methoxycarbonylphenyl)dibenzo[*a,e*]cyclooctatetraene (368 mg, 0.890 mmol). The contents were melted by warming the tube briefly over a small yellow flame. The tube was flushed with nitrogen, sealed, and placed in an oil bath at 210 °C. The tube was removed after 6 h, cooled to room temperature, and opened. The contents were recrystallized from absolute alcohol, decolorizing with Norit, to give the title

ester as colorless needles (218 mg, 60%): mp 134–138 °C; NMR ($CDCl_3$) δ 3.87 (s, 3, OCH_3), 7.5–6.7 (m, 17, vinyl and aromatic protons), 7.91 (dd, J_1 = 9.5 Hz, J_2 = 1.0 Hz, aromatic protons ortho to the methoxycarbonyl group); UV (EtOH) 275 nm (ε 31 300).

Anal. Calcd for $C_{30}H_{22}O_2$: C, 86.92; H, 5.39. Found: C, 87.11; H, 5.39.

5,11-Bis(*p*-methoxycarbonylphenyl)dibenzo[*a*,*e*]cyclooctatetraene. In a small test tube was placed 5,6-bis(*p*-methoxycarbonylphenyl)dibenzo[*a*,*e*]cyclooctatetraene (518 mg, 1.10 mmol). Thermal rearrangement was effected by the same means as that used in the preceding experiment. Recrystallization of the product from acetone provided colorless crystals (420 mg, 81%), mp 189–192 °C.

Anal. Calcd for $C_{32}H_{24}O_4$: C, 81.34; H, 5.12. Found: C, 81.31; H, 5.14.

5-Phenyl-6-(*p*-carboxyphenyl)dibenzo[*a*,*e*]cyclooctatetraene (17). A solution of the methyl ester **16** (1.86 g, 4.65 mmol) and KOH (1.3 g) in 95% ethanol (200 mL) was refluxed for 3.5 h. The ethanol was distilled at reduced pressure, and the residue was dissolved in water (100 mL), acidified with concentrated HCl (3 mL), and extracted with chloroform. The chloroform extract was washed with water, dried ($MgSO_4$), filtered, and evaporated to give the crude product. Recrystallization of the product from acetone gave colorless crystalline **17** (1.59 g, 89%), mp 242–244 °C.

Anal. Calcd for $C_{29}H_{20}O_2$: C, 86.97; H, 5.15. Found: C, 87.11; H, 5.12.

Resolution of 17. The acid **17** (1.51 g, 3.78 mmol) was combined with a solution of (−)-cinchonidine (1.19 g, 3.78 mmol) in acetone (800 mL) containing water (10 mL), and the resulting solution was allowed to stand at room temperature for 12 h. Evaporation of the solvent gave a residue which was crystallized from a mixture of ligroine and chloroform. Two crops (A and B) of crystals were collected. The mother liquor was evaporated, and the residue crystallized from acetone to give two new crops (C and D). Crops A and B had $[\alpha]^{23}_D$ +6.40 and −0.13° ($CHCl_3$), respectively. Crops C and D had $[\alpha]^{23}_D$ −83.4 and −71.0°, respectively. Crops A and B (total weight, 0.826 g) were combined and stirred with a mixture of chloroform (10 mL), ether (100 mL), and 5% HCl (20 mL). The organic layer was separated, washed with water, dried ($MgSO_4$), filtered, and evaporated to give (+)-**17**, $[\alpha]^{23}_D$ +10° ($CHCl_3$). Crops C and D were combined, acidified, and worked up as before to give (−)-**17**, $[\alpha]^{23}_D$ −19.1° ($CHCl_3$). Recrystallization of the levorotatory acid from alcohol gave (−)-**17**: mp 227–229 °C; $[\alpha]^{23}_D$ −21.0° ($CHCl_3$).

Preparation of (+)-16. To a solution of (+)-**17** in chloroform was added excess diazomethane in ether. After treatment with acetic acid to destroy unreacted diazomethane, the reaction mixture was washed with saturated sodium bicarbonate and then water, and the organic layer was dried ($MgSO_4$), filtered, and evaporated. Recrystallization (MeOH) of the residue gave (+)-**16**: mp 130–140 °C; $[\alpha]^{23}_D$ +5.10° ($CHCl_3$); $[\alpha]^{23}_D$ +30° (adiponitrile).

5-Phenyl-11-(*p*-carboxyphenyl)dibenzo[*a*,*e*]cyclooctatetraene [(±)-23]. A solution of **20** (71.4 mg) and KOH (1.0 g) in 95% ethanol (20 mL) was refluxed for 2.5 h. Workup of the reaction mixture in the usual way provided crude **23**, which was recrystallized from methanol/benzene to give colorless prisms (39 mg), mp 270–272 °C.

Anal. Calcd for $C_{29}H_{20}O_2$: C, 86.97; H, 5.15. Found: C, 86.93; H, 5.25.

Preparation of (−)-23. In a 125-mL Erlenmeyer flask were combined 5-phenyl-11-(*p*-carboxyphenyl)dibenzo[*a*,*e*]cyclooctatetraene (217 mg, 0.543 mmol), anhydrous (−)-brucine (214 mg, 0.543 mmol), hot acetone (40 mL), and 5 drops of water. The resulting clear solution was permitted to stand at room temperature for 12 h. No precipitate formed. Approximately one-third of the solvent was distilled at atmospheric pressure, and the remaining solution was allowed to stand for 5 h. After this time, a crop of small crystals (153 mg), mp 216–220 °C dec, $[\alpha]^{23}_D$ −40 ° ($CHCl_3$), had precipitated. This material was dissolved in a mixture of chloroform (5 mL) and ether (20 mL) and stirred vigorously for 30 min with 5% HCl (15 mL). The layers were separated, and the organic layer was washed with water, dried ($MgSO_4$), and filtered. Evaporation of the solvents gave a crystalline residue (56 mg), mp 220–225 °C, $[\alpha]^{23}_D$ −78.3° (adiponitile), which was used without further purification in the racemization kinetics experiments.

Rate of Rearrangement and Rate of Loss of Optical Activity of (+)-5-Phenyl-6-(*p*-methoxycarbonylphenyl)dibenzo[*a*,*e*]cyclooctatetraene [(+)-16]. A solution of (+)-**16** (120 mg) in adiponitrile (5 mL) was prepared. A 2-drop amount of the solution was transferred to a tared vial, weighed, and set aside for the rearrangement rate analysis. The remaining solution was transferred to a 4-cm polarimeter cell, and the rotation (α) was recorded. The solution was transferred from the polarimeter cell to a test tube equipped with a condenser. The solution was flushed with nitrogen for 1–2 min, and then the nitrogen flow was reduced to maintain a small internal pressure in the tube. The tube was immersed in a thermostated oil bath. After an appropriate amount of time had elapsed, the tube was immersed in a beaker of cold water to quench the reaction. A 2-drop amount of the solution was again removed and weighed. The rotation was measured. The procedure was repeated 7 or 8 times until the rotation had diminished to about one-fourth the initial reading. An infinity titer was obtained by heating the solution for 3–4 h at 200 °C (extrapolated optical reaction was 7–10 half-lives). In each case the rotation was zero, and the ultraviolet spectrum was identical with the spectrum of rearranged ester obtained from racemic starting material.

The rate of rearrangement was followed using an ultraviolet spectrophotometer. Each of the 2-drop portions of the solution removed at the different time intervals was rinsed into a numbered 50-mL volumetric flask with 95% alcohol and diluted to the mark. The spectrum of the solution was recorded between 220 and 400 nm. The spectrum of the rearranged ester contains a maximum near 270 nm. The ratio of molar extinction coefficients of product to starting material at this wavelength is approximately 2. The absorbance of the alcohol solutions at 270 nm was recorded as "raw absorbance". The "corrected absorbance", A, was calculated by multiplying the "raw absorbance" by the ratio of the weight of the 2 drops removed at the zero reading to the weight of the 2 drops removed at the end of the particular interval.

The rate of loss of optical activity was cleanly first order, and the rate constant for this process, k_α, was derived from the expression $\log \alpha = -k_\alpha t$ + constant by a least-squares analysis of the data. The rate of rearrangement was also first order, and the associated rate constant, k_r, was calculated from the expression $1 + \log (A_\infty - A) = -k_r t/2.303$ + constant. Rate constants are recorded in Table I, and activation parameters are given in Table III.

Rate of Racemization of (−)-5-Phenyl-11-(*p*-carboxyphenyl)dibenzo[*a*,*e*]cyclooctatetraene [(−)-23]. Approximately 20 mg of (−)-**23** was dissolved in 4.5 mL of adiponitrile, and the optical rotation of the solution was measured and recorded. The procedure for obtaining data was identical with that previously described, except that samples for UV spectra were removed only at the zero and infinity readings. The UV spectra of these two samples were identical.

The infinity titer was obtained by heating the sample at 170 °C for 3.5 h (ca. 10 half-lives). In each experiment the rotation of the sample after this treatment was zero. The rates of racemization, measured at three temperatures, were first order, and the rate constant was obtained from an expression identical with that used for calculating the rate of loss of optical activity of (+)-**16**. The rate constant is recorded in Table II, and activation parameters are in Table III.

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Registry No.—**13**, 3034-86-4; **14**, 33416-97-6; **15**, 67904-60-3; **16**, 67904-59-0; (+)-**16**, 67904-59-0; **17**, 67904-61-4; (+)-**17**, 68129-80-6; (−)-**17**, 68129-79-3; **18**, 10602-02-5; **19**, 10602-00-3; (±)-**20**, 67904-62-5; (−)-**23**, 67938-57-2; (±)-**23**, 67904-63-6; 5,11-bis(*p*-methoxycarbonylphenyl)dibenzo[*a*,*e*]cyclooctatetrene, 67904-64-7; *p*-bromophenylacetylene, 766-96-1; benzenediazonium 2-carboxylate, 1608-42-0; phenylacetylene, 25640-27-1; lithium (*p*-lithiophenyl)acetylide, 67904-65-8; methyl (*p*-carbomethoxyphenyl)propiolate, 67904-66-9.

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