destruction of **2** and had to be avoided. The highly volatile hydrocarbon so produced (mp >225 °C)[19] clearly has 4-fold symmetry: ^1H NMR ($CDCl_3$, 200 MHz) δ 2.98–2.91 (m, 4 H), 2.65–2.54 (m, 4 H), 2.15 (d of t, J = 13.7, 9.9 Hz, 4 H), 1.65 (d, J = 13.7 Hz, 4 H); ^{13}C NMR ($CDCl_3$) 48.44, 46.85, 46.31 ppm.

Studies aimed at crafting **13** into **5** are currently in progress.[20]

Registry No. 2, 85850-64-2; **7**, 6675-71-4; **9**, 85850-65-3; **10**, 85850-66-4; **11**, 85850-67-5; **12a**, 85850-68-6; **12b**, 85850-69-7; **13**, 85850-70-0; **14**, 85864-53-5; **15a**, 85850-71-1; **15b**, 85850-72-2; TSC≡CH, 13894-21-8.

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(19) These conditions do not result in complete reduction of the tosylate. The amount of pure **2** obtained after chromatography and sublimation exceeded 10%.

(20) We express our warm appreciation to the National Institutes of Health for their generous support of this program (Grant AI-11490).

Electrostatic Control of Regioselectivity in Competing Bimolecular Eliminations

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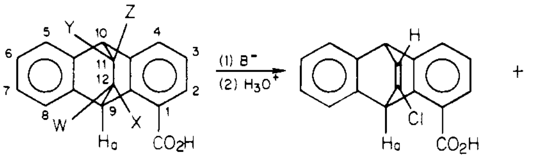
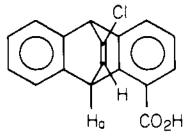
Previously we demonstrated substituent electrostatic field effects on various reactions of carboxyl groups at the 1- and 2-positions of geometrically isomeric 11,12-dichloro-9,10-dihydro-9,10-ethanoanthracenes.[1,2]

We now report preliminary results of a study of base-induced eliminations of HCl from the anions of the four isomeric 11,12-dichloro-9,10-dihydro-9,10-ethano-1-anthroic acids, **1–4**. In each case the ratio of vinyl halides, **5**/**6**, appears to be determined primarily by the relative electrostatic repulsive interactions between the carboxylate anion and the attacking base.



5

1, X = Z = Cl; W = Y = H
2, X = Z = H; W = Y = Cl
3, X = Y = H; W = Z = Cl
4, X = Y = Cl; W = Z = H



6

The preparation, separation and characterization of acids **1** and **2** have been previously described.[2] Isomers **3** and **4** (via the corresponding methyl esters) were similarly prepared by the cycloaddition of methyl 1-anthroate and *trans*-1,2-dichloroethene followed by hydrolysis of the separated[3] esters. The geometric assignments for **3** and **4** are based upon the single-crystal X-ray analysis of the methyl ester of **3**.[4,5]

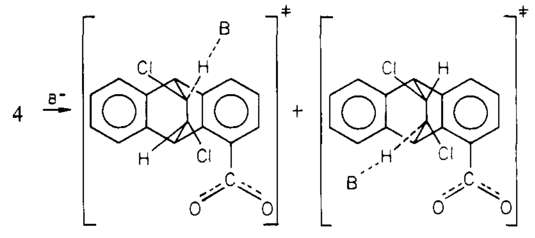
Table I. Observed and Calculated Ratios of **6**/**5** from Dehydrochlorinations[a] at 80 °C

compd	obsd ratio[b]	calcd ratio[c]
1	2.4 (71/29)	3.0 (75/25)
2	13.3 (93/7)	9.7 (91/9)
3	24 (96/4)	19 (95/5)
4	1.70 (63/37)	1.53 (61/40)

[a] A 0.50 M solution of KO-*t*-Bu in *t*-BuOH was used as the base. The substrate concentration in the basic solution was 0.095 M. A 1.1 mole ratio of 18-crown-6/total K^+ was employed. [b] Average of two runs. Estimated uncertainty is ±3%. [c] See discussion.

Dehydrochlorinations of degassed solutions of **1–4** (KO-*t*-Bu/*t*-BuOH) were conducted in the presence of crown ether (18-crown-6).[6] Combined yields of **5** plus **6** exceeded 90%. The ratios **6**/**5** were determined by area integrations for H_a. The results are shown in Table I.

We propose that the ratio of products formed in each dehydrochlorination is primarily determined by transition-state potential-energy differences arising from variable repulsive energies generated between the charge on the carboxylate anion and the charge on the attacking base (possibly distributed in part onto the β-carbon).[9] Calculations of these repulsive energies assume certain constant features for the transition states (see illustrations for transition states from **4**). Direct through-space distances between the carboxylate anionic center and either C_β or the oxygen of the attacking base were estimated by using Dreiding models. Differences in total repulsive potential energies for each pair of competing transition states were computed from Coulomb's law, with variables being the effective dielectric constant[10] and the fractions of charge on the oxygen of the attacking base and on C_β. Differences in repulsive potential energies were converted to



$\mathbf{6}^{\ddagger}$ $\mathbf{5}^{\ddagger}$

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(1) Grubbs, E. J.; Fitzgerald, R.; Phillips, R. E.; Petty, R. *Tetrahedron* **1971**, *27*, 935.

(2) Wang, C. T.; Grubbs, E. J. *J. Org. Chem.* **1977**, *42*, 534.

(3) The methyl esters of **3** and **4** were separated by repeated fractional crystallizations from hexane. All new compounds including pure samples of **5** and **6** afforded proper elemental analyses as well as reasonable NMR spectra.

(4) Full details of the crystal structure determination will be reported (Noordik, J. *Acta Crystallogr., Sect. C.*, in press). We thank Dr. Noordik for his assistance with the X-ray crystallography. Questions regarding this aspect of our work should be addressed to him at the University of Nijmegen, The Netherlands.

(5) Additional studies involving pK_a determinations of the isomeric acids confirm these assignments and will be presented in the full report of this work.

(6) Under conditions promoting aggregation (tetrahydrofuran, no crown ether) regioselectivity is diminished. For example, under these conditions, the KO-*t*-Bu-induced elimination from **1** gives a ratio, **6**/**5**, of only 1.3 (compared with 2.4 in *t*-BuOH and crown ether).

(7) The basic oxygen was assumed to be linearly extended along the C_β–H axis at 2.7 Å from C_β.[8]

(8) This is a typical distance between oxygen atoms in hydrogen-bonded alcohols (Pimentel, G. C.; McClelland, A. L. "The Hydrogen Bond"; W. H. Freeman: San Francisco, 1960).

(9) Evidence for the bimolecular nature of eliminations (possessing some carbanion character) in systems that are similarly conformationally constrained has been reported. See: (a) Bartsch, R. A.; Mintz, E. A.; Parlman, R. M. *J. Am. Chem. Soc.* **1974**, *96*, 4249. (b) LeBel, N. A.; Beirne, P. D.; Subramanian, P. M. *Ibid.* **1964**, *86*, 4144. (c) Cristol, S. J.; Hause, N. L. *Ibid.* **1952**, *74*, 2193 and references therein.

(10) This is an "empirical effective dielectric constant" as defined earlier[11,12] (a number that allows one to fit an observed substituent effect to an equation such as the Bjerrum or Eucken equation, representing Coulombic interactions).

(11) Hoefnagel, A. J.; Wepster, B. M. *J. Org. Chem.* **1982**, *47*, 2318.

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rate ratios by using the Arrhenius equation.[13] An iterative least-squares computer program leads to a best fit with an effective dielectric constant of 13.7 ±1.6 D and the fraction of charge on the *tert*-butoxy oxygen (f_0) equal to 0.85 ± 0.13 (with the remainder on C_β).[14] The calculations converge to the same values within the range 0–1.0 for f_0 and 5–50 for D_E. Calculations in which a significant charge is allowed to develop on the departing chlorine are not consistent with experimental results.[15] For example, in the elimination from **4**, by using the best-fit effective dielectric constant of 13.7 and assuming a 0.2 charge on chlorine (0.8 on the oxygen of the base), the calculated ratio **6**/**5** is 0.62. That is, the predicted regioselectivity is actually reversed.

There is a growing belief that bimolecular syn-periplanar eliminations involve transition states with considerable carbanion character.[16] Our results for both **3** and **4** (for which syn elimination is required) and as well as for **1** and **2** (which proceed from an anti-clinal conformation) suggest some carbanion character obtains (with little charge on chlorine) but with the majority of charge on the attacking base.

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

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[12] King, E. J. "Acid–Base Equilibria"; Pergamon Press: Oxford, 1965; p 160.

[13] The implicit assumption that differences in entropy of activation are negligible is supported by our observation that no measurable changes in product ratios were observed for elimination of HCl performed at 50 °C.

[14] Possible factors contributing to the magnitude of D_E and to the quality of agreement of calculated and experimental elimination ratios with use of a single D_E for the variety of transition-state interactions will be discussed in the full paper.

[15] With as little as 0.3 fraction of a unit charge on chlorine, calculations fail to converge. With a 0.1 charge on chlorine (0.53 on the base and 0.37 on C_β) convergence leads to a value of 10.2 ± 1.2 D for the dielectric constant, but the fit to experimental data is poorer.

[16] See: Bach, R. D.; Badger, R. C.; Lang, T. J. *J. Am. chem. Soc.* **1979**, *101*, 2845 and references cited therein.

Mechanism of Formation of Weiss' *endo*- and *exo*-Tetracyclo[5.5.1.0^{2,6}.0^{10,13}]tridecane-4,8,12-trione[1]

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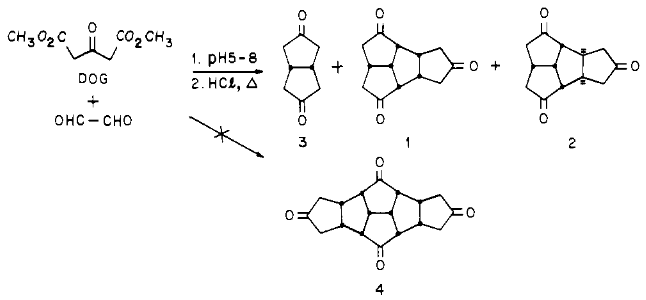
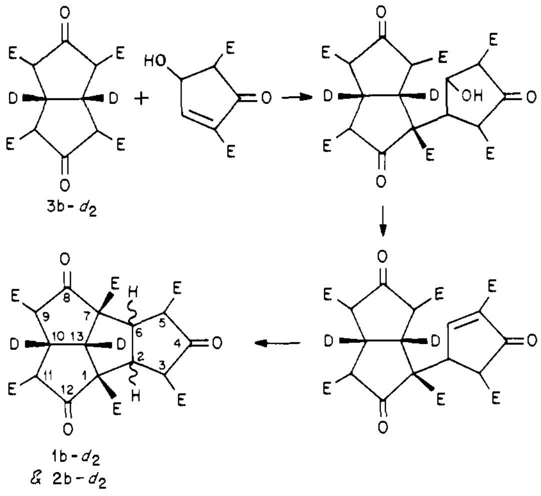
Now that the dodecahedrane story has reached denouement,[2] interest in polyquinane chemistry is keen and will undoubtedly continue to grow as the synthetic methodology that has been developed is applied to other "theoretically interesting" hydrocarbons and to the increasing number of known cyclopentanoid natural products.[3] This activity also promises to stimulate mechanistic investigations as unexpected new reactions are discovered. We are pleased to report the solution to a mechanistic mystery that has perplexed polyquinane chemists for a decade, viz., the reason that Weiss' *endo*-tetracyclic triketone **1**[4] (Scheme I) predominates (by ~2:1) over the *exo*-isomer, **2**.[5] These products accompany bicyclo[3.3.0]octane-3,7-dione (**3**) after hydrolysis–decarboxylation of the material that forms when dimethyl 3-oxoglutarate (DOG) and glyoxal are allowed to react in aqueous buffers.[4,5] Molecular mechanics calculations of the Westheimer type using the program GEMO[6] suggest that **1** is less stable than **2** by 8.1 kcal/mol, which is mainly attributable to torsion angle strain (4.9 kcal/mol) and bond angle strain (2.0 kcal/mol).

Scheme I



Scheme II



Compound **1** is an attractive precursor for dodecahedrane, as it possesses 13 of the requisite 20 carbon atoms, all in the proper positions. In addition, all the necessary activation for further construction is present at the nontertiary carbon atoms. Last, but no less important, **1** is prepared in two easy steps, albeit in low yield (~3%).[5] Even more tantalizing was the possibility that the hexacyclic tetraketone **4** with 18 of dodecahedrane's 20 carbon atoms in place might also be formed in an analogous manner. Unfortunately, no **4** could be isolated by meticulous chromatography or even detected by intensive spectroscopy.[7] Since the straightforward mechanism suggested[8] for the formation of **1** and **2** (Scheme II) makes the creation of some **4** (as well as two other stereoisomers) appear inevitable, the elucidation of the mechanism was imperative in order to understand why no **4** was found.

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[1] Dedicated to Dr. Ulrich Weiss (NIH) on the occasion of his 75th birthday. Part 4 in a series on the Weiss reaction: parts 3, 2, and 1 are given in ref 9–11, respectively.

[2] Ternansky, R. J.; Balogh, D. W.; Paquette, L. A. *J. Am. Chem. Soc.* **1982**, *104*, 4503–4.

[3] Annis, G. D.; Paquette, L. A. *J. Am. Chem. Soc.* **1982**, *104*, 4504–6. Wrobel, J.; Takahashi, K.; Honkan, V.; Lannoye, G.; Cook, J. M.; Bertz, S. H. *J. Org. Chem.* **1983**, *48*, 139–41.

[4] Edwards, J. M.; Qureshi, I. H.; Weiss, U.; Akiyama, T.; Silverton, J. V. *J. Org. Chem.* **1973**, *38*, 2919–20. Akiyama, T.; Silverton, J. V. *Acta Crystallogr., Sect. B* **1975**, *B31*, 2336–8.

[5] Rice, K. C.; Sharpless, N. E.; Weiss, U.; Highet, R. J. *Tetrahedron Lett.* **1975**, 3763–6.

[6] Cohen, N. C. *Tetrahedron*, **1971**, *27*, 789–97.