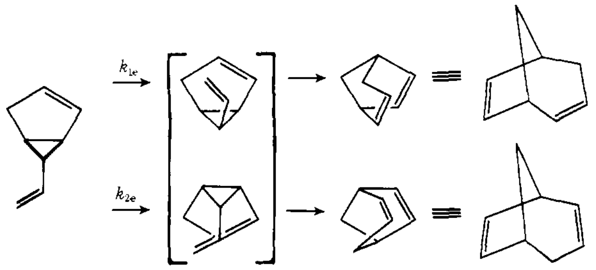
optically active versions of 1-methylspiro[2.4]hepta-4,6-diene demonstrated that one-center epimerization at the spiro carbon atom was definitely not prominent; the three experimental rate constants for distinct cyclopropane geometrical isomerizations could be accommodated with the three two-center epimerization rate constants.[6]

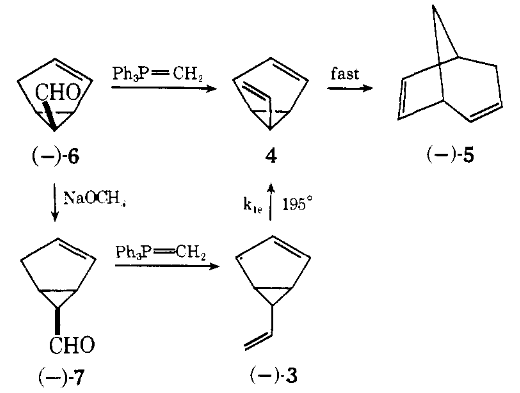
We sought to learn whether a particular *trans*-1,2-divinylcyclopropane, 6-*exo*-vinylbicyclo[3.1.0]hex-2-ene (**3**), isomerizes to the 6-endo isomer **4** through a one-center epimerization, at C(6), or a two-center epimerization, at C(1) and C(5). This choice of substrate would permit a quantitative determination of k_{1e} and k_{2e} through comparison of absolute stereochemistry and relative optical purity of substrate and final product, bicyclo[3.2.1]octa-2,6-diene (**5**).



endo-Bicyclo[3.1.0]hex-2-ene-6-carboxaldehyde (±-**6**), prepared through peracetic or *m*-chloroperbenzoic acid oxidation of norbornadiene,[7] was combined with 0.5 equiv of *l*-(−)-ephedrine. The unreacted aldehyde was recovered, purified, and found to be optically active, $[\alpha]_D$ −54.4° (*c* 1.01, $CHCl_3$). Wittig condensation[8] converted a portion of this aldehyde to bicyclo[3.2.1]octa-2,6-diene, (−)-**5**, $[\alpha]_{365}$ −77.0 ± 0.4°; another portion with sodium methoxide in methanol[9] at reflux for 1.5 h gave rise to the exo-aldehyde (−)-**7**, $[\alpha]_D$ −60.4°, which was converted to 6-*exo*-vinylbicyclo[3.1.0]hex-2-ene, (−)-**3**, $[\alpha]_{365}$ −283.1 ± 0.3°, through another Wittig reaction (see Scheme I).

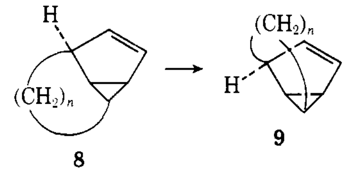
The absolute configurations for these molecules are indeed as formulated below. (−)-Bicyclo[3.2.1]octa-2,6-diene was reduced with diimide to afford (+)-(1*R*,5*R*)-bicyclo[3.2.1]oct-2-ene.[10] (−)-*exo*-6-Vinylbicyclo[3.1.0]hex-2-ene and the stereochemically analogous (−)-(1*S*,1*S*)-*trans*-divinylcyclopropane,[4,11] have very similar ORD spectra from 365 to 589 nm. In the absence of other strong chromophores in the two molecules compared, the ORD spectra should reflect absolute stereochemistry reliably.[12]

Scheme I



Pyrolysis of (−)-*exo*-6-vinylbicyclo[3.2.0]hex-2-ene at 195 °C for 1 h in a sealed, degassed ampoule gave (−)-bicyclo-[3.2.1]octa-2,6-diene, $[\alpha]_{365}$ −75.8 ± 0.3. Thus, within limits much smaller than probable experimental imprecisions, the entire reaction follows the one-center epimerization alternative; $k_{2e} = 0$.

Although bicyclo[3.1.0]hex-2-ene exhibits the two-center epimerization process along with 1,3-sigmatropic shifts of the C(1)–C(5) bond,[13] the 6-*exo*-vinyl system **3** shows only the one-center epimerization. Dauben and Kellogg[14] found that the thermal rearrangement **8** → **9**, restricted by geometrical constraints to the one-center epimerization mode, did occur, while in cyclopropane and phenylcyclopropane,[5] systems without such constraint and free to rearrange by either mode, two-center epimerization is the exclusive or nearly exclusive operative process. The present results demonstrate clearly for the first time one-center epimerization in a cyclopropane for which an alternative two-center option is geometrically feasible and gives the thermodynamically undisadvantaged, enantiomeric product.



n = 4 or 5

Similar work with other constrained *trans*-divinylcyclopropanes, monocyclic *trans*-divinylcyclopropanes, and derivatives of vinylcyclopropane itself will be needed to discover the minimal structural features facilitating kinetic dominance of one-center over two-center epimerizations in cyclopropanes.

Acknowledgment. This work has been supported through Grant GP-40933X by the National Science Foundation.

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Structural Studies of Tautomeric Systems: the Importance of Association for 2-Hydroxypyridine–2-Pyridone and 2-Mercaptopyridine–2-Thiopyridone

Sir:

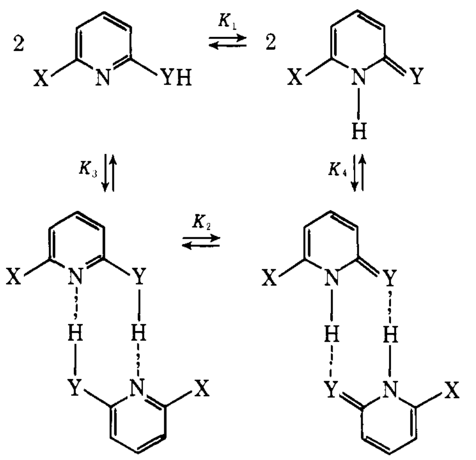
The fact that the positions of tautomeric equilibrium for hydroxypyridines–pyridones and related systems are reversed by transfer from polar solvents to the vapor phase has been established recently.[1] The usual procedure for eliminating solvation effects of polar solvents, and thereby to approach the vapor phase environment, is to use dilute solutions in nonpolar solvents.[2] We wish to report that due to dominating association effects this approach succeeds in the case of 2-hydroxypyridine

Table I. Equilibrium Constants for Scheme I

Substrate	Solvent	K_T	$K_1{}^a$	K_2	K_3	K_4
1–2	Decane or cyclohexane	1.6	2.56	*b*	*b*	$(5.6 \pm 1.7) \times 10^6$
3–4	Cyclohexane	0.09^d	0.008 ± 0.001^c	*c*	*c*	$(9.4 \pm 1.0) \times 10^5$
	Chloroform	2.6	6.8 ± 0.40^c	*c*	*c*	$(2.7 \pm 0.5) \times 10^3$
5–6	Chloroform	2.2	4.8 ± 0.5	4.3 ± 1.5	$(7 \pm 1) \times 10^3$	$(7 \pm 1) \times 10^3$

^{a} $K_1 = (K_{T_{\text{monomer}}})^2$. ^{b} The hydroxypyridine dimer was not detected. ^{c} The mercaptopyridine dimer was not detected. ^{d} The change in K_T with solvent is consistent with the changes in dipole moments of **3–4** (ref 1).

Scheme I



1, X = H; Y = O
3, X = H; Y = S
5, X = Cl; Y = O

2, X = H; Y = O
4, X = H; Y = S
6, X = Cl; Y = O

(**1**)-2-pyridone (**2**) in saturated hydrocarbons only if solutions on the order of 10^{-7} M are studied at ambient temperature or if more concentrated solutions are heated to >100 °C. Our interpretation is supported by direct measurements of association and tautomeric ratios for related systems in chloroform. These results have significance for determinations, interpretations, and application of protomeric equilibrium constants.

The ultraviolet spectrum of **1–2** ($\lambda_{\max}$, 305 nm) in decane at 10^{-5} M when compared with that of 2-methoxypyridine ($\lambda_{\max}$, 275 nm, ϵ 4000) and 1-methyl-2-pyridone ($\lambda_{\max}$, 310 nm, ϵ 3000) shows the 2-pyridone form to be dominant and the amount of 2-hydroxypyridine present, if indeed it is detectable, to be less than 10%. That situation is clearly different from the gas phase where the hydroxy form predominates.[1,3] However, if the decane solution is heated to 110–130 °C or if the spectrum is measured at 1.25×10^{-7} in cyclohexane,[4] the 2-hydroxypyridine tautomer is readily detectable. Under the latter conditions an equilibrium constant of 1.6 ± 0.5 (NH/OH), comparable to the gas phase value of 0.4 ± 0.2, may be obtained.[5] The temperature and concentration dependence are readily accommodated by the well-known tendency of 2-pyridone to form stable dimers which are broken up by heating or extreme dilution, although the equilibrium constant for association in the saturated hydrocarbons is higher by factors of 10^4 and 10^6 than those reported for benzene or dioxane.[6] Scheme I and Table I give the salient features of this association.[7] Direct measurement of the association was precluded by the low solubility of the pyridone in hydrocarbon solvents.

The ultraviolet spectrum of 2-mercaptopyridine (**3**)-2-thiopyridone (**4**) over the range of 10^{-3} to 10^{-5} M in cyclohexane and 10^{-2} to 10^{-5} M in chloroform shows a ninefold and fourfold increase in the relative amount of the thiol tautomer **3** with decreasing concentration. In this case, a direct measure of 66% dimer at 1.27×10^{-3} M in chloroform was provided by vapor phase osmometry. The data fit the known association[6] of **3** for Scheme I for the values given in Table I.

In a careful study of the tautomeric equilibria of substituted 6-chloro-2-hydroxypyridine tautomers, Simchen determined equilibrium constants for monomers since he noted that these compounds are strongly associated.[8] Ultraviolet and vapor phase osmometry data for the 6-chloro-2-hydroxypyridine isomers **5** and **6** in chloroform over the concentration range of 10^{-2} to 10^{-5} M provide the equilibrium and thermodynamic values given in Table I. Although the effect of association on the equilibrium is only a factor of two in this case, the data do require that two dimers, shown as the hydroxypyridine and pyridone dimers, be present, with the former predominant.[9]

The results for **1–2** and **3–4** show that the position of protomeric equilibrium can be significantly affected by association[10] and that the extent of association, like the values of the equilibrium constants between the monomers,[1,11] may be changed by orders of magnitude as a function of molecular environment. The results for **5–6** show that such environmental dependence is not observed for all cases and suggest each situation must be individually evaluated. Interpretations of apparent protomeric equilibrim constants in terms of relative chemical binding energies appear to be unreliable unless the effects of both solvation and association are considered. Extrapolations of such constants from one environment to another are clearly precarious.[12] Further studies are needed to provide a basis for understanding bonding, solvation, and association in protomeric equilibria.

Acknowledgment. We are grateful to the National Science Foundation and the National Institutes of Health for support of this work.

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(2) (a) For example the equilibrium constant between **1** and **2** in isoctane has been determined to be >10 in favor of **2** by A. Gordon and A. R. Katritzky, *Tetrahedron Lett.*, 2767 (1968). (b) We have reported that only **2** is detectable at 10^{-4} M in cyclohexane and noted the possible complications of association.[1]

(3) The gas phase values change little from 110 to 250 °C and therefore can be extrapolated to 25 °C without substantial change.[1]

(4) A path length of 3 m is required. An ultraviolet spectrometer was constructed for these measurements.

(5) Calorimetric determinations of the basicities and heats of solution of 2-methoxypyridine and 1-methyl-2-pyridone have recently been used to estimate the enthalpy difference between **1** and **2** in cyclohexane as +1.1 kcal/mol by M. J. Cook, A. R. Katritzky, L. G. Hepler, and T. Matsui, *Tetrahedron Lett.*, 2685 (1976). While the success of that approach depends on some quantitative compensations in solvations, it has the interesting advantage of not being a direct measurement on the protomers **1–2** and thus avoiding problems of association. The enthalpy of association of **1–2** can be estimated as −20 kcal/mol from the K_4 value in Table I and the theoretical loss of translational entropy on dimerization.

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(7) The possibility of a hydroxypyridine dimer in equilibrium with the monomer

2 cannot, of course, be excluded by the present data. If such a dimer is formed, its association constant with respect to monomer 2 is less than the association constant for monomer 1.

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(9) Acceptable alternatives to Scheme I include hydroxypyridine dimer in equilibrium with a mixed hydroxypyridine–pyridone dimer or an equilibrium between all three possible dimers, but the hydroxypyridine form is always required by the data to be ominant.

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(12) In biochemical applications transference of equilibrium constants for the purine or pyrimidine bases from aqueous solutions to associated bases within nucleic acids could be in error by orders of magnitude. On a more positive note, the demonstration that 2 is 6 kcal/mol more strongly associated in cyclohexane than in dioxane suggests that the energy of enzyme–substrate binding could be strongly influenced by the molecular environment at the binding site. W. P. Jenks, "Catalysis in Chemistry and Enzymology", McGraw-Hill, New York, N.Y., 1962; T. C. Bruice, "The Enzymes", P. R. Boyer, Ed., Academic Press, New York, N.Y., 1970, Chapter 4.

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Originally Received August 3, 1976

Exploratory Field Desorption Mass Analysis of the Photoconversion of Adsorbed Polycyclic Aromatic Hydrocarbons

Sir:

Experiments conducted with polycyclic aromatic hydrocarbons (PAH) adsorbed on silica gel, alumina,[1-4] and on surfaces of crystalline PAH[5] demonstrate increased photochemical reactivity over that observed in solution. PAH might similarly undergo accelerated photoconversion when adsorbed on carbon soot.[6-8] In this report, we describe the application of field desorption mass spectrometry (FDMS) to study the photooxidation of PAH adsorbed on carbon. Mass spectra of PAH irradiated directly on carbon microneedle emitters are presented and discussed.

Field ionization mass spectrometry has been used to detect primary, gas-phase, photodecomposition products.[9-11] FDMS, a related technique which is becoming increasingly useful in analytical chemistry,[12] could be similarly applicable to the investigation of surface phase photochemisry. In FDMS the sample is adsorbed directly onto an electrode (the emitter), where it is subsequently ionized and desorbed by application of a high electric field. Although the mechanism of ionization is a subject of current debate, volatilization of the sample prior to ionization is generally believed not to occur. Photochemical reactions of material adsorbed on an emitter take place in the ionization region and, thus, direct analysis of the reaction products is possible. At present, the most commonly used emitter consists of carbon microneedles grown on a thin tungsten wire.[13,14] X-ray studies show the carbon structure of emitter microneedles to be very similar to that of graphite[14] and, hence, soot.[15] Since airborne PAH are principally associated with soot,[8] the results of photooxidation experiments conducted on field desorption emitters should aid in understanding naturally occurring photochemical processes.

A Hitachi-Perkin Elmer RMU-7, single focusing mass analyzer fitted with a field ionization/field desorption ion source, constructed in the authors' laboratory, was used in this work. Similar sources are described elsewhere.[16] The RMU-7 was modified to extend its mass range to *m/e* 500 at an accelerating voltage of 3.6 kV and to provide it with a stable, Hall probe regulated, programmable magnet scan controller. The instrument has a resolution of about 600 at *m/e* 500.

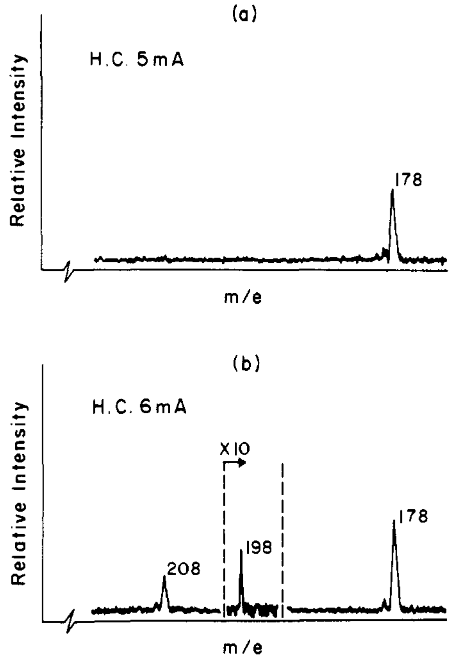

Figure 1. Field desorption mass spectra: (a) anthracene (*m/e* 178), nonirradiated; (b) anthracene, irradiated 1 h.

The sensitivity of the instrument for acetone (*m/e* 58 in the field ionization mode is 2×10^{-8} A/Torr. In the field desorption mode the sensitivity of the RMU-7 to benzo[*a*]pyrene (*m/e* 252), that is the ratio of the total integrated ion current at *m/e* 252 to the amount of sample used ($\sim$0.6 ng), is about 5×10^{-14} C/ng. The field desorption limit of detectability for benzo[*a*]pyrene is about 25 pg (0.1 μl of a 10^{-6} M benzene solution deposited on the emitter).

Photooxidation experiments were performed on anthracene, benzo[*a*]anthracene, pyrene, benzo[*a*]pyrene, chrysene, and coronene. Solutions of PAH in bromobenzene ($\sim 10^{-3}$ M) were prepared from reagent grade chemicals after purification by sublimation. Approximately 1 μl of solution was deposited on an emitter, leaving $\sim$0.1 μg of sample adsorbed after solvent evaporation. Field desorption mass spectra of each compound were obtained to establish purity and to provide references for comparison with spectra of the irradiated samples. Reference spectra of all compounds were found to exhibit only molecular ion mass peaks with no evidence of impurities. A typical reference spectrum of anthracene is shown in Figure 1a.

Sample material, adsorbed on an emitter, was irradiated in air with a high pressure mercury arc lamp for 30-60 min. Radiation was filtered with a 5-cm quartz water cell and the emitter support post was immersed in a Dewar containing acetone and dry ice. These measures were taken to prevent thermal reactions and evaporation of surface-adsorbed species. Light intensity at the sample surface was approximately 200 mW/cm^2. Immediately following irradiation, samples were placed in the field desorption ion source for mass analysis.

Photooxidation of anthracene, benzo[*a*]anthracene, pyrene, and benzo[*a*]pyrene on field desorption emitters is observed; photomodification of chrysene and coronene under the same conditions is not observed. All compounds, with the exception of coronene, have been shown to react similarly under exposure to ultraviolet radiation when adsorbed on silica gel.[3]

The mass spectrum of irradiated anthracene is shown in Figure 1b. In addition to the molecular ion mass peak at *m/e* 178, the spectrum exhibits peaks at *m/e* 198 and 208. The peak at *m/e* 208 corresponds to anthraquinone, an expected photooxidation product.[5] The identity of the small peak at *m/e* 198 is unknown. The absence of peaks due to impurities, instrument background, or cluster ions (singly or doubly charged) in the