Table II. Calculated Log K_X/K_H by Means of TMKW[a] Cavity Model

Acid	R, Å	μ, D	θ	D_E[b]	Log $(K_X/K_H)_{calcd}$	Log $(K_X/K_H)_{exptl}$
I	4.52	1.4	30° 26′	3.80	0.56	0.461
II	5.24	1.4	14° 49′	4.10	0.43	0.306
III	5.53	1.4	67° 27′	4.26	0.15	0.252

[a] Tanford modification of the Kirkwood–Westheimer cavity model. [b] Reference 13.

inductive model. We also show that the field model adequately accounts for the experimental facts.

We have synthesized some 5- and 6-hydroxybicyclo[2.2.2]octane-2-carboxylic acids[6] and determined their pK_a values in 50% (by weight) aqueous ethanol at 25°.[10] The data are summarized in Table I. In each of these cases both the substituent and the reaction center are, to a good approximation, in the same steric environment. This implies that the steric approach of solvent molecules to these centers is approximately the same in the three cases. In addition, examination of molecular models shows that there is little chance for direct steric interaction between the substituent and the reaction center. Comparison of the relative pK_a values, therefore, allows a direct evaluation of the relative polar effects of these substituents.

The σ-inductive model[11] predicts that the effect of substituents at C-6 and C-5 on a reaction center at C-2 would be $[(1/f)^2 + (1/f)^4 + 2(1/f)^6]$ and $[2(1/f)^3 + (1/f)^5]$, respectively, where f is the attenuation factor per carbon. Using factors of 2–3,[5] the predicted relative magnitude of the σ-inductive influence of a substituent at C-6 compared to C-5 would be 1.22–1.61. Comparison of I and II (Table I) shows that the inductive order is in the correct direction; however, III is less acidic than II. The σ-inductive model predicts just the opposite. This reversed attenuation effect points to an internal inconsistency in the model and casts serious doubt on its usefulness in predicting relative rates and equilibrium constants.

In order to evaluate the field model, the data in Table I were analyzed by means of the Tanford modification of the Kirkwood–Westheimer cavity model.[13] The parameters used in the calculation as well as the calculated and experimental equilibrium constant ratios are listed in Table II. While agreement is only qualitatively good, the field model does predict the correct order of acidities.

Acknowledgment. This work was supported by the National Science Foundation (Grant No. GP 14437) and by the Department of Interior, Office of Water Resources Research, as authorized under the Water Resources Research Act of 1965 (P. L. 88-379).

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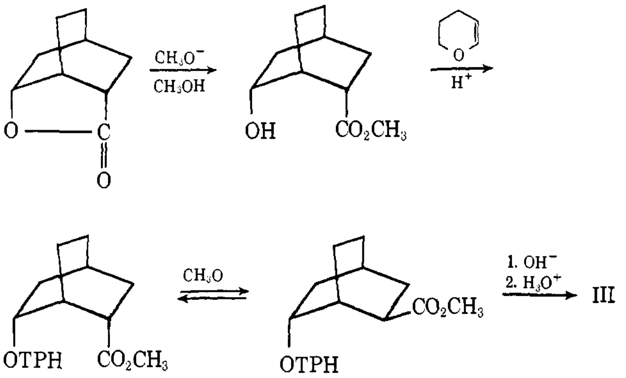
(6) Mixtures of the ethyl esters of I and II were prepared from ethyl *endo*-bicyclo[2.2.2]oct-2-ene-5-carboxylate (V) by two methods: (a) oxymercuration–demercuration[7] and (b) hydroboration followed by oxidative work-up.[8] The corresponding acetates were separated by silica gel column chromatography and subsequently hydrolyzed to I and II. III was prepared by the following scheme



IV was prepared by catalytic hydrogenation of V followed by hydrolysis. The melting points of I, II, III, and IV are 150–150.5, 111.5–112.5, 136.5–138, and 83–84.5° (lit.[9] 84–85°), respectively. All spectral data (nmr, ir, and mass spectral) and all neutralization equivalents were consistent with the assigned structures.

(7) H. C. Brown and F. Geogphegan, Jr., *J. Amer. Chem. Soc.*, **89**, 1522 (1967).

(8) H. C. Brown and G. Zweifel, *ibid.*, **83**, 1241 (1961).

(9) R. Seka and O. Tramposh, *Ber. Deut. Chem. Ges. B*, **75**, 1379 (1942).

(10) The pK_a values were determined by a previously described method: C. L. Liotta, K. H. Leavell, and D. F. Smith, Jr., *J. Phys. Chem.*, **71**, 3091 (1967).

(11) According to the σ-inductive model,[12] if one considers a substituent at a position S on a molecule, the polarization of the bond between the substituent and the atom to which it is attached can be transmitted to another position on the molecule, $S + n$, n bonds removed from the point where the initial effect was exerted, by the successive polarization of the intervening σ bonds. The resultant effect, $\lambda_{S \pm n}$, will be equal to the initial effect, λ_S, multiplied by a constant factor per bond ($1/f < 1$) and summed over all pathways as illustrated by the following equation

$$\lambda_{S \pm n} = \lambda_S \sum_p [(1/f)^{(S \pm n)}]_p$$

(12) S. Ehrenson, *Progr. Phys. Org. Chem.*, **2**, 195 (1964).

(13) J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, **6**, 506 (1938); J. G. Kirkwood and F. H. Westheimer, *ibid.*, **6**, 513 (1938); F. H. Westheimer, W. A Jones, and R. A. Lad, *ibid.*, **10**, 478 (1942); F. H. Westheimer and M. W. Shookhoff, *J. Amer. Chem. Soc.*, **61**, 555 (1939); C. Tanford, *ibid.*, **79**, 5348 (1957).

(14) NSF Undergraduate Research Participant, Summer 1971.

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3-Vinylpentadienyl Anions. Rearrangement of 3-Vinylheptadienyl Anion to 2-Ethylcycloheptadienyl Anion

Sir:

According to HMO calculations, 3-vinylpentadienyl anions (DE_π = 2.00β) should have almost as much resonance stabilization as 1-vinylpentadienyl (= heptatrienyl) anions (DE_π = 2.05β). Although 3-vinylpentadienyl cations have been studied,[1] the only report involving one of the corresponding anions describes the use of the parent anion as an intermediate in the synthesis of tetravinylmethane,[2] and the spectral properties of the anion were not given. We wish to report the high-yield preparation and some nmr spectral properties of five cross-conjugated anions of this class, and the unexpectedly facile thermal rearrangement of one

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(1) T. S. Sorensen, *Can. J. Chem.*, **43**, 2744 (1965).

(2) J. G. Berger, E. L. Stogryn, and A. A. Zimmerman, *J. Org. Chem.*, **29**, 950 (1964).

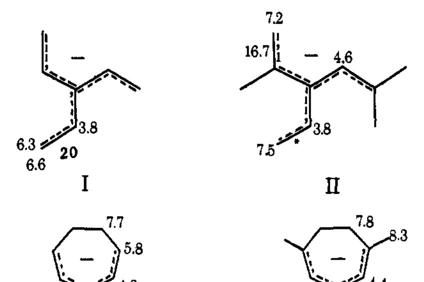

Figure 1. Chemical shifts (τ) and rotation barriers (boldface, in kilocalories per mole) in 3-vinylpentadienyl anions. Asterisks denote bonds about which rotation barriers are apparently low (<14 kcal/mol) because of the simplicity of the nmr spectrum.

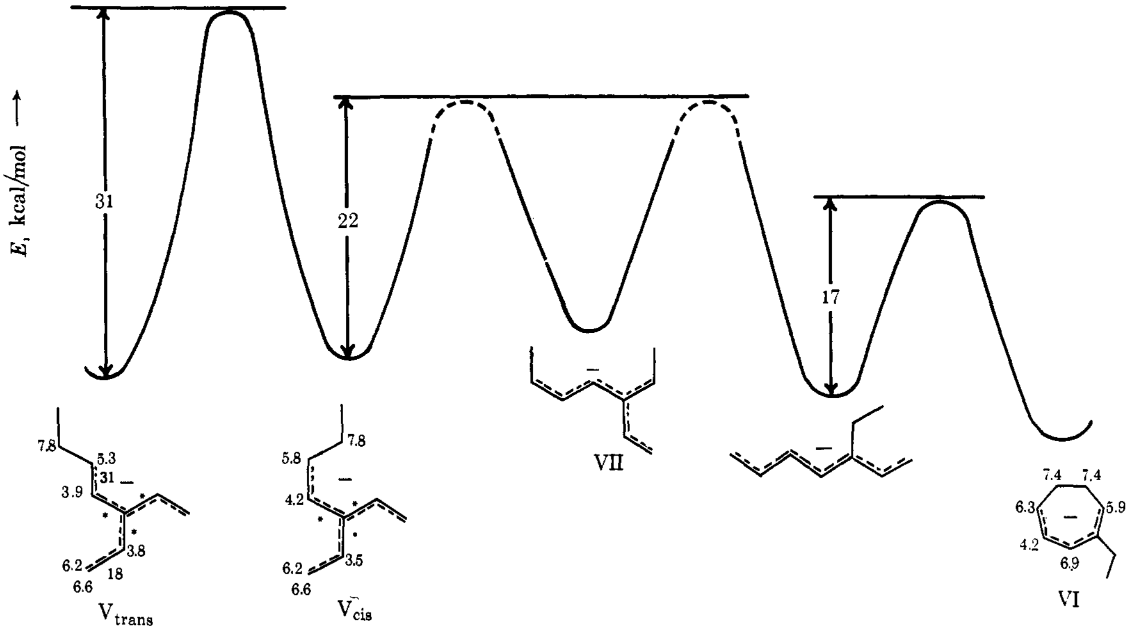

Figure 2. Approximate energy diagram for the V → VI conversion. The remarks in the Figure 1 caption apply to this figure as well.

member of the series *via* a 2-vinylpentadienyl anion and a 1-vinylpentadienyl (=heptatrienyl) anion to a cycloheptadienyl anion.[3]

Anions I–V were prepared in quantitative yield[4] from the corresponding trivinylmethane derivatives[5] using *n*-butyllithium in THF–hexane. Layer separation, indicating reaction,[6] took place in a few minutes below room temperature except for II, which required several hours at room temperature. The favored conformations of these anions probably closely approximate the two planar conformations possible for 3-vinylallyl systems: I, II, and V favor the "symmetric" (threefold axis) planar conformation, and III and IV favor the "asymmetric" planar conformation.

Rotation barriers, measured by variable-temperature nmr studies or by direct interconversion, and proton chemical shifts in anions I–V are given in Figures 1 and 2. Coupling constants are not given, but were unexceptional (*e.g.*, in the "vinyl" groups present, J_{trans} = 15.5–16.5 Hz, J_{cis} = 9–11 Hz, and J_{gem} = 2–3 Hz); in many cases assignments were verified by spin decoupling. Configurational assignments for V_{trans} and V_{cis} were based on a coupling constant of 15 Hz between the two critical protons in the former as compared to 10 Hz in the latter. Comparison of the values in the figures shows that as in pentadienyl anions,[7] replacement of a hydrogen on an end carbon atom by an alkyl group greatly affects chemical shifts and rotation barriers, both of which probably reflect changes in charge distribution. For example, comparing the rotation barriers for I and V_{trans}, the ethyl group raises the adjacent barrier by 11 kcal/mol while lowering each far barrier by 2 kcal/mol.

The 3-vinyl-1,4-heptadiene used to prepare V was 55% trans and 45% cis, and gave corresponding amounts of V_{trans} and V_{cis}. The nmr spectrum of V_{trans} was unchanged on standing at probe temperature (33°), but the spectrum assigned to V_{cis} disappeared with a half-life of 7 min and was replaced by the spectrum of VI.[8] As depicted in Figure 2, this rearrangement probably proceeds *via* two sigmatropic proton shifts[8] and a heptatrienyl–cycloheptadienyl rearrangement.[9] The 2-vinylpentadienyl intermediate VII is a representative of a new class of cross-conjugated anions

(3) Taken in part from the M.S. Thesis of C. M. Cole, University of Arizona, 1971.

(4) Exception: II was accompanied by a lesser amount of an as yet uncharacterized but probably isomeric species.

(5) The trivinylmethane precursors for I and III–V were prepared in 50–85% yield from 1,4-pentadiene, 1,3,6-heptatriene, 2,6-dimethyl-1,3,6-heptatriene, and 1,4-heptadiene, respectively (all from Chemical Samples Co.), by the sequence (a) *n*-butyllithium–THF–hexane, (b) ethylene oxide, (c) Chugaev reaction.[2] The precursor for II (W. Sucrow, *Angew. Chem.*, **80**, 626 (1968)) was very kindly provided by Dr. Sucrow. III and V were purified by preparative glpc using SE-30 silicone oil on Chromosorb P, and IV using DEGS on base-washed Chromosorb W.

(6) R. B. Bates, D. W. Gosselink, and J. A. Kaczynski, *Tetrahedron Lett.*, 199 (1967).

(7) R. B. Bates, D. W. Gosselink, and J. A. Kaczynski, *ibid.*, 205 (1967).

(8) Characterized by nmr spectral comparison with 2-methylcycloheptadienyllithium (R. B. Bates, S. Brenner, W. H. Deines, D. A. McCombs, and D. E. Potter, *J. Amer. Chem. Soc.*, **92**, 6345 (1970)).

(9) (a) R. B. Bates, W. H. Deines, D. A. McCombs, and D. E. Potter, *ibid.*, **91**, 4608 (1969); (b) K. Kloosterziel and J. A. A. van Drunen, *Recl. Trav. Chim. Pays-Bas*, **88**, 1984 (1969).

predicted by HMO theory to have $DE_\pi = 1.88\beta$, and might thus be expected to be *ca.* 2 kcal/mol less stable than a similarly substituted 3-vinylpentadienyl anion. It is not clear which of the maxima adjacent to VII is 22 kcal/mol above V_{cis}, but the higher one must be. The value for the activation energy for $V_{trans} \rightarrow V_{cis}$ is calculated from the observed half-life of 30 min at 140° for the $V_{trans} \rightarrow$ VI conversion, and the last activation energy in the sequence is assumed to have about the same value as the heptatrienyl–cycloheptadienyl anion cyclization.[9] Apparently 2- and 3-vinylpentadienyl anions suitably substituted for these sigmatropic rearrangements will best be prepared below room temperature.

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Iron(II) Phthalocyanines as Nuclear Magnetic Resonance Shift Reagents for Amines[1]

Sir:

The known existence of a large ring current in the phthalocyanine ring[2] and the known ability of the iron in iron(II) phthalocyanine to complex amines[3] suggested that this phthalocyanine might function as a useful nmr shift reagent for amines. This possibility has been investigated and it has been found that, in fact, iron(II) phthalocyanine does serve as an efficient and convenient shift reagent for amines.[4] It has also been found that through ligand exchange the complexes of iron(II) phthalocyanine with certain amines can sometimes function as convenient shift reagents for other amines.

These iron(II) phthalocyanine reagents are complementary to the group IV metal phthalocyanine reagents previously reported[6–10] because they bind the species of interest in a different way, *i.e.*, by coordinate covalent bonds rather than by simple covalent bonds. They are also complementary to the lanthanide reagents[11,12] since they are applicable to a much narrower range of bases than the lanthanide reagents. This specificity is expected to be of value in studies of polyfunctional compounds.

The use of iron(II) phthalocyanine as a shift reagent is illustrated by work carried out on methylamine and *n*-butylamine. In the case of methylamine the free amine was condensed in large excess on iron phthalocyanine and the excess amine allowed to evaporate off. The product when dissolved in deuteriobenzene gave, as is seen in Figure 1, a well-resolved A_2X_3 spectrum. In the case of *n*-butylamine a slight excess of the free amine in benzene was allowed to react with iron(II) phthalocyanine at room temperature overnight. The product was isolated by evaporation and purified by fractional precipitation from ether with hexane. A deuteriochloroform solution of it gave, as Figure 2 shows, a spectrum with well-resolved multiplets for each type of proton. For both complexes the areas of the resonances were consistent with a 2:1 ratio between amine and phthalocyanine.

An illustration of the use of the amine complexes of iron(II) phthalocyanine as shift reagents is provided by work done with the bis-*n*-butylamine complex. Here several successive additions of pyridine were made to a dilute deuteriochloroform solution of the *n*-butylamine complex, and after each addition a 100-MHz Fourier transform spectrum was taken. Each of these spectra showed resonances attributable to the bis-pyridine complex, the bis-*n*-butylamine complex, and what is presumed to be the monopyridine–mono-*n*-butylamine complex. The resonances of the pyridyl protons of the bispyridyl complex and the mixed complex overlapped partially in the case of the 2,6 protons and fully in the case of the 3,5 and 4 protons. Over the range studied the pyridyl protons showed no concentration dependence.

Similarly the addition of *n*-propylamine to a deuteriochloroform solution of the *n*-butylamine complex gave a solution showing the methyl resonance of complexed *n*-propylamine. The other amine resonances were, of course, overlapped by the *n*-butylamine resonances. (This overlap could have been alleviated or avoided by using other suitable complexes as reagents, for example, suitable aromatic amine complexes.)

That iron(II) phthalocyanines can function well as qualitative shift reagents is dependent on a number of factors besides those already mentioned. Of importance, since both iron(II) phthalocyanine itself and iron(III) species in general are paramagnetic,[5] is the low solubility of iron(II) phthalocyanine in organic solvents and its resistance to oxidation by air to iron(III) species. Also important is the rate of the iron–amine exchange in the complexes—slow enough to preclude broadening and shifting of the amine resonances but fast enough to permit convenient interchange of one ligand for another. The slowness of the N–H exchange rate and the rapidity of the N relaxation rate are also of significance since they preclude substantial N–H resonance broadening.[13,14]

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[1] Support for this work was provided by National Science Foundation Grant No. GP-22739 and by an NDEA Fellowship. The work was presented in part at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971.

[2] T. R. Janson, A. R. Kane, J. F. Sullivan, K. Knox, and M. E. Kenney, *J. Amer. Chem. Soc.*, **91**, 5210 (1969).

[3] P. A. Barrett, D. A. Frye, and R. P. Linstead, *J. Chem. Soc.*, 1157 (1938).

[4] Although iron(II) phthalocyanine is paramagnetic, its bisamine complexes are diamagnetic.[5] Paramagnetism thus plays no role in the functioning of iron(II) phthalocyanine as a shift reagent for amines.

[5] A. B. P. Lever, *Advan. Inorg. Chem. Radiochem.*, 7, 27 (1965).

[6] J. E. Maskasky and M. E. Kenney, *J. Amer. Chem. Soc.*, **93**, 2060 (1971).

[7] A. R. Kane, J. F. Sullivan, D. H. Kenny, and M. E. Kenney, *Inorg. Chem.*, **9**, 1445 (1970).

[8] A. R. Kane, R. G. Yalman, and M. E. Kenney, *ibid.*, 7, 2588 (1968).

[9] J. N. Esposito, L. E. Sutton, and M. E. Kenney, *ibid.*, **6**, 1116 (1967).

[10] J. N. Esposito, J. E. Lloyd, and M. E. Kenney, *ibid.*, **5**, 1979 (1966).

[11] C. C. Hinckley, *J. Amer. Chem. Soc.*, **91**, 5160 (1969).

[12] A recent note listing many lanthanide shift reagent papers is W. De W. Horrocks, Jr., J. P. Sipe III, and J. R. Luber, *ibid.*, **93**, 5258 (1971).

[13] Other examples of rapid ^{14}N relaxation have been known for some time: G. V. D. Tiers and F. A. Bovey, *J. Phys. Chem.*, **63**, 302 (1959).

[14] Ruthenium(II) phthalocyanine[15] has properties similar to those of