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THE TRANSMISSION OF SUBSTITUENT EFFECTS IN ISOMERIC DICHLOROETHANO-BRIDGED ANTHRACENE DERIVATIVES[1, 2]

E. J. GRUBBS, R. FITZGERALD, R. E. PHILLIPS, and R. PETTY
Department of Chemistry, San Diego, State College, San Diego, California 92115

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Abstract—The syntheses and characterization of the *syn* (**2b**) and *anti* (**2a**) isomers of methyl-*cis*-11,12-dichloro-9,10-dihydro-9,10-ethano 2-anthroate as well as methyl-9,10-dihydro-9,10-ethano 2-anthroate (**2c**) are described. Geometric assignments for **2a** and **2b** were based upon dipole moments and chemical degradation. The rates of base-catalyzed hydrolyses of the three esters in aqueous ethanol are reported. The acid dissociation constants for the corresponding three bridged-anthracene carboxylic acids **3a**, **3b** and **3c** in aqueous methanol and their rates of reaction with diphenyldiazomethane in ethanol and in toluene have been measured. The angular dependence of the substituent effects in this system is discussed.

INTRODUCTION

THE search for a model which will quantitatively describe the influence of polar and dipolar substituents upon reactivity at remote sites within a molecule continues to enlist the efforts of a growing number of investigators. The problem's appeal, perhaps, attests to its fundamental importance, but belies the frustration attending the failure to find a universally applicable model. Tests of the relative applicability of the classical inductive theory[4] and the Kirkwood-Westheimer[5] electrostatic approach have taken several forms. One such method has employed comparisons of measured reactivities (or ratios of reactivities) of rigid bicyclic and spirane derivatives with calculated values. The calculated values are determined from the number of sigma bonds intervening between the substituent and reaction site combined with appropriate fall-off factors on the one hand and from molecular geometric parameters and effective dielectric constants required in the K and W method on the other.[6] An alternate probe is based upon the fact that dipole-charge electrostatic interaction models of the K and W type predict an angular dependence of dipole orientation upon reactivity, whereas the classical inductive model does not. Traditionally this has led to the construction of rigid molecules bearing substituents held in a configuration such that the inductive and electrostatic models give opposing predictions of substituent effect upon reactivity.* Dewar and Grisdale[11] have suggested an alternate electrostatic model which has been applied reasonably successfully in dissecting substituent effects in aromatic systems. However, this theory does not explicitly account for angular dependence of substituent effects.

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*Roberts and Carboni[7] first suggested the utility of such systems in connection with their studies of substituted phenylpropiolic acids.

Golden and Stock[7a] reported a convincing example of the reversal of the "normal" inductive effect caused by a "reversed" angular orientation of the dipole. Other examples of this approach have been reported using substituted cinnamic and naphthoic acids.[8-10]

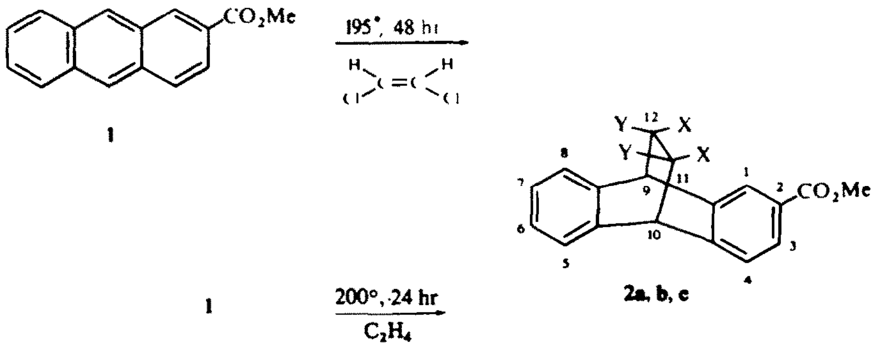
We have recently described our newly initiated efforts to evaluate substituent effect models.[3, 12] We have chosen to explore dependency of these effects on dipole orientation in rigid geometrically isomeric systems. This paper reports our findings obtained from the ethano-bridged anthracene derivatives.

RESULTS

Syntheses and experiments related to geometric assignments

The *syn* and *anti* isomers of methyl-*cis*-11, 12-dichloro-9, 10-dihydro-9, 10-ethano 2-anthroate (**2b** and **2a**) and the "unsubstituted" analog **2c** were prepared as shown in Scheme I. The corresponding acids (**3a** X=H, Y=Cl; **3b** X=Cl, Y=H; and **3c** X=Y=H) were obtained by basic hydrolysis. The isomers **2a** and **2b** were separated by a combination of column chromatography and fractional crystallization. the dipole moments of **2a** and **2b** were determined in benzene.* they are listed in Table 1 along with those for compounds **2c**, **4**,[14] and **5**[15] (also in benzene) measured during the course of the present study for purposes of independently estimating the values for **2a** and **2b**.

SCHEME I



	X	Y
2a	H	Cl
2b	Cl	H
2c	H	H

The two dichloro acids **3a** and **3b** were individually subjected to degradation. The Curtius rearrangement was employed, followed by deamination via diazotization and reduction in hypophosphorus acid[17] as shown in Scheme II. In each case *cis* and only *cis*-11,12-dichloro-9,10-dihydro-9,10-ethanoanthracene (**5**) was isolated in approximately 40% overall yield.

Rate and acidity measurements

(a) *Dissociation constants*. The apparent p*K*'s for the three acids, **3a**, **3b** and **3c** were determined potentiometrically in 50% aqueous ethanol (v/v) at 25°. The results are shown in Table 2

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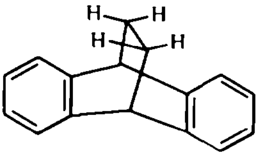
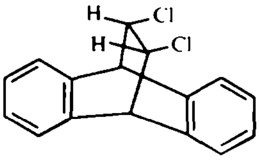
*Dielectric constants of solutions were measured using a Dipolmeter Type DM 01 (Wissenschaftlich-Technische Werkstätten GmbH, Weilheim, Germany). The Guggenheim method[13] was employed for obtaining dipole moments.

TABLE 1. DIPOLE MOMENTS OF SEVERAL BRIDGED-ANTHRACENE DERIVATIVES

Compound	Measured μ (Debye)	Calculated* μ (Debye)
2a	2·60	1·69
2b	3·80	4·32
2c	2·31	—
 4	0·92	—
 5	2·92	—

* In calculating these values we have assumed the geometry of ethanoanthracene adopted by Arbusov and Vereshchagin.[16] The chlorines on carbons 11 and 12 were assumed to form tetrahedral angles with the C_{11}—C_{12} bond and to lie in a plane which forms a 120° angle with the plane of carbons 9, 10, 11 and 12. The bond lengths were taken to be: C—Cl (1·77 Å), C_{sp^3}—C_{sp^3} (1·54 Å), C_{sp^3}—C_{sp^2} (1·50 Å), bonds in benzene rings (1·39 Å), and C_2—C_{17} (carboxylate carbonyl carbon) (1·46 Å).

SCHEME II

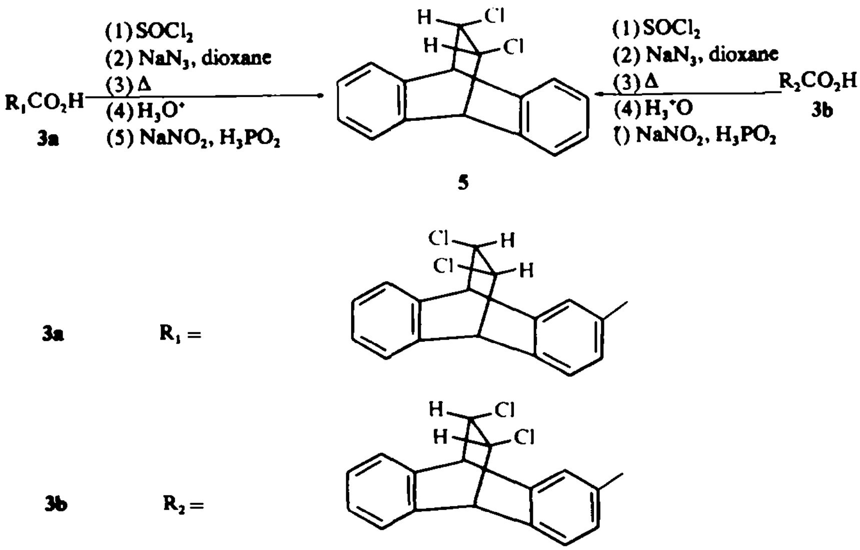


TABLE 2. APPARENT p*K*'s IN 50% AQUEOUS ETHANOL (v/v) AT 25°

Compound	Apparent p*K*
3a	5·67 (5·69)
3b	6·07 (6·10)
3c	6·25 (6·28)

(b) *Rates of reaction of diphenyldiazomethane with* **3a**, **3b** *and* **3c**· The rate measurements were performed as described in the Experimental. No correction was made for the etherification accompanying the esterification in ethanol.[18] The initial acid concentration employed was approximately tenfold in excess over the diphenyldiazomthane initial concentration. Rate constants for the esterifications in absolute ethanol and in toluene are shown in Table 3.

TABLE 3. SECOND-ORDER RATE CONSTANTS FOR THE REACTION OF DIPHENYLDIAZOMETHANE WITH **3a**, **3b** AND **3c** AT 26·7°

Acid	Initial acid concentration, (moles/l) × 10^3	Solvent	k_2[a] (l/mole sec) × 10^2
3a	3·121	C_2H_5OH	1·677
	2·969	C_2H_5OH	1·693
3b	2·985	C_2H_5OH	1·353
	3·003	C_2H_5OH	1·348
3c	3·022	C_2H_5OH	0·954
	3·170	C_2H_5OH	0·988
3a	3·279	$C_6H_5CH_3$	2·85
	3·028	$C_6H_5CH_3$	2·62
	3·279	$C_6H_5CH_3$	2·75
3b	3·136	$C_6H_5CH_3$	1·101
	3·035	$C_6H_5CH_3$	1·101
	3·096	$C_6H_5CH_3$	1·081
3c	3·086	$C_6H_5CH_3$	0·388
	3·352	$C_6H_5CH_3$	0·374

[a] Statistically derived probable errors were less than 1% for individual runs.

(c) *Rates of base-catalyzed hydrolyses of esters* **2a**, **2b** *and* **2c**. The rate constants were determined as described in the Experimental Section and are listed in Table 4.

DISCUSSION

Structural assignments for the isomeric esters **2a** *and* **2b** *and acids* **3a** *and* **3b**

The dipole moments determined for **2a** and **2b** are only in fair agreement with calculated values. This is not surprising in view of the uncertainties in bond lengths and angles within the isomeric chloro esters and the model compounds. Nonetheless, these observed differences rendered desirable a demonstration that neither **2a** nor **2b** possessed a dichloroethano bridge with chlorines *trans* to one another.* Although equilibrated

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* Two such isomers are possible as Diels-Alder adducts of *trans* 1,2-dichloroethylene and methyl 2-anthroate.

TABLE 4. SECOND-ORDER RATE CONSTANTS FOR THE BASIC HYDROLYSIS OF **2a**, **2b** AND **2c** IN 96% ETHANOL 4% WATER (v/v) AT 25·0°

Ester	Initial ester concentration, (moles/l) × 10^4	$k_2{}^a$, (l/mole sec) × 10^4
2a	3·00	6·88
2a	3·00	6·76
2b	3·00	2·64
2b	3·01	2·66
2c	4·09	1·52
2c	3·94	1·45

[a] The statistically derived probable errors were of the order of 2–3% for individual runs.

mixtures of 1,2-dichloroethylene contain a preponderance of the *cis* form, the ratio (approximately 60/40) is not large.[19, 20] It is not posible to reliably estimate the rate of geometric isomerization of *cis* dichloroethylene in our reaction medium from data obtained under grossly different conditions.[19, 20] There was no evidence found for the presence of more than two isomers from the condensation of *cis* dichloroethylene with methyl 2-anthroate.* Nonetheless, to remove any uncertainties, **2a** and **2b** were hydrolyzed to the corresponding acids **3a** and **3b**. Acids **3a** and **3b** were then separately degraded to *cis*-11,12-dichloro-9,10-ethanoanthracene (**5**) as shown in Scheme II.

Rates and acidities

The apparent p*K*'s for **3a** and **3b** show a striking dependence of acidity upon the angular orientation of the dipoles. The change in acidity is in accord with expectations based upon a dipolar field effect model. As pointed out earlier, the classical inductive effect model does not predict such an angular dependence upon dipole orientation. It can be further seen that the order of acidities (**3a** > **3b** > **3c**) is paralleled by the rates of basic hydrolyses for the corresponding methyl esters (**2a** > **2b** > **2c**). In fact, a plot of log $k_{\text{hydrolysis}}$ versus p*K* for these esters and acids affords a straight line with a correlation coefficient of 0·997. The pitfalls of placing too great an importance on a "three point plot" are all too obvious. Nonetheless, this is at least suggestive of a linear free energy relationship.

The data shown in Tables 2, 3 and 4 (and in particular the comparisons of acidities and/or reactivities for **3a**, **3b and 2a**, **2b**) suggest that dipolar field effects are operative. However, it is also apparent that these results cannot be adequately interpreted on the basis of an unmodified Kirkwood–Westheimer equation. Using such a model the *syn* acid **3b** would have been expected to exhibit the highest p*K* in the series and the smallest rate of reaction with diphenyldiazomethane. And similarly the *syn* ester **2b** should have shown the smallest rate of hydrolysis.

The relevant geometric parameters for the isomeric chloro acids **3a** and **3b** required in the application of the Kirkwood–Westheimer equation are approximately as follows (for

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* A recent analysis of the dichloroethylenes remaining after a condensation of *cis* dichloroethylene (which also serves as solvent) with 2-acetoxy-anthracene at approximately 200° for 48 hr showed the mixture to be 92·7% *cis* and 7·3% *trans*. the starting dichloride composition was 93·3% *cis* and 6·7% *trans*.

each C—Cl dipole, the distance, r, separating its midpoint from the carboxyl proton is followed by the angle, θ, formed by the dipole and this line): C_{12}—Cl_{syn}, 6·82 Å, −72°; C_{11}—Cl_{syn}, 7·46Å, −84°; C_{12}—Cl_{anti}, 7·92 Å, 27°; C_{11}—Cl_{anti}, 8·47 Å, 5°. These values were calculated using the bond angles and lengths already mentioned. The carboxyl proton was placed at 1·45 Å beyond the carboxyl carbon on an extension of the line joining it to C_2. The dibenzobicyclo [2.2.2] octadiene ring system is extremely rigid. It is impossible to construct this system with steel Dreiding models using normal tetrahedral units for carbons C_9—C_{12}. However it can be constructed with obvious strain using Fieser Plastic Dreiding models. In spite of this rigidity a small amount of molecular adjustment from dipole–dipole repulsions and charge–dipole attractions or repulsions appears possible through ring deformation involving motions of C_{11} and C_{12}. The possible effect of such deformation on the geometry of the *syn* isomer (**3b**) or its anion is of particular concern. It is instructive to consider the effects of ring deformation in which charge–dipole repulsion cause the C_{12}—CO_2^- distance to increase and the C_{11}—CO_2^- distance to diminish. When this is done and the original angle θ associated with the C_{12}—Cl dipole is forced to open to as large as −85°, the angle associated with the *syn* C_{11}—Cl dipole simultaneously decreases to about −65°. It is clear from this type of analysis that ring deformations such as these will not alter the predicted order of acidities of the three acids based upon the K and W electrostatic field model.

A major problem repeatedly encountered in interpreting substituent effect data is the evaluation of the importance of possible highly selective solvent interactions. In the preliminary account of this work the tentative suggestion of a linear free energy relationship between pK's and logarithms of ester hydrolysis rate constants was offered as an argument against specific solvent effects being the source of reactivity differences within the two series.[3] However the similarities between the solvents (50% versus 96% aqueous ethanol) and reactions in these two series do not offer a stringent test for specific solvation. With this in mind, the rates of diphenyldiazomethane esterification of the acids **3a**, **3b** and **3c** were determined in two drastically differing solvents, namely ethanol and toluene. The results are shown in Table 3. Again it is seen that the orders of reactivities remain the (**3a**>**3b**>**3c**). The log k versus pK plots for these esterifications also suggest linearity.* Thus the importance of highly specific solvent effects appears to be quite limited in these systems.

Somewhat surprisingly, *a reversal of the normal (inductive model) substituent effect is not observed in comparisons of reactivity between* **2b** *and* **2c** *and* **3b** *and* **3c**. The reasons for this unexpected behavior are not completely clear. One possibility is that inductive effects may be superimposed upon field effects in this system. It should be

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* The mechanism for the reaction of diphenyldiazomethane and carboxylic acids has not been as extensively studied in toluene as in alcohols. It is no doubt complicated by the existence (and perhaps reaction) of dimers. Nonetheless, rate constants for diphenyldiazomethane esterifications of series of acids in toluene lead to excellent linear free energy relationships when combined with appropriate sigma constants derived from acidities determined in water. For example Bowden and co-workers[18] have obtained such a correlation (coeff. 0·991) for the DDM reaction with thirteen substituted acetic and propionic acids. The sigma constants (σ_I) were those employed by Charton.[21] The average of correlation coefficients for basically the same set of acids undergoing the same reaction in six different alcohol solvents was 0·992. In the DDM esterification of phenylacetic acid (at 30°) in toluene Bowden[18] noted that the rate coefficients extrapolated to zero acid concentration from the "first order measurements" were close to those calculated for 0·006 M acid (the lowest initial concentration employed) under second order conditions. Using 10 cm cells, initial acid concentrations were lowered to approximately 0·003 Molar in the present study.

remembered that the Kirkwood–Westheimer model encompasses both a direct electrostatic and an inductive effect.[22] The inductive "portion" of the total effect is approximated by the polarization of the molecular cavity. Nonetheless, the "point dipole" approximation may be invalid in certain systems.* In these cases (with appropriate geometry) the polarization may be opposed to the direction anticipated on the basis of the "point dipole orientation" as employed in the K and W equation. Wilcox[23] recently discussed this problem in somewhat different terms emphasizing the importance of polarizable species contiguous with the molecular cavity in moderating the transmission of substituent effects. Accordingly in isomers **2a** and **2b** and **3a** and **3b**, the C—Cl bonds should be considered as dipoles of finite length within the molecular cavity. Since the negative ends (Cl's) are closer to the edge of the cavity, they would act through regions of higher effective dielectric constant than that through which the positive ends (C's) act. The unexpected acid strength (and reactivity) of **3b** compared with **3c** and similarly the unexpected reactivity of **2b** compared with **2c** may reflect a diminished field exerted at the carboxylate center by the outer (negative) dipole ends. This could result in a dominating field originating near carbons 11 and 12 in spite of the slightly closer proximity of the Cl atoms.

In this connection it may be noted that Tanford's modification[24] of the K and W model reveals the critical dependence of charge interactions on the depth of the charges and dipoles within the molecular cavity.

EXPERIMENTAL

M.p. are uncorrected unless specified. IR spectra were determined on a Perkin–Elmer Model 321 or 621 Infrared Recording Spectrophotometer. NMR spectra were obtained using a Varian Model A–60 spectrometer. TMS was used as an internal standard in the specified solvent. UV spectra were determined on a Cary Model 14 Recording Spectrophotometer. Elemental analyses were performed by Mr. C. F. Geiger.

2-*Anthroic acid*. The acid was prepared by the zinc reduction of 2-anthraquinone carboxylic acid (MCB, white label) in aqueous ammonium hydroxide. It was obtained as yellow fluorescent crystals in 64% yield after two crystallizations from AcOH, m.p. 283–285° (Lit.[25] m.p.279°). Neutralization equivalent Calcd: 222; Found: 227.

Methyl 2-*anthroate* (**1**). The esterification of 2-anthroic acid was effected by conc HCl in MeOH. The ester was isolated in 95% yield, m.p. 186·5–188°. One recrystallization from benzene raised the m.p. of the yellow-green crystals to 187–188·5° (84%) [Lit.[25]m.p. 128°]; NMR ($CDCl_3$): 3·99 (s, 3H, —OMe), 7·22–8·87 (m, 9H, aromatic); IR ($CDCl_3$: ν_{max} 1717 cm^{-1}; mass spectrum (80 eV); *m/e* 236 (molecular ion), *m/e* 221 (parent ion—CH_3), *m/e* 205 (parent ion—OME), *m/e* 177 (parent ion—CO_2Me); mol wt (by decrease of chloroform vapor pressure), Calcd: 236; Found: 237. (Found: C, 81·41; H, 4·97. $C_{16}H_{12}O_2$ requires C, 81·34; H, 5·13).

No explanation seems apparent for the discrepancy in m.p. for this compound cited in the present work and reported earlier.[25] The spectral and analytical data obtained for **1** remove any doubt concerning its structure.

Methyl-syn *and* anti-cis-11,12-*dichloro*-9,10-*dihydro*-9,10-*ethano* 2-*anthroate* (**2b** *and* **2a**). A soln of 2·0 g (0·0085 mole) of methyl-2-anthroate in 19 g (0·198 mole) *cis*-1,2-dichloroethylene was introduced into a 200 × 20 mm heavy-walled glass tube. The soln was thoroughly degassed, sealed, and then heated in a Parr apparatus at 195° for 48 hr. After cooling, the reaction mixture was subjected to chromatography over Merck acid-washed alumina. The column was eluted with benzene. Repeated fractional crystallizations from benzene or EtOH were also employed. Progress being made the course of the separations was easily followed by observation of the relative intensities of the Me singlets corresponding to unreacted **1** and the two isomeric dichloroethano-bridged products, *syn* **2b** and *anti* **2a**. In benzene these singlets appear at 3·65,

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* In fact, it is probably a rather poor approximation in most real systems as Dewar and Grisdale[11] have pointed out. Specifically it is only applicable to the extent that the length of the dipole is very short compared with the distance separating it from the charge at the reaction site.

3·52 and 3·57 ppm respectively. From a 3·53 g mixture of *syn* **2b** and *anti* **2a** was obtained 332 mg of **2b**, m.p. 160–162°. (Found: C, 65·19; H, 4·40. $C_{18}H_{14}Cl_2O_2$ requires: C, 64·91; H, 4·23) and 554 mg of **2a**, m.p. 181–182·5°. (Found: C, 64·48; H, 4·58; Cl, 21·13. $C_{18}H_{14}Cl_2O_2$ requires: C, 64·91; H, 4·23; Cl, 21·29).

A subsequent preparation and separation of these two isomers employing, primarily, fractional crystallization led to **2b** in 28% yield (based on unrecovered **1**), m.p. 164–165° and **2a** in 31% yield. m.p. 183–184°. IR **2b** (CCl_4): ν_{max} 1730 cm^{-1}; UV (C_2H_5OH): λ_{max} 246 (9,910); NMR ($CDCl_3$): 3·90 (s, H, —OMe). 4·48 and 4·58 (2 narrow m., 4H, 9,10 and 11,12 protons), 7·0–8·1 (m, 7H, aromatic); IR **2a** (CCl_4): ν_{max} 1730 cm^{-1}; UV (EtOH): λ_{max} sh, 245 (9,320); NMR ($CDCl_3$): 3·90 (s, 3H, —OMe), 4·45 and 4·57 (2 narrow m., 4H, 9,10 and 11,12 protons), 6·9–8·06 (m, 7H, aromatic).

Methyl-9,10-*dihydro*-9,10-*ethano* 2-*anthroate* (**2c**). Methyl 2-anthroate (2·0 g, 0·0085 mole) in 2·6 g toluene was allowed to react with ethylene in a high pressure autoclave at 200° for 24 hr under a pressure of 700 psi. The light brown liquid product of the reaction was passed through a column of acid-washed alumina eluting with benzene. The desired ester, obtained first as a colorless oil, was crystallized three times from EtOH affording 1·4 g (63%) of colorless crystals, m.p. 110–111°. (Found: C, 82·11; H, 6·01. $C_{18}H_{16}O_2$ requires: C, 81·80; H, 6·13); IR (CCl_4): ν_{max} 1727 cm^{-1}; UV (C_2H_5OH): λ_{max} 247 (10,500); NMR ($CDCl_3$): 1·70 (narrow m, 4H, 11,12-protons), 3·88 (s, 3H, —OCH_3), 4·38 (broad s, 2H, 9,10-protons), 6·9–8·0 (m, 7H, aromatic).

syn-cis-11,12-*Dichloro*-9,10-*dihydro*-9,10-*ethano*-2-*anthroic acid* (**3b**). A mixture of 171 mg (0·514 mmole) of the *syn* ester **2b** and 1·39 g KOH in 15 ml EtOH was boiled under reflux for 1 hr. The resulting ppt was dissolved in water, filtered, and the filtrate acidified with 3N HCl. The product was collected and recrystallized from benzene and then from ether affording 78 mg (48%) of **3b** as colorless crystals, m.p. 258–260°. (Found: C, 63·89; H, 3·91; Cl, 21·86. $C_{17}H_{12}Cl_2O_2$ requires: C, 63·99; H, 3·76; Cl, 22·22). Neutralization equivalent; Calcd: 319; Found: 319; IR (KBr disk): ν_{max} 1670 cm^{-1}; UV (EtOH): λ_{max} 244 (8,930).

anti-cis-11,12-*Dichloro*-9,10-*dihydro*-9,10-*ethano*-2-*anthroic acid* (**3a**). The acid was obtained by basic hydrolysis of 231 mg, 0·692 mmole of the ester **2a** as described above. The crude product was crystallized twice from benzene affording 178 mg (81%) of **3a** as colorless crystals, m.p. 295–297°. (Found: C, 64·30; H, 3·81. $C_{17}H_{12}Cl_2O_2$ requires: C, 63·99; H, 3·76). Neutralization equivalent; Calcd: 319; Found 326; IR (KBr disk): ν_{max} 1700 cm^{-1}; UV (EtOH): λ_{max} sh 243 (8,300).

9,10-*Dihydro*-9,10-*ethano* 2-*anthroic acid* (**3c**). A similar hydrolysis of **2c** (300 mg, 1·14 mmole) led to 226 mg (80%) of colorless crytals (from benzene), m.p. 231–233°. (Found: C,81·98 ; H, 5·68. $C_{17}H_{14}O_2$ requires: C, 81·58; H, 5·64). Neutralization equivalent: Calcd: 250; Found: 253; IR (KBr disk): ν_{max} 1679 cm^{-1}; UV (EtOH): λ_{max} 245 (9,620).

Degradation of anti-cis-11,12-*dichloro*-9,10-*dihydro*-9,10-*ethano*-2-*anthroic acid* (**3a**) *to* cis-11,12-*dichloro*-9,10-*dihydro*-9,10-*ethanoanthracene* (**5**). Because of the limitations on quantities of **3a** and **3b** available for degradation experiments, the intermediates in the following reaction sequence were not purified or characterized between each successive step.

To 0·122 g, 0·383 mmole of the *anti* acid **3a** was added 5 ml of freshly distilled thionyl chloride. The mixture was boiled under reflux for 2 hr and then concentrated under reduced pressure.

The partially crystalline acid chloride was dissolved in 1·5 ml dioxan and added slowly to a soln of 35·0 mg, 0·538 mmole of sodium azide in 3 ml of 83% aqueous dioxan maintained at 6–9°. Two additional 1 ml rinses with dioxan were used to insure the quantitative transfer of the acid chloride. The mixture was stirred at 5–9° for 30 min. Water (2 ml) was added and the mixture stirred for an additional 30 min at 1°. Addition of 10 ml of water precipitated the acyl azide which was isolated by ether extraction affording 120 mg of tan-colored crystals.

The crude acyl azide was dissolved in 5·0 ml dioxan and boiled under reflux for 45 min. The cooled soln containing the isocyanate was diluted to 15 ml with dioxan and placed into a constant addition funnel fitted to a high-dilution addition assembly. The isocyanate soln was added, at a rate of about 1·5 drops per min, to a soln of 30 ml dioxan and 13 ml conc HCl. The addition via the high dilution reservoir to the boiling aqueous, acidic dioxan soln required 8 hr. An additional 2 ml conc HCl was added and the soln was boiled for 10 hr. The amine was extracted into ether. It was then partially separated from neutral contaminants by dissolution in HCl aq, washing with ether and reprecipitating with base to give 86 mg tan crystals. Since the amine is only partially soluble in hydrochloric acid, it was dissolved in 50% hypophosphorous acid, the soln was filtered, and the amine reprecipitated from the filtrate with ammonium hydroxide. In this way 52 mg white crystals were obtained from 60 mg crude tan product.

A 49 mg sample of this amine was dissolved in 3 ml 33% hypophosphorous acid at 2°. A soln of $NaNO_2$ (12 mg, 0·17 mmole) in 1·5 ml water was added over a 5 min period at 2–3°. Gas evolution ceased after stirring for 1 hr. The mixture was then stirred at room temp for 1·5 hr. The ppt was collected, washed with water and dried leaving 42 mg of cream-colored crystals, m.p. 193–202°. this represents an overall yield from **3a** of 40%. The IR spectrum (KBr disk) of this product was nearly identical to that of an authentic sample of **5**.[15] The IR spectrum was grossly different from that of a sample of **6**.* The *cis*-dichloride (42 mg) obtained from the degradation was further purified by a combination of sublimation and crystallization from CCl_4 affording 14 mg colorless crytals, m.p. 206–207·5°; mixture m.p. with authentic **5** (m.p. 208–208·5°), 206·5–207·5°; mixture m.p. with an authentic sample of *trans*-11,12-dichloro-9,10-dihydro-9,10-ethanoanthracene* (m.p. 115–117°), 104–195°. The IR spectra (KBr disks) of the two samples showing no depression of mixture m.p. were essentially identical.

A similar degradation of 0·125 g, 0·392 mmole of **3b** afforded 43 mg (40% overall yield) tan crytals, m.p. 201–207°. The IR spectrum (KBr disk) of this product was nearly identical to that of an authentic sample of **5**. A sample (36 mg) of this degradation product was further purified by sublimation and crystallization from CCl_4 affording 22 mg pure *cis*-dichloroethanoanthracene, m.p. 209–209·5°; mixture m.p. with authentic **5**, 207·5–208°; mixture m.p. with authentic **6**, 105–192°.

Measurements of apparent acid dissociation constants in 50% (vol/vol) aqueous ethanol

The p*K* determinations were performed potentiometrically with the aid of a Beckman Research pH Meter. The electrodes (glass, Beckman model 40485 and calomel, Beckman model 39170 A5) were standardized using succinic acid–lithium hydrogen succinate (in aqueous EtOH) and potassium hydrogen phthalate (in aqueous EtOH) buffers. Titrations were carried out using approximately 0·01 N NaOH in 50% by volume aqueous EtOH. Distilled water was boiled for 1 hr and allowed to cool under N_2 before preparing stock solns. Titrations were conducted under N_2 in a water-jacketed cell maintained at 25·0 ±0·1°.

Determination of rate constants for the base-catalyzed hydrolyses of **2a**, **2b** *and* **2c**

The rates were measured at 25° in 96% EtOH–4% water by volume. Equal volumes of the hydrolyzing base (approximately 0·06 N NaOH) and the ester in the 96% aqueous EtOH (brought to 25° separately) were rapidly mixed. Aliquots of the soln containing the hydrolyzing ester were periodically removed, quenched with standardized HCl and back titrated with dilute standardized NaOH to a bromothymol blue end point. Nine or ten points were obtained in a typical run covering the first two half-lives. Rate constants were calculated on an IBM 1620 computer using a program for a second-order rate expression with least squares error analysis.

Product isolations of the three acids formed in the hydrolyses were effected under conditions approximating those used in the rate determinations. Each reaction was allowed to proceed to near completion. The resulting acid was then precipitated with dilute HCl. The *anti* (**3a**), and unchlorinated (**3c**) acids were recrystallized several times from benzene. The *syn* acid (**3b**) was recrystallized twice from diethyl ether. The results are summarized:

Starting ester (mg)		*Recovered acid* (mg)		*m.p. acid*	% Yield
2a	86	**3a**	44	293–296	54
2b	47	**3b**	27	261–263	60
2c	52	**3c**	26	232–234	53

Determination of rate constants for the diphenyldiazomethane esterifications of **3a**, **3b**, *and* **3c**.

A. *Reagents*. Commercial abs EtOH was further purified by treatment with Na followed by diethyl succinate and then distillation.[26] Toluene was purified as described.[27] Diphenyldiazomethane was prepared as follows. A soln of benzophenone hydrazone in ether was stirred with anhyd $MgSO_4$ and Ag_2O for 50 min as 15°. The mixture was filtered and the filtrate containing the product was evaporated to dryness under reduced pressure. The diphenyldiazomethane was then dissolved in the solvent of choice and its concentration determined from the absorbance at 525 mμ and the reported extinction coefficient.[27, 28]

B. *Kinetic procedures*. The rates were measured directly in a 10 cm silica cell fitted with a thermal spacer-jacket through which water of constant temp was circulated. The acid and diphenyldiazomethane solns were

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* Kindly supplied by Professor S. Cristol.

brought to the desired temp separately and then rapidly mixed. Measurements of absorbance at 525 mμ were made at 1–2 min intervals through approximately two half-lives. The resulting data were processed by the computer to give the best straight-line fit of log absorbance *vs* time. The second-order rate constants were calculated by dividing the pseudo-first-order rate constant by the initial organic acid concentration.

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