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Optically Active 9,10-Dihydro-9,10-etheno and -ethanoanthracenes. I. Syntheses of Optically Active 1,5-Disubstituted-9,10-dihydro-9,10-etheno and -ethanoanthracenes.

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1,5-Dimethoxycarbonyl-9,10-dihydro-9,10-ethenoanthracene was synthesized by the reaction of 1,5-dimethoxycarbonylanthracene with dichloroethylene followed by dechlorination with zinc-copper couple. Optical resolution of 1,5-dicarboxy-9,10-dihydro-9,10-ethenoanthracene prepared from the dimethyl ester could be achieved by strychnine to give optically pure (−)-dicarboxylic acid and (+)-diacid with an optical purity of 87.3%. Catalytic reduction of (−)-dicarboxylic acid afforded (−)-ethano-dicarboxylic acid. Transformation of the carboxyl groups in various substituent groups to give optically active C_2-symmetrical etheno- and ethanoanthracene derivatives belonging to the same series of absolute configuration as that of the starting material is described.

The present authors have studied the relation of structure and optical rotatory properties of a number of optically active triptycene derivatives bearing various substituents at various positions of the benzene rings.[1] The absolute configurations of optically active 2,5-dimethoxy-7-substituted- and 2,7-disubstituted-triptycenes have been studied by both X-ray analysis[2] and chemical correlation.[3] It was found that the cautious analyses of CD spectra of these triptycene derivatives lead to antipodal absolute configurations.[4,5]

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1) a) A. Sonoda, F. Ogura, and M. Nakagawa, This Bulletin, **35**, 853 (1962); b) F. Ogura, Y. Sakata, and M. Nakagawa, *ibid.*, **45**, 3646 (1972); c) F. Ogura and M. Nakagawa, *ibid.*, **46**, 651 (1973): d) M. Kuritani, Y. Sakata, F. Ogura, and M. Nakagawa, *ibid.*, **46**, 605 (1973).

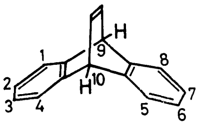
2) N. Sakabe, K. Sakabe, K. Ozeki-Minakata, and J. Tanaka, presented at the 9th International Congress of Crystallography (Kyoto), (1972), *Acta. Crystallogr.*, **B28**, 3441 (1972).

3) M. Kuritani, Y. Sakata, F. Ogura, and M. Nakagawa, *Chimia*, **1972**, 470.

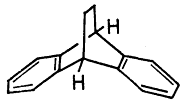
4) J. Tanaka, F. Ogura, M. Kuritani, and M. Nakagawa, *ibid.*, **1972**, 471.

5) J. Tanaka, K. Ozeki-Minakata, F. Ogura, and M. Nakagawa, *Nature, Phys. Sci.*, (London), **241**, 22 (1973).

9,10-Dihydro-9,10-etheno- and ethanoanthracenes (I and II) prepared by Cristol⁶⁾ are stable compounds with a fairly rigid cage structure. 9,10-Dihydro-9,10-etheno- and ethanoanthracene derivatives substituted dissymmetrically in the benzene rings should be resolved in the optical antipodes. In fact, optical resolution and CD spectral properties of some etheno- and ethanoanthracene derivatives have been reported.⁷⁾ Considering the direction of polarization of transition of benzene chromophores,⁸⁾ we have carried out the syntheses and optical resolution of a series of 9,10-dihydro-9,10-etheno- and ethanoanthracenes bearing the same substituent groups at 1,5-positions (III and IV). It is contemplated that systematic studies on the CD spectral properties of series of III and IV with the same absolute configuration may afford valuable information on the relation of structure and rotatory properties.



I



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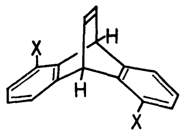
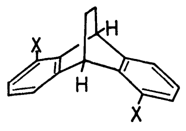


III



IV

The present paper deals with the synthesis and optical resolution of 1,5-dicarboxy-9,10-dihydro-9,10-ethenoanthracene (X) and the transformation of carboxyl groups in optically active X in various substituents to give a series of optically active 1,5-disubstituted derivatives with the same absolute configuration. The reaction sequence of the synthesis of X and ethanoanalogue (XII) starting from 1,5-dichloroanthraquinone is outlined in Fig. 1. The reaction of *cis*- or *trans*-dichloroethylene with 1,5-dimethoxycarbonylanthracene (V) derived from dichloroanthraquinone was carried out in a sealed tube at 180—190°C. As expected, *cis*-dichloroethylene gave an adduct (VI) and the *trans*-isomer afforded two kinds of adducts which could be separated on silica gel column chromatography into crystalline VII and VIII. Treatment of the adduct (VI or VII or VII or a mixture of VII and VIII) with zinc-copper couple in boiling methanol by the reported method⁹⁾ yielded the same 1,5-dimethoxycarbonyl-9,10-dihydro-9,10-ethenoanthracene (IX) in a good yield. Hydrolysis of IX gave dicarboxylic acid (X). Catalytic hydrogenation of IX and X afforded ethano-derivatives (XI and XII), respectively.

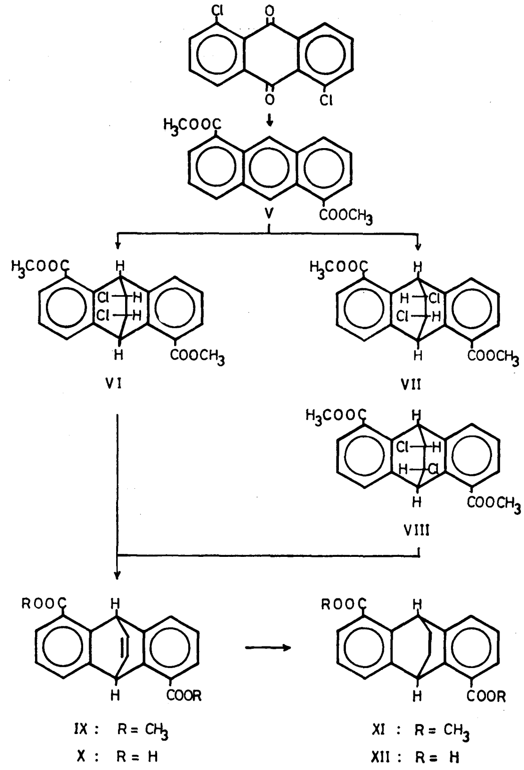


Fig. 1. Synthesis of 1,5-dicarboxy-9,10-dihydro-9,10-etheno- and ethanoanthracenes (X and XII).

The optically resolution of X could b eachieved by strychnine. A solution of X and equimolar strychnine in 99% ethanol was refluxed to give crystalline salt. Optically pure salt obtained by repeated recrystallization of the salt from ethanol was treated with aqueous 50% acetic acid to yield (−)-X. Decomposition of crude salt obtained by concentration of the mother liquor of first recrystallization with aqueous 50% acetic acid afforded (+)-X with an optical purity of 87.3%.¹⁰⁾

The reaction sequence of the transformation of carboxyl groups in optically active X in various substituents is shown in Fig. 2. X was converted into diamino derivative (XIII) by the Curtius reaction *via* acid chloride, azide, and isocyanate. Hydrogenation of XIII over platinum catalyst gave diamino-ethano derivative (XIV). XIV in chloroform was oxidized with peracetic acid to give dinitro-ethanoanthracene (XVIII). (−)-Diamino derivative (XIII) was converted into (−)-dihydrobromide (XV) and the single crystal of (−)-XV was subjected to X-ray structure analysis by the Bijvoet method to determine the absolute configuration. Diazotization of XIII in acetic acid with sodium nitrite followed by hydrolysis afforded etheno-phenol (XVI) which was converted into etheno-dimethyl ether (XVII) by the reaction with dimethyl sulfate. 1,5-Dimethoxycarbonyl-ethenoanthracene (IX) obtained from dicarboxylic acid (X) was treated with lithium aluminum hydride to give bis-hydroxymethyl deriva-

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6) S. J. Cristol and N. L. Hause, *J. Amer. Chem. Soc.*, **74**, 2193 (1952).

7) M-J. Brienne and M. J. Jaques, *C. R. Sci. Acad. Paris, Ser C*, **272**, 1889 (1971); S. Hagishita and K. Kuriyama, *Tetrahedron*, **28**, 1435 (1972).

8) J. R. Platt, *J. Chem. Phys.*, **19**, 263 (1951); J. Petruska, *ibid.*, **34**, 1111 (1961); A. C. Albrecht and W. T. Simpson, *ibid.*, **23**, 1480 (1955); J. Tanaka, This Bulletin, **36**, 833 (1963).

9) S. J. Cristol and D. C. Lewis, *J. Amer. Chem. Soc.*, **89**, 1476 (1967); S. J. Cristol and W. Y. Lin, *J. Org. Chem.*, **34**, 1 (1969).

10) Attempts to resolve (±)-X with cinchonidine resulted in (−)-X with poor optical purity (5.13%).

tive (XIX). The reaction of thionyl chloride with XIX resulted in bis-chloromethyl-etheno derivative (XX). Bis-iodomethyl-etheno compound (XXI) obtained on treatment of XX with sodium iodide in acetone was reduced by lithium aluminum hydride in tetrahydrofuran to give dimethylethenoanthracene (XXII). Catalytic reduction of XXII afforded dimethyl-ethano compound (XXIII).

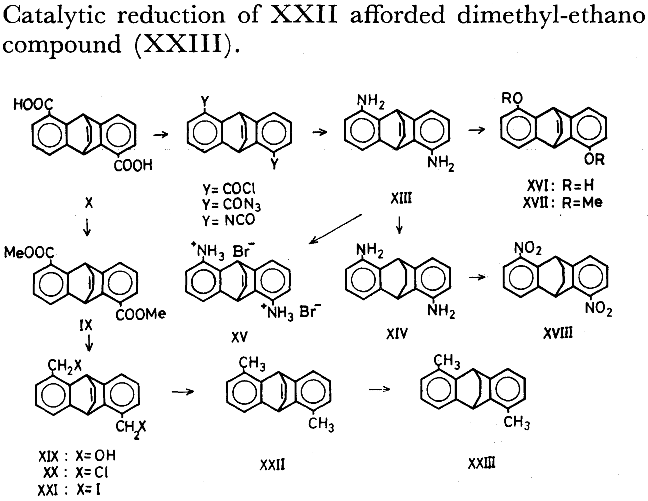

Fig. 2. Transformation of X into 1,5-disubstituted-9,10-dihydro-9,10-etheno- and ethanoanthracenes.

Optically active 1,5-disubstituted-9,10-dihydro-9,10-etheno- and ethanoanthracenes thus prepared clearly belong to a series of the same absolute configuration as that of starting X, because the rigid cage structure of the molecule excludes the possibility of occurrence of the Walden inversion and racemization during the course of transformation.

Experimental

The melting points below 260°C were determined on a Mettler FP2 apparatus and those over 260°C on a Shimadzu Kofler micro hot stage, and are not corrected. Anhydrous pure solvents were used unless otherwise stated. Ligroin with bp 60—80°C was used. The IR and UV spectra were obtained on Hitachi EPI-2, JASCO DS-301 and Hitachi EPS-3T spectrophotometers, respectively. A Yanagimoto ORD-185 and a JASCO J-20 with CD attachment spectropolarimeters were used for the measurements of rotation and CD spectra, respectively. Inflection or shoulder is denoted by an asterisk. Methanol or ethanol containing 10 vol% of 0.1N hydrochloric acid (MeOH–HCl or EtOH–HCl) was used for the measurements of UV, ORD, and CD spectra in an acidic medium. The UV, ORD, and CD spectral data are summarized in Tables 1, 2, and 3. The NMR spectra in deuteriochloroform were measured on a Varian A-60 spectrometer using TMS as an internal standard. Chemical shifts are given in τ-unit.

*1,5-Dimethoxycarbonyl-9,10-dihydro-9,10-(*cis*-11,12-dichloro)-ethanoanthracene (VI).* A mixture of 1,5-dimethoxycarbonylanthracene[1d] (V, 6.54 g, 0.0222 mol) and *cis*-dichloroethylene (18.75 g, 0.2065 mol) in a sealed tube was heated to 180—185°C for 3 days. The crystals deposited on standing the reaction mixture overnight were washed with benzene to give colorless crystals (6.46 g). The residue obtained by evaporating the combined washings and filtrate was dissolved in carbon tetrachloride–benzene (1:1) and the solution was passed through a column of alumina (150 g), yielding an additional amount of crystals, 1.23 g (total 7.69 g, 88.9%). The combined crystals were recrystallized twice from carbon tetrachloride to give pure VI, mp 204.8—205.2°C, IR (KBr-disk): 1718 ($\nu_{C=O}$) cm^{-1}, NMR: 1.98—2.73 (m, 6H, aromatic), 3.83 (m, 1H, bridgehead), 4.09 (m, 1H, bridgehead), 5.50 (t, 2H, bridge), 6.02 (s, 6H, -COOCH$_3$), UV: $\lambda_{\max}^{\text{dioxane}}$ (ε) 291 (4430), 227* (23000), 211 (39500) nm.

Found: C, 61.23; H, 4.14; Cl, 18.22%. Calcd for $C_{20}H_{16}Cl_2O_4$: C, 61.39; H, 4.12; Cl, 18.13%.

1,5-Dimethoxycarbonylanthracene (V, 0.9 g) was recovered from benzene eluate of the alumina column.

*1,5-Dimethoxycarbonyl-9,10-dihydro-9,10-(*trans*-11,12-dichloro)-ethanoanthracene (VII and VIII).* A mixture of V[1d] (5.0 g, 0.017 mol) and *trans*-dichloroethylene (16.5 g, 0.170 mol) in a sealed tube was heated to 180—190°C for 48 hr. Treatment of the reaction mixture by a similar method to that used for VI afforded pale yellow crystals (6.33 g, 95.2%) along with recovered V (0.02 g). A solution of the crystals (5.364 g) in benzene–carbon tetrachloride (1:1) was passed through a column of silica gel (300 g) and eluted with the same mixed solvent. The eluate was divided into 36 fractions, each fraction being 100 ml. As fractions 10—16 gave a spot at the same R_f on tlc (silica gel), they were combined and evapo-

Table 1. UV spectra of etheno- and ethanoanthracenes

Compound	Solvent	$\lambda_{\max}$ in nm (ε)
(±)-IX	MeOH	306 (6610), 284* (2840), 243* (16400), 223 (31100), 205 (33500)
(−)-X	MeOH	305 (6440), 222 (33200), 205 (35100)
(±)-XI	MeOH	290.5 (5270), 230 (21100), 202 (46400)
(±)-XII	MeOH	291 (5130), 263* (1500), 259.5* (1600), 257 (1700), 253.5 (2430), 229 (20700), 210.5 (29100), 206.5 (29400), 202 (30400), 197.5 (38300)
(−)-XIII	MeOH	296 (3140), 224 (41300), 207* (30900), 204 (32700), 200 (31800)
	MeOH-HCl	295* (100), 278 (2510), 270 (1680), 215 (42600), 211* (38500)
(−)-XIV	MeOH	288 (3610), 232* (20800), 212* (35900), 199 (48800)
	EtOH-HCl	290 (210), 270 (1110), 263 (1010), 250* (950), 209* (35000)
(+)-XVII	99% EtOH	285 (2440), 277 (2290), 219 (42000)
(−)-XVIII	EtOH	309* (4210), 262 (11100), 217 (14600)
(−)-XIX	MeOH	284 (3430), 276 (1990), 267* (1050), 257* (1160), 220 (44100), 215* (38700), 207* (35500), 203* (37500), 200* (38300), 196* (41700), 193* (42600)
(−)-XXII	isooctane	281 (1260), 273 (830), 237* (4270), 220 (53300), 215* (38900), 195 (30000)
(−)-XXIII	isooctane	274 (460), 268* (580), 265* (660), 260.5 (1060), 254.5 (1210), 249 (980), 243 (970), 215* (40200), 207.5 (58000), 204 (63700), 200.5 (65000), 196* (71200), 194* (78000), 192* (93300)

Table 2. ORD spectra of etheno- and ethanoanthracene at 20°C

Compound	Solvent	Concentration (g/100 ml)	$[\alpha]$ ($\lambda_{\max}$ in nm)
(−)-X	dioxane	0.237	−333.3° (D), −411.0° (546)
	MeOH	0.004925	−7920° (312), −3860° (297), −6090° (287), −1750° (272), −29250° (236)
(−)-XIII	MeOH	0.00615	−1040° (436), −1580° (405), −2340° (365), −8730° (310), +2930° (289), −63400° (242)
	MeOH–HCl	0.00745	−820° (365), −1260° (308), +5130° (279), −7070° (275), −6640° (273), −12300° (266*), −12700° (260), −11000° (252)
(−)-XIX	MeOH	0.00589	−760° (365), −1150° (304), +2170° (285), −6210° (280), −5980° (278), −9120° (270), −7560° (257), −63800° (224)

Table 3. CD spectra of etheno- and ethanoanthracenes

Compound	Solvent	$\lambda_{\max}$ ($\Delta\varepsilon$) in nm
(−)-IX	MeOH	307 (−5.5), 282 (−7.4), 226 (−65.0), 205 (+46.0)
(−)-X	MeOH	307 (−5.0), 281 (−6.4), 226 (−65.0), 204 (+47.0)
(−)-XI	MeOH	293 (−9.7), 242* (−16.0), 222 (−22.6), 209 (−31.7), 196 (+22.0)
(−)-XIII	MeOH	297 (−8.69), 276 (+3.35), 260 (+3.20), 228 (−11.1), 206 (+80.8)
	MeOH–HCl	294 (−0.24), 276 (+6.73), 269 (+4.78), 239* (−7.23), 215 (−40.3), 195 (+10.1)
(−)-XIV	MeOH	292 (−8.35), 272 (+1.57), 237 (−35.1), 214 (−30.5), 201 (+39.0)
	MeOH–HCl	291 (−0.17), 270 (+2.02), 264 (+1.63), 230* (−6.39), 222 (−6.87), 207 (−24.2)
(+)-XVII	99% EtOH	285 (+5.85), 277 (+4.85), 250 (−14.44), 223 (+153.43), 203 (−82.52)
(−)-XVIII	EtOH	318 (−8.03), 285 (−6.50), 258 (+0.15), 238 (−5.93), 227 (+1.09), 204 (−10.70)
(−)-XIX	MeOH	283 (+5.83), 274 (+3.01), 265 (−1.12), 257 (−1.75), 251 (−1.53), 241 (+0.67), 220 (−103.7), 198 (+40.8)
(−)-XXII	Isooctane	281 (+4.89), 274 (+3.29), 266 (+2.70), 255 (+1.47), 245 (+1.78), 222 (−50.03), 214 (−28.72), 202 (+25.01)
(−)-XXIII	Isooctane	274 (+3.13), 268* (+2.56), 265 (+2.71), 260* (+1.91), 232* (−11.19), 214 (−37.69), 200 (+9.33)

rated to give crystals (2.733 g) which were recrystallized from benzene–ligroin to afford colorless needles, mp 211.6—211.7°C, 2.136 g. Fractions 17—23 gave two spots on tlc indicating that they contain VII and VIII. Fractions 24—36 gave a spot on tlc and were therefore combined and evaporated, yielding crystals (1.225 g). Recrystallization from benzene–ligroin afforded colorless granulous crystals, mp 256.3—256.4°C 0.925 g.

Lower Melting Isomer: IR (KBr-disk): 1720 ($\nu_{C=O}$) cm^{-1}, NMR: 2.00—2.87 (m, 6H, aromatic), 4.13 (t, 2H, bridgehead), 5.77 (m, 2H, bridge), 6.02 (s, 6H, $-COOCH_3$), UV: $\lambda_{\max}^{\text{dioxane}}$ (ε) 290 (4260), 228 (24100), 211 (37200) nm.

Found: C, 61.65; H, 4.18; Cl, 18.12%. Calcd for $C_{20}H_{16}Cl_2O_4$: C, 61.39; H, 4.12; Cl, 18.13%.

Higher Melting Isomer: IR (KBr-disk): 1715 ($\nu_{C=O}$) cm^{-1}, UV: $\lambda_{\max}^{\text{dioxane}}$ (ε) 292 (4200), 287* (4140), 230* (23200), 211.5 (43500) nm.

Found: C, 61.19; H, 4.01; Cl, 18.09%. Calcd for $C_{20}H_{16}Cl_2O_4$: C, 61.39; H, 4.12; Cl, 18.13%.

1,5-Dimethoxycarbonyl-9,10-dihydro-9,10-ethenoanthracene (IX). From cis-*Adduct (VI).* Zinc-copper couple[11] (76 g) was added to a solution of VI (3.00 g, 7.67 mmol) in methanol (400 ml) and benzene (140 ml). The mixture was refluxed for 4 days under stirring. The hot reaction mixture was filtered and the insoluble material was washed successively with hot methanol and hot benzene. The combined filtrate and washings were concentrated and mixed with water (1000 ml) and extracted with benzene. The extract, after washing and drying, was evaporated under reduced pressure to give colorless crystals 2.43 g (95.3%) which were recrystallized from methanol to yield pure IX, mp 150.5—151.0°C, IR (KBr-disk): 1724 ($\nu_{C=O}$) cm^{-1}, NMR: 2.27—3.16 (m, 8H, aromatic and olefinic), 3.30—3.55 (m, 2H, bridgehead), 6.03 (s, 6H, $-COOCH_3$).

Found: C, 75.25; H, 4.99%. Calcd for $C_{20}H_{16}O_4$: C, 74.99; H, 5.03%.

From Lower Melting trans-*Adduct (VII or VIII).* A mixture of lower melting *trans*-adduct (0.301 g, 0.77 mmol), zinc-copper couple[10] (7.6 g), methanol (40 ml) and benzene (15 ml) was refluxed under stirring for 48 hr. The reaction mixture was worked up according to a procedure similar to that used for VI, and the crude IX in benzene was chromatographed on alumina (15 g). Colorless crystals 0.288 g (92.2%) obtained from the first benzene eluate (300 ml) were recrystallized twice from methanol, yielding pure IX as colorless rhomboids, mp 151.4—151.7°C. The IR spectrum was found to be identical with that of IX derived from *cis*-adduct.

Found: C, 74.97; H, 5.13%. Calcd for $C_{20}H_{16}O_4$: C, 74.99; H, 5.03%.

From Higher Melting trans-*Adduct (VII or VIII).* Zinc-copper couple[11] (7.6 g) was added to a mixture of higher melting *trans*-adduct (0.297 g, 0.76 mmol), methanol (40 ml) and benzene (30 ml), and the mixture was refluxed for 77.5 hr under stirring. Crystals obtained on working up the reaction mixture by a similar procedure to that used for *cis*-adduct were found to be contaminated with the starting chloro compound (25% on the basis of NMR spectrum). The crystals in benzene (20 ml) and methanol (60 ml) were treated with zinc-copper couple[10] (8.0 g) for further 28 hr. Working up the reaction mixture yielded colorless crystals, 0.143 g (58.8%), which were recrystallized 3 times from methanol to give pure IX, mp 149.8—151.1°C. The IR spectrum was identical with that of IX obtained from *cis*-adduct.

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[11] R. D. Smith and H. E. Simmons, "Organic Syntheses," Vol. 41, p. 72 (1961).

Found: C, 74.97; H, 5.03%. Calcd for $C_{20}H_{16}O_4$: C, 74.99; H, 5.03%.

A mixture of VII and VIII gave IX under the same reaction conditions.

1,5-Dicarboxy-9,10-dihydro-9,10-ethenoanthracene (X). A solution of potassium hydroxide (100 g) in water (200 ml) was added to a solution of IX (4.305 g, 13.44 mmol) in methanol (300 ml) and the mixture was refluxed for 5 hr. After the methanol had been removed by distillation, the mixture was made acidic to Congo red with concentrated hydrochloric acid under cooling. Colorless precipitate formed was washed thoroughly with cold water and dried *in vacuo* at 100°C to give X, 3.86 g (98.4%). This material was recrystallized successively from acetic acid and methanol to afford pure X, colorless crystals, mp 303—309°C (decomp.), IR (KBr-disk): 1678, 1691 ($\nu_{C=O}$) cm^{-1}.

Found: C, 73.50; H, 4.21%. Calcd for $C_{18}H_{12}O_4$: C. 73.96; H, 4.14%.

X could be converted into IX on heating with methanol and sulfuric acid.

1,5-Dimethoxycarbonyl-9,10-dihydro-9,10-ethanoanthracene (XI), Dimethyl ester (IX, 0.324 g, 1.011 mmol) in dioxane (50 ml) was reduced over platinum oxide (21.4 mg). The crystals (0.316 g) obtained on evaporation of the solvent were recrystallized twice from methanol to yield pure XI, colorless crystals, mp 140.1—140.3°C, IR (KBr-disk): 1713 ($\nu_{C=O}$) cm^{-1}, NMR: 2.15—3.03 (m, 6H, aromatic), 4.34 (m, 2H, bridgehead), 6.06 (s, 6H, -COOCH$_3$), 8.27 (t, 4H, ethane bridge).

Found: C, 74.36; H, 5.06%. Calcd for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63%.

Hydrolysis of XI under the similar reaction conditions used for IX afforded ethano-dicarboxylic acid (XII).

1,5-Dicarboxy-9,10-dihydro-9,10-ethanoanthracene (XII). Catalytic hydrogenation of X (0.0987 g, 0.338 mmol) in methanol (40 ml) over platinum oxide (14.9 mg) afforded XII as colorless crystals (0.1024 g) which were recrystallized twice from methanol to give pure XII, mp 318—327°C (decomp.), IR (KBr-disk): 1690 ($\nu_{C=O}$) cm^{-1}.

Found: C, 73.30; H, 5.02%. Calcd for $C_{18}H_{14}O_4$: C, 73.46; H, 4.80%.

XII could be converted into XI on treatment with methanol and sulfuric acid.

Optical Resolution of (±)-1,5-Dicarboxy-9,10-dihydro-9,10-ethenoanthracene (X). A solution of equimolar strychnine (4.58 g, 0.0137 mol) in 99% ethanol (600 ml) was added to a solution of (±)-X (4.00 g, 0.0137 mol) in the same solvent (3500 ml). After being refluxed for 3 hr, the mixture was concentrated to *ca.* 1000 ml and allowed to stand overnight. Crystalline salt deposited (3.43 g) was recrystallized 4 times from 99% ethanol to give optically pure salt, mp 322—326°C (decomp.), 1.43 g.

Found: C, 74.41; H, 5.45; N, 4.43%. Calcd for $C_{39}H_{34}N_2O_6$: C, 74.74; H, 5.47; N, 4.47%.

Since the measurement of rotation of the strychnine salt was difficult owing to its poor solubility in organic solvents, the increase in optical purity of the salt was followed by measurements of rotation of dicarboxylic acids obtained from the mother liquors of recrystallization on acidification with acetic acid.

Optically pure salt thus obtained was decomposed with aqueous 50% acetic acid to yield optically pure (−)-X, mp 315—322°C (decomp.), 0.65 g.

Found: C, 73.45; H, 4.24%. Calcd for $C_{18}H_{12}O_4$: C, 73.96; H, 4.14%.

The mother liquor of the first recrystallization was concentrated to give crystalline salt (5.05 g). Decomposition of the salt with aqueous 50% acetic acid afforded (+)-enantiomer, 2.35 g, $[\alpha]_D$ +291.2° (*c*, 0.215, dioxane), optical purity, 87.3%.

(−)-1,5-Dimethoxycarbonyl-9,10-dihydro-9,10-ethenoanthracene (IX). Concentrated sulfuric acid (3 ml) was added to a solution of (−)-X (0.196 g) in methanol (30 ml) and the mixture was refluxed for 16.5 hr. The reaction mixture was worked up by the usual way to afford (−)-etheno-diester (IX), 0.198 g (92.4%). Pure (−)-IX was obtained by recrystallization from methanol, mp 151.5—151.8°C, $[\alpha]_{405}$ −1160° (*c* 0.00546, methanol).

Found: C, 75.22; H, 5.14%. Calcd for $C_{20}H_{16}O_4$: C, 74.99; H, 5.03%.

(−)-1,5-Dimethoxycarbonyl-9,10-dihydro-9,10-ethanoanthracene (XI). Reduction of (−)-IX (22.6 mg) in dioxane (10 ml) over platinum oxide (6.6 mg) yielded colorless liquid which could be crystallized on trituration with methanol. Recrystallization from methanol gave pure (−)-XI, colorless crystals, mp 121.8—122.4°C, 19.4 mg, $[\alpha]_{405}$ −1170° (*c* 0.00600, methanol).

Found: C, 74.21; H, 5.66%. Calcd for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63%.

(−)-1,5-Diamino-9,10-dihydro-9,10-ethenoanthracene (XIII). A mixture of (−)-X (0.441 g, 1.508 mmol), thionyl chloride (5 ml) and tetrahydrofuran (40 ml) was refluxed for 3 hr. Crude acid chloride (0.716 g) obtained by evaporation of volatile material under reduced pressure was dissolved in tetrahydrofuran (16 ml), and a solution of sodium azide (0.359 g, 5.521 mmol) in water (8 ml) was added under ice-cooling. After being stirred for 3 hr at the same temperature, the reaction mixture was mixed with ice-water and extracted with benzene. The extract, after washing and drying, was concentrated under reduced pressure to give crystalline acid azide. Thoroughly dried acid azide (0.561 g) in benzene (40 ml) was refluxed for 5 hr. Isocyanate (0.584 g) obtained as a brown liquid on evaporation of the solvent under reduced pressure was mixed with a solution of potassium hydroxide (3 g) in 99% ethanol (35 ml) and water (8 ml). After the mixture had been refluxed for 12 hr, the reaction mixture was poured onto ice-water and extracted with benzene. Concentration of the extract, after washing and drying, afforded crude diamine (XIII, 0.281 g) as a brown solid. A solution of the crude XIII in benzene–ether (9: 1) was passed through a column of silica gel (30 g) and the filtrate was chromatographed on the same adsorbent. Elution with dichloromethane afforded (−)-XIII (0.128 g, 79.1%) which was recrystallized from ether-ligroin to give pure (−)-XIII, mp 188.3—189.6°C (racemate, mp 187.6—189.5°C), IR (Nujol mull): 3320, 3230 (ν_{N-H}), 1627 (δ_{N-H}) cm^{-1}, NMR: 2.72—3.75 (m, 8H, aromatic and olefinic), 4.85 (t, 2H, bridgehead), 6.45 (s, 4H, -NH$_2$).

Found: C, 81.89; H, 6.10; N, 11.81%. Calcd for $C_{16}H_{14}N_2$: C, 82.02; H, 6.02; N, 11.96%.

(−)-1,5-Diamino-9,10-dihydro-9,10-ethanoanthracene (XIV). Hydrogenation of (−)-XIII (0.167 g, 0.712 mmol) in methanol (20 ml) over platinum oxide afforded crude (−)-XIV (0.158 g) which was chromatographed on silica gel and eluted with benzene–ether (9: 1) to yield (−)-XIV (0.146 g, 86.7%). Recrystallization of this material from benzene-ligroin gave pure (−)-XIV, mp 213.3—213.8°C (racemate, mp 188.8—188.9°C), IR (Nujol mull): 3340, 3230 (ν_{N-H}), 1625 (δ_{N-H}) cm^{-1}, NMR: 2.90—3.43 (m, 6H, aromatic), 5.68 (s, 2H, bridgehead), 6.60 (s, 4H, -NH$_2$), 8.30 (t, 4H, bridge).

Found: C, 81.49; H, 6.84; N, 11.73%. Calcd for $C_{16}H_{16}N_2$: C, 81.32; H, 6.83; N, 11.86%.

(−)-1,5-Diamino-9,10-dihydro-9,10-ethenoanthracene Dihydrobro-

mide (XV). A mixture of hydrobromic acid (47%, 2 ml) and water (2 ml) was added to a solution of (−)-XIII (0.0211 g) in 99% ethanol (10 ml). Homogeneous solution obtained on warming the mixture was allowed to stand at room temperature. Fine needles deposited after a week were dissolved on addition of the same solvent (5 ml) under warming. The homogeneous solution in a loosely stoppered flask was kept in a dark place at room temperature. After 3 months, single crystal of (−)-XV was obtained as a rod.

Found: C, 46.54; H, 4.53; Br, 38.22%. Calcd for $C_{16}H_{16}Br_2N_2 \cdot H_2O$: C, 46.40; H, 4.38; Br, 38.59%.

(−)-1,5-Dinitro-9,10-dihydro-9,10-ethanoanthracene (XVIII). To a warm solution of peracetic acid prepared by heating a mixture of chloroform (0.1 ml), 90% hydrogen peroxide (0.15 ml), concentrated sufuric acid (2 drops) and acetic anhydride (0.1 ml) was added dropwise a solution of (−)-XIV (51.7 mg) in chloroform (5 ml). After the mixture had been refluxed for 2.5 hr under stirring, the reaction mixture was poured onto water and extracted with chloroform. The extract, after washing and drying, was concentrated under reduced pressure to afford crystals (37.1 mg, 57.2%). A solution of the crystals in carbon tetrachloride–benzene (1:1) was passed through a column of alumina (7 g). The crystals (23.3 mg) obtained from the early filtrate (150 ml) were recrystallized twice from benzene–methanol to give pure (−)-XVIII, feather-like crystals, 10.7 mg, mp 206.3—207.3°C (racemate, mp 225.1—225.6°C), IR (Nujol mull): 1532 ($\nu_{as\ N-O}$), 1347 ($\nu_{s\ N-O}$) cm^{-1}, NMR: 2.00—2.90 (m, 6H, aromatic), 4.47 (broad s, 2H, bridgehead), 8.15 (broad s, 4H, ethane bridge).

Found: C, 64.71; H, 4.13%. Calcd for $C_{16}H_{12}N_2O_4$: C, 64.86; H, 4.08%.

(+)-1,5-Dimethoxy-9,10-dihydro-9,10-ethenoanthracene (XVII). To a solution of (+)-XIII (0.0573 g, 0.2446 mmol) in acetic acid (2 ml) was added dropwise a solution of sodium nitrite (0.047 g, 0.6812 mmol) in water (1.0 ml) under ice-cooling. After being stirred for further 1.5 hr at the same temperature, the solution of diazonium salt was added dropwise to boiling 6N sulfuric acid (24 ml) and reflux was continued for 1.5 hr. The reaction mixture was repeatedly extracted with ether. The ethereal extract, after washing and drying, was concentrated under reduced pressure. Crude (+)-phenol (XVI, 0.0434 g, 75.1%) obtained as a brown solid was methylated without purification. In the case of racemate, crude XVI was converted into diacetate by the usual method, and treated with lithium aluminum hydride in tetrahydrofuran to give pure (±)-XVI.

(±)-Diacetate: mp 176.7—177.1°C. Found: C, 74.99; H, 5.03%. Calcd for $C_{20}H_{16}O_4$: C, 74.99; H, 5.03%.

(±)-Phenol (XVI): mp 231.4—234.8°C (decomp.). Found: C, 81.05; H, 5.08%. Calcd for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12%.

A mixture of crude (−)-XIV (43.4 mg), dimethyl sulfate (0.15 g), potassium carbonate (0.75 g) and acetone (13 ml) was refluxed for 18.5 hr. The reaction mixture was worked up in the usual way to give crude crystals (46.6 mg, 72% based on (+)-XIII). The crude crystals dissolved in carbon tetrachloride–benzene (1:1) were passed through a column of alumina (20 g). Colorless crystals (15.3 mg) obtained from the early eluate (200 ml) were recrystallized from methanol–benzene to yield pure (+)-XVII, colorless needles, 9.3 mg, mp 206.9—207.3°C (sealed tube) (racemate 210.0—210.4°C), NMR: 3.60—2.77 (m, 8H, aromatic and olefinic), 4.43 (t, 2H, bridgehead), 6.23 (s, 6H, $-OCH_3$).

Found: C, 82.13; H, 6.09%. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10%.

(−)-1,5-Bis(hydroxymethyl)-9,10-dihydro-9,10-ethenoanthracene XIX). A solution of (−)-IX (0.158 g, 0.494 mmol) in tetrahydrofuran (10 ml) was added to a suspension of lithium aluminum hydride (0.295 g) in the same solvent. After refluxing for 21 hr, ethyl acetate (5 ml), ice-water (5 ml) and 6N sulfuric acid (60 ml) were added successively to the reaction mixture under ice-cooling, and then extracted with ether. The extract, after washing and drying, afforded yellow liquid (0.143 g) on evaporation under reduced pressure. The liquid was chromatographed on silica gel (10 g) and eluted with benzene–ether (9:1) to give pale yellow liquid (0.113 g, 86.7%) which could be crystallized from benzene–acetone, yielding pure (−)-XIX, colorless crystals, 0.0454 g, mp 154.5—155.1°C (racemate, mp 204.5—205.5°C), IR (Nujol mull): 3260 (ν_{O-H}) cm^{-1}.

Found: C, 81.72; H, 6.10%. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10%.

(−)-1,5-Dimethyl-9,10-dihydro-9,10-ethenoanthracene (XXII). To a solution of (−)-XIX (79.1 mg, 0.2993 mmol) in benzene (20 ml) was added thionyl chloride (2 ml). After the mixture had been refluxed for 10 hr, the volatile material was removed under reduced pressure to give crude XX (84.9 mg). Crude (−)-XX thus prepared was used in the following reaction. (±)-XX was recrystallized from ligroin to give pure material, mp 195.6—197.5°C, NMR: 2.47—3.23 (m, 8H, aromatic and olefinic), 4.41 (t, 2H, bridgehead), 5.23 (s, 4H, $-CH_2Cl$).

Found: C, 71.71; H, 4.78%. Calcd for $C_{18}H_{14}Cl_2$: C, 71.77; H, 4.69%.

Crude (−)-XX (84.9 mg) in acetone (15 ml) was refluxed for 6 hr with sodium iodide (0.2 g) under shielding from light. Crude crystals of (−)-XXI (102.4 mg) obtained by working up the reaction mixture in the usual way were dissolved in tetrahydrofuran (40 ml) and the solution was added to a stirred suspension of lithium aluminum hydride (0.2 g) in the same solvent (40 ml). After being refluxed for 25 hr, the reaction mixture was treated successively with ethyl acetate, water and 6N sulfuric acid and extracted with ether. The extract, after being washed and dried, was concentrated under reduced pressure. The resulting colorless liquid (58.6 mg, 84.3%) was distilled *in vacuo* to give pure (−)-XXII, bp 90—100°C/15 mmHg (bath temp.) which gave a spot on tlc, NMR: 2.72—3.36 (m, 8H, aromatic and olefinic), 4.66 (t, 2H, bridgehead), 7.58 (s, 6H, $-CH_3$).

(±)-XXII was obtained as crystals, mp 159.4—162.9°C (from methanol) which gave an identical UV spectrum in isooctane with that of (−)-XXII.

Found: C, 92.82; H, 7.03%. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94%.

(−)-1,5-Dimethyl-9,10-dihydro-9,10-ethanoanthracene (XXIII). (−)-XXII (21.1 mg) in 99% ethanol was reduced over platinum oxide. The product dissolved in carbon tetrachloride was chromatographed on alumina (10 g). Crude crystals obtained from the early eluate (100 ml) were recrystallized from methanol to give pure (−)-XXIII, mp 92.4—94.7°C (racemate, mp 49.0—55.0°C), NMR: 2.79—3.18 (m, 6H, aromatic), 5.46 (s, 2H, bridgehead), 7.59 (s, 6H, $-CH_3$), 8.36 (t, 4H, ethane bridge).

Found: C, 91.99; H, 7.83%. Calcd for $C_{18}H_{18}$: C, 92.26; H, 7.74%.