washed with water, dried (anhydrous magnesium sulfate), and filtered, and the filtrate was concentrated in vacuo, affording crude 1 (202 mg, 65%). An analytical sample of 1 was obtained as a pale yellow microcrystalline solid, mp 155–156 °C, via careful recrystallization of the crude product from ethyl acetate–hexane mixed solvent: ^{1}H NMR ($CDCl_3$) δ 3.1–3.2 (br s, 2 H), 3.6–3.7 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 36.8 (d), 43.8 (d), 44.7 (d), 51.7 (d), 127.1 (s); IR (CCl_4) 1550 (vs), 1365 (m), 1330 (m), 1260 (m), 1220 (m), 1110 (m), 985 cm^{-1} (m); mass spectrum (70 eV), *m/e* (relative intensity) (no molecular ion), 144.0 (18.6), 132.0 (21.1), 131.0 (25.3), 128.0 (24.5), 127.0 (34.6), 126.0 (27.8), 117.9 (10.1), 116.0 (53.6), 115.0 (100), 114.0 (13.9), 105.0 (11.0), 104.0 (19.0), 103.0 (27.4), 102.0 (27.0), 101.0 (12.7), 92.1 (11.0), 91.0 (13.9), 90.0 (12.7), 89.0 (28.7), 79.9 (9.3), 78.0 (28.7), 77.0 (42.7), 76.0 (24.1), 74.9 (16.5), 74.0 (11.0), 64.9 (21.1), 63.0 (55.3), 62.0 (14.8), 54.9 (14.3), 52.9 (19.8), 52.0 (32.1), 51.0 (64.6), 50.0 (30.0), 45.9 (55.7), 43.9 (52.7).

Anal. Calcd for $C_{10}H_8N_4O_8$: C, 38.47; H, 2.58. Found: C, 38.50; H, 2.69.

Acknowledgment. Financial[14] support of our study by the United States Army Armament, Munitions, and Chemical Command, The Air Force Office of Scientific Research, The Robert A. Welch Foundation (Grant B-963), and the North Texas State University Faculty Research Committee is gratefully acknowledged.

Registry No. 1, 91861-20-0; 2, 176-32-9; 3, 25834-57-5; 4, 4576-45-8; 5, 4576-44-7; 6, 4514-82-3; 7, 14725-77-0; 8, 91861-21-1; 9, 91861-22-2; 10, 91861-23-3; cyclopentanone, 120-92-3; ethylene glycol, 107-21-1.

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[14] Research sponsored by Air Force Office of Scientific Research, Air Force Systems Command, USAF, under Grant Number AFOSR-84-0085.

Reversal of Attenuation in Substituent Effects. Influence of Substituent Angular Orientation

Edward J. Grubbs,* Charles Wang, and Larrie A. Deardurff

Department of Chemistry, San Diego State University, San Diego, California 92182

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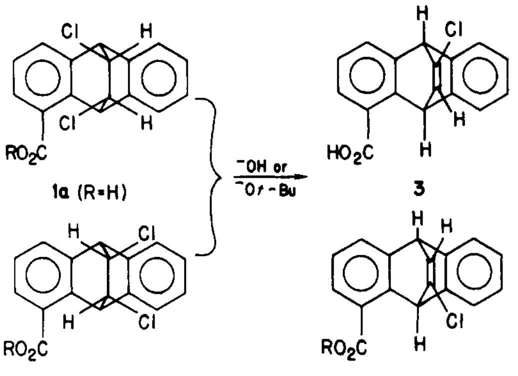
The replacement of hydrogen by an electronegative atom such as fluorine, chlorine, or bromine on the hydrocarbon skeleton of a carboxylic acid usually produces the expected acidity enhancing effect.[1] As the number of carbons positioned between the dipole and the reaction site increases, the magnitude of the substituent effect normally diminishes.[2] This phenomenon has been interpreted in terms of either the Kirkwood–Westheimer electrostatic field model or in terms of diminishing polarizations of bonding electrons as the number of intervening carbons increases. We now report pK_a data which demonstrate a reversed distance attenuation, the origin of which is ascribed primarily to dipole angular orientation differences.

Results

During the course of a recent study[3] on elimination reactions, the two vinyl chlorides 3 and 4 were generated via base-induced eliminations from *syn*- and *anti-cis*-11,12-dichloro-9,10-dihydro-9,10-ethano-1-anthroic acids **1a** and **2a**. Isomeric assignments for 3 and 4 were made on the basis of the magnitude of the coupling of the C-9 and C-10 protons with the vinyl hydrogen. The C-9 proton (peri to the carboxylate group) absorbs at a lower field than does the C-10 proton.[4] Thus for 3 the lower field doublet lies at δ 6.43 (J = 7.0 Hz) and the higher field doublet at δ 5.32 (J = 2.1 Hz). For 4 essentially the reverse is true with the low-field doublet at δ 6.34 (J = 2.1 Hz) and the high-field doublet at δ 5.36 (J = 7.0 Hz). In each case the smaller J value corresponds to four-bond rather than three-bond coupling.



1a (R=H)

2a (R=H)

3

4

The apparent pK_a's of 3 and 4 were determined by potentiometric titration in 50% by volume aqueous ethanol. For comparison, 9,10-dihydro-9,10-etheno-1-anthroic acid (**5**) was prepared by zinc dechlorination of a mixture of **1b** and **2b** (R = CH_3) followed by hydrolysis. Its pK_a, that for the corresponding 9,10-ethano derivative **6**, and those for 3 and 4 are shown in Table I.

Table I. Apparent pK_a's of Several Bridged Anthracene-1-carboxylic Acids in 50% Aqueous Ethanol at 25 °C

acid	pK_a	acid	pK_a
3	5.72 ± 0.01	5	5.94 ± 0.01
4	5.90 ± 0.01	6	5.96 ± 0.01[5]

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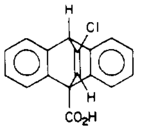
[1] Reversed (i.e., acid weakening) substituent effects have been observed in several systems possessing appropriate geometric orientations of the dipole and carboxylate group. See: Bowden, K.; Hojatti, M. *J. Chem. Soc., Chem. Commun.* **1982**, 273 and references therein.

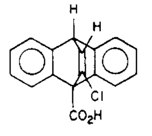
[2] Fall-off factors in the range of 2–3 have been cited. See, for examples: Wilcox, C. F.; Leung, C. *J. Am. Chem. Soc.* **1968**, *90*, 336 and references therein.

[3] Grubbs, E. J.; Schmidt, S. P.; Wang, C. T.; Goodrow, M. H.; Lewis, R. M.; Deardurff, L. A.; Coffey, D., Jr. *J. Am. Chem. Soc.* **1983**, *105*, 4115.

[4] The proton spectrum of 11-chloro-9,10-dihydro-9,10-ethenoanthracene (the "decarboxylated analog" of **3** or **4**) shows two bridgehead proton doublets centered at about 5.3 ppm. The two doublets have coupling constants of about 7 and 2 Hz, respectively. The assignments for **3** and **4** are supported by the observation of nearly identical coupling constants for related isomeric vinyl chlorides bearing as the only other substituent a methyl, a methoxyl, a nitro, or a carboxylic acid at C-9. Results obtained from the potassium *tert*-butoxide induced elimination of HCl from *cis*- or *trans*-11,12-dichloro-9,10-dihydro-9,10-ethano-9-anthroic acid (the analogues of **1a** and **2a** bearing CO_2H at C-9) are also in accord with the assignments made for **3** and **4**. From either of these substrates (bearing CO_2H at C-9) only one vinyl chloride is obtained, namely, the 11-chloro isomer (i). None of the isomeric vinyl halide ii was detected. Transition-state electrostatic calculations similar to those successfully applied to eliminations from **1a**, **2a**, and the trans analogues[3] predicted a ratio i/ii = 97/3 from the 11,12-dichloro-9,10-dihydro-9,10-ethano-9-anthroic acids. The coupling constant involving the C-10 H of i is 2 Hz. That for ii obtained by another route is approximately 7 Hz. These data will be fully presented in a later publication dealing with the elimination reactions.



i



ii

[5] Value reported by Golden, R.; Stock, L. M. *J. Am. Chem. Soc.* **1972**, *94*, 3080. See also footnote 5 in ref 6.

[6] Wang, C. T.; Grubbs, E. J. *J. Org. Chem.* **1977**, *42*, 534.

0022-3263/84/1949-4080$01.50/0

Table II. Parameters[8] and Calculated Values of log K/K_H for Acids 3 and 4

	parameters			Tanford sphere		measured log K/K_H
	R, Å	μ, D	θ, deg	D_E	log K/K_H	
3	6.8	1.44	30	4.8	0.29	0.22
4	5.0	1.44	80	4.0	0.13	0.04

Discussion

The most striking feature of these data is the fact that the stronger of the two acids 3 and 4, namely, 3 possesses the carbon–chlorine dipole one more carbon remote from the carboxylic acid group than is the case for 4. This reversal of the usual attenuation is contrary to expectations based upon a classical inductive model. By contrast it is understandable, at least qualitatively, in terms of the Kirkwood–Westheimer (K–W) field model. Application of the K–W expression to these acids is however limited by two principal uncertainties. First X-ray data for these or closely related substrates are not available. Thus the C-11–C-12–Cl bond angle is not known with certainty. Nonetheless for vinyl chloride the value is 121.6°[7] and it is probable that the values for 3 and 4 also lie close to 120°. A second uncertainty regards the question as to whether the C–Cl bond should be treated as the substituent dipole or, in view of the delocalization, whether the entire three atom vinyl chloride group should be considered. In the latter case, the "mid-point" of the dipole becomes less certain as does the "dipole" angular disposition and thus the K–W angle. For sake of simplicity, the C–Cl bond is treated below as the dipole and the K–W angles are then estimated from Dreiding models. For construction purposes the normal "ethylene" unit was employed for the C-11–C-12 linkage. The carboxyl proton was placed at 1.45 Å beyond the carboxyl carbon on an extention of a line joining it to C-1. The dipole moment of vinyl chloride was employed for μ in the K–W expression. The resulting parameters and calculated log K/K_H values for 3 and 4 are summarized in Table II.

Calculated and experimental results are in reasonable agreement. Use of the Tanford ellipsoid model gives similar values (for 3 log $K/K_H = 0.14$; for 4 log $K/K_H = 0.09$). If the C^{sp^2}–C^{sp^2}–Cl bond angle is enlarged beyond 120°, the corresponding K–W angle for 3 more closely approaches 90°, leading to a predicted vanished substituent effect. Simultaneously the log K/K_H value calculated for 4 increases. In such a case the ellipsoid model would more accurately match the measured values as previously observed for **1a** and **2a**.[6]

These results suggest that the difference between the angular orientations of the carbon–chlorine dipoles in 3 and 4 (and thus the differences between the two K–W angles) is primarily responsible for the reversal in expected distance attenuation.

Experimental Section[9]

Dehydrochlorinations of *syn*- and *anti*-*cis*-11,12-Dichloro-9,10-dihydro-9-10-ethano-1-anthroic Acids (1a and 2a). The dichloro acids[6] were dehydrohalogenated by using methanolic sodium hydroxide. Samples of **1a** and **2a** (approximately 190 mg, 0.597 mmol) were mixed with 2 mL of methanol containing approximately 80 mg (2.0 mmol) of sodium hydroxide. The samples were placed in the thick-walled reaction tubes, degassed, sealed, and heated for 48 h at 144 °C. The product mixtures were diluted with 50 mL of water and acidified with 2 N HNO_3. The precipitated acids were thoroughly washed with distilled water and dried. Yields ranged from 93–98%.

11-Chloro-9,10-dihydro-9,10-etheno-1-anthroic Acid (3). The 11-chloro isomer was obtained in pure form via chromatography. A 25-mm diameter column was packed with a mixture prepared from 50 g of 100-mesh silicic acid, 10 g of Celite, 5.1 mL of water, and 27 mL of methanol. The column was packed with 4:1 (by volume) hexane–ether. A 720-mg sample of a mixture of dehydrochlorinated acids was introduced to the column in the solid form as a sandwich between two sand layers. The column was then eluted with the 4:1 hexane–ether. An early fraction afforded 95 mg of predominantly 3 as a white solid. This was dissolved in hexane and the volume reduced to 15 mL before refrigerating. The pure acid (50 mg) was collected as white crystals, mp 213–214 °C.

The mass spectrum shows the molecular ion at m/e 283. A peak at m/e 247 corresponds to the loss of chlorine. The infrared spectrum (KBr disk) shows the CO_2H carbonyl band at 1680 cm^{-1}. The NMR spectrum (Me_2SO-d_6) shows the C-9 proton doublet at δ 6.43 ($J = 7.0$ Hz), the C-10 proton doublet at δ 5.32 (2.1 Hz), and the vinyl and aromatic proton multiplet at δ 6.8–7.9.

Anal. Calcd for $C_{17}H_{11}ClO_2$: C, 72.22; H, 3.92. Found: C, 71.99; H, 4.07.

12-Chloro-9,10-dihydro-9,10-etheno-1-anthroic Acid (4). Pure samples of the 12-chloro isomer were obtained by fractional crystallization of the mixture of 3 and 4 from carbon tetrachloride. In a typical experiment, a 110-mg sample of the acid mixture was recrystallized twice from CCl_4. In each case the product which began to crystallize was collected after only a small percentage of the acid had deposited. This afforded 10 mg of 4 as white crystals, mp 271.5–272.5 °C.

The mass spectrum shows the molecular ion at m/e 283 and a peak at m/e 247 ($M^+ - Cl$). The infrared spectrum (KBr disk) shows the CO_2H carbonyl band at 1680 cm^{-1}. The NMR spectrum (Me_2SO-d_6) shows the C-9 proton doublet at δ 6.34 ($J = 2.1$ Hz), the C-10 proton doublet at δ 5.36 ($J = 7.0$ Hz), and the vinyl and aromatic protons at δ 6.8–7.8.

Anal. Calcd for $C_{17}H_{11}ClO_2$: C, 72.22; H, 3.92; Found: C, 72.00; H, 3.83.

9,10-Dihydro-9,10-etheno-1-anthroic Acid (5). A 1.12-g (33.5 mmol) sample of a mixture of methyl *syn*- and *anti*-*cis*-11,12-dichloro-9,10-dihydro-9,10-ethano-1-anthroates **1b** and **2b**[6] was added to 183 mL of methanol and 30 g of activated zinc powder. The mixture was boiled under reflux with stirring for 10 days. The mixture was filtered and the precipitate rinsed with methanol. The filtrate was concentrated under reduced pressure, leaving a yellow oil. The oil was crystallized from cyclohexane affording 0.617 g (70%) of dechlorinated ester as a white solid, mp 87–90.5 °C. This was recrystallized from hexane yielding 0.433 g of the pure product, mp 93–94.5 °C.[10]

The infrared spectrum (KBr disk) shows the ester carbonyl at 1680 cm^{-1}. The NMR spectrum ($CDCl_3$) shows the vinyl and aromatic multiplet δ 6.2–7.0, the bridgehead proton multiplets centered at δ 5.85 and δ 4.58, and the methyl ester singlet at δ 3.4.

This ester was boiled under reflux in 35 mL of 0.31 M methanolic NaOH for 3 h. The methanol was evaporated and 50 mL of water was added to the residue. The resultant mixture was filtered. The filtrate was acidified with 6 N HCl. The precipitate was filtered, washed with water, and dried, affording 0.33 g (80%) of 5, mp 218–221 °C. One recrystallization from ethanol afforded 0.23 g of the acid, mp 220–222 °C.

The mass spectrum shows the molecular ion at m/e 248. The infrared spectrum (KBr disk) shows a broad O–H band centered

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(7) "Handbook of Organic Structural Analysis", Yukawa, Y., Ed.; W. A. Benjamin, Inc.: New York, 1965; p 514.

(8) The dipole moment of vinyl chloride was employed for μ (see p 502 of ref 7).

(9) Melting points are uncorrected. Infrared spectra were obtained on a Perkin-Elmer Model 621 spectrophotometer. Nuclear magnetic resonance spectra were determined on a Varian EM-390 spectrometer. Mass spectra were obtained on a Hitachi Perkin-Elmer Model RMU mass spectrometer. The pK_a measurements were made on a Beckman research pH meter equipped with a Beckman No. 39000 glass electrode and a Beckman No. 39071-A3U calomel electrode. Elemental analyses were performed by M-H-W Laboratories, Garden City, MI, and Galbraith Laboratories, Inc., Knoxville, TN.

(10) The (+) isomer of this ester has been reported to melt at 115.7–116.5 °C. No spectral data were given in that communication. The spectral properties of 5 and its precursor ester presently described are in full agreement with the proposed structures.

at 3000 cm^{-1} and the carbonyl (CO_2H) at 1670 cm^{-1}. The NMR spectrum (Me_2SO-d_6) shows the vinyl and aromatic proton multiplet δ 6.7–7.5 and the bridgehead proton multiplets centered at δ 6.30 and δ 5.22.

Anal. Calcd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87. Found: C, 82.14; H, 4.84.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the San Diego State University Foundation for support of this research.

Registry No. 1a, 60573-55-9; 2a, 60618-78-2; 3, 91798-50-4; 4, 91798-51-5; 5, 91782-23-9; 6, 38378-63-1.

Diastereoselective Synthesis of an (Arene)chromium Tricarbonyl Complex

Kevin R. Stewart, Samuel G. Levine,* and Jon Bordner

Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695

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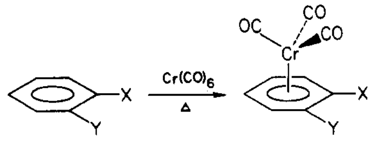
The distinctive chemical and physical properties of (arene)chromium tricarbonyl(CT) complexes[1,2] have been investigated from several points of view since 1959 when their direct preparation from the parent arene was first described[3] (eq 1). The stereochemical properties of these compounds have attracted particular attention. A complexed benzene with unlike *ortho* substituents 1 (X ≠ Y) is chiral and several such derivatives have been obtained in optically active form by classical optical resolution procedures.[4,5] Furthermore, the generation of a new chiral center within X or Y is typically found to occur with very high diastereoselectivity.[6] These facts combine to suggest the potential utility of compounds of type 1 as chiral synthons and, therefore, the desirability of developing alternative, more general methods for their production in optically active form. Solladie-Cavallo and co-workers[7] have resolved racemates of type 1 (X = CHO) via reaction with (*S*)-(−)-5-(α-phenylethyl)semioxamazide and chromatographic separation of the diastereomeric semioxazones 1 (X = $PhCHCH_3NHCOCONHN{=}CH$). The same investigators also tried the strategy of asymmetric induction in the complexation process, but with disappointing results. Acetals of type 2a derived from (*S*,*S*)-(+)-butane-2,3-diol underwent complexation with, at most, 20% asymmetric induction. In this report we describe the facile and inexpensive preparation of an optically active derivative of *o*-aminobenzaldehyde and its conversion to a CT complex with nearly complete asymmetric induction. Unfortunately, this complex was resistant to hydrolysis except under strenuous conditions and its conversion to optically active (*o*-aminobenzaldehyde)CT was not achieved.



(1)

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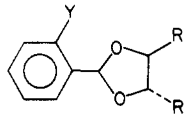
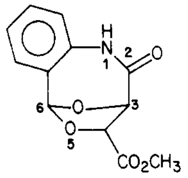


2a, R = CH_3
2b, R = CO_2CH_3, Y = NO_2
2c, R = CO_2CH_3, Y = NH_2

Dimethyl 2-nitrobenzylidine-L-tartarate (**2b**) was prepared from 2-nitrobenzaldehyde and (+)-dimethyl L-tartarate in 55% yield. Catalytic hydrogenation of the acetal followed by heat-induced lactamization produced the benzoxazocine 4 (87% yield) as a colorless solid, mp 167.5 °C. The complexation reaction was conducted by heating 3 with chromium hexacarbonyl in refluxing dioxane under argon in a Strohmeier apparatus[8] for 72 h. Chromatographic removal of unreacted starting material and NMR examination[9] of the total complexation product disclosed that two diastereomers were present in a ratio of about 50:1. One recrystallization gave the major isomer as a yellow needles, mp >300 °C, in 42% yield. The structure and stereochemistry of the complex were determined by single-crystal X-ray analysis which led to the ORTEP[10] plot shown in Figure 1; this structure and the derived perspective drawing 4 reveal that complexation has taken place on that face of the aromatic ring which is syn to the 3,6-epoxy bridge.



3 (benzoxazocine numbering)

The X-ray crystal structure of 4 also provides a reasonable explanation for the high degree of diastereoselectivity of the complexation reaction. Firstly, no short nonbonded distances involving the $Cr(CO)_3$ grouping are found. Secondly, inspection of the stereoplot (Figure 1) leads to the inference that the alternative complexation product would be subject to significant steric compression. This qualitative assessment was substantiated by calculation. By considering the aromatic ring to determine a mirror plane and by projecting the atomic centers of the CT group across the plane, one arrives at a model of the alternative complexation product.[11] A survey of interatomic distances within the model now reveals that the C-4 hydrogen is compressed by the oxygen of the nearest CO group. This interatomic distance is calculated as 1.84 Å whereas the sum of the pertinent van der Waals radii is 2.6 Å. It is worth pointing out that the carbonyl oxygens of the CT group are located approximately 3.5 Å above the plane of the aromatic ring and that steric guidance of the

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[1] Jaouen, G. In "Transition Metal Organometallics in Organic Synthesis"; Alper, H., Ed.; Academic Press: New York, 1978; Vol. 2, pp 65–120.

[2] Semmelhack, M. F. *Pure Appl. Chem.* **1981**, *53*, 2379.

[3] Nicholls, B.; Whiting, M. C. *Proc. Chem. Soc.* **1958**, 152.

[4] Mandelbaum, A.; Neuwirth, Z.; Cais, M. *Inorg. Chem.* **1963**, *2*, 902.

[5] Meyer, A. *Liebigs Ann. Chem.* **1973**, 379.

[6] For example, see: Meyer, A.; Debard, R. *J. Organomet. Chem.* **1972**, *36*, C38.

[7] Solladie-Cavallo, A.; Solladie, G.; Tsamo, E. *J. Org. Chem.* **1979**, *44*, 4189.

[8] Strohmeier, W. *Chem. Ber.* **1961**, *94*, 2490.

[9] Signals due to the C-6 proton of the major and minor complexation products from 4 were seen at δ 6.05 and 6.13, respectively.

[10] Johnson, C. K. ORTEP Report ORNL-3794, **1965**, Oak Ridge National Laboratory, TN.

[11] The orientation of the chromium tricarbonyl group with respect to the aromatic ring in determined by the electronic character of the carbon atoms of that ring and therefore should not be altered by the mirror inversion. The energy value of this conformation is, however, unknown.

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