different in solid state for the three molecules, appears identical in aqueous solutions.

We have previously shown[2] that the electronic distribution of the protonated nitrogens of Ach and monoprotonated Ni was closely the same. The similar values for the stretching vibrations of methyl groups bonded to nitrogen in the spectra of Ach, β-MeAch, Mu, and Ni indicate that in the neighborhood of the nitrogen atom the electronic density is closely the same for all these molecules.

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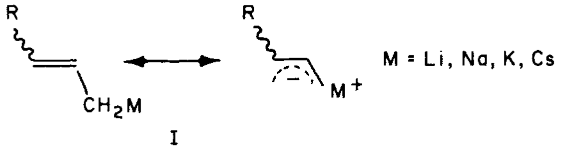
Gas Phase Acidities of the 2-Butenes. Regarding the Use of Organometallics as Models for Free Carbanions

Sir:

Interest has focused in recent years on the generation and characterization of allyl organometallics, I, in which M is an alkali metal. Perhaps the most startling feature of these systems is their thermodynamic preference to adopt cis rather than trans skeletal geometries.[1-4] For example, Schlosser and Hartmann[1i] have recently reported that equilibrium mixtures of the 1-methylallyl compounds (I, $R = CH_3$) of lithium, sodium, potassium, and cesium are comprised of 67, 93, 96, and >99.9% of the cis isomers, respectively. These ratios correspond to free energy differences (favoring the cis compounds) of 0.4, 1.2, 1.4, and >3.1 kcal/mol for the four metals, respectively, which are to be compared with a cis-trans ΔG° (trans favored) of 0.7 kcal/mol for 2-butene itself.[6] Similar cis/trans ratios have been reported for equilibrium mixtures of more highly substituted alkenyl organometallics, which generally show enhanced preference for cis skeletal arrangements with increasing electropositivity of the metal.



I

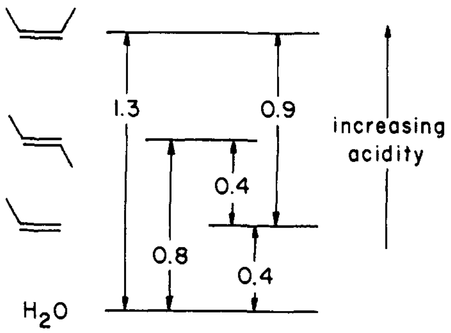


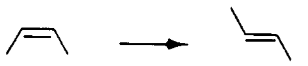
Chart I

The preferences noted for alkenyl organometallics to adopt cis skeletal geometries have often been ascribed to those of the underlying allyl carbanions. It has also recently been pointed out that "the properties of resonance-stabilized organometallic contact pairs approach closer and closer to those of true (free) carbanions as the metal is varied from the less electropositive (lithium) to the more electropositive (cesium)."[1i] In order to provide evidence for or against such notions as these, we have undertaken to measure the relative acidities of *cis*- and *trans*-2-butene in the gas phase, using pulsed ion cyclotron resonance (ICR) spectroscopy.[7] Our data, displayed in Chart I, indicates a ΔG°_{298} for the proton transfer reaction (eq 1),

(1)

(obtained by independent measurements of the acidities of *cis*- and *trans*-2-butene relative to both water and propene), of −0.5 ± 0.2 kcal/mol (i.e., favoring of formation of the cis 1-methylallyl anion). It needs to be emphasized that the ICR experiment provides no direct information regarding the geometrical structures of ions in the gas phase. This is because only a species' charge to mass ratio is measured directly. Therefore, the interpretation of our data requires that three assumptions be made: (1) that on the time scale of the ICR experiment, the cis and trans isomers of the 1-methylallyl anion do not interconvert; (2) that deprotonation of the 2-butenes results in formation of allylic rather than vinylic anions; (3) that reprotonation of the cis and trans 1-methylallyl anions leads to the corresponding 2-butenes rather than to the thermodynamically less stable C_4H_8 isomer, 1-butene. Our first assumption is supported by the fact that, in solution, cis-trans interconversion barriers of alkenyl organometallics are sizable. Thus, rotation about the allylic bond in a variety of 1-phenylallyl organometallics requires between 15 and 20 kcal/mol,[8a,b] while degenerate isomerization in allyllithium occurs with a somewhat smaller (10.5 kcal/mol[8c]) barrier. In view of known preferences for charge localized cations to be more heavily solvated than delocalized species,[9] it seems likely that the barriers hindering cis-trans isomerization in the free anions will be even larger than those measured in solution. Although no experimental data are available, an ab initio molecular orbital calculation indicates a barrier of 25 kcal/mol for rotation in the allyl anion.[10] Our second assumption, regarding the site of deprotonation in the 2-butenes, seems quite secure, since proton detachment from ethylene (leading to the vinyl anion) is at least 15 kcal/mol more difficult than allylic deprotonation.[13] Our final assumption, that reprotonation of the cis and trans methylallyl anions leads back to their respective alkene precursors and not to 1-butene, will be satisfied on thermodynamic grounds (1-butene is 1.3 and 2.0 kcal/mol less stable than *cis*- of *trans*-2-butene, respectively) since the rates of the proton transfer reactions considered here are nearly diffusion controlled. It should be stressed that the breakdown of any of these three assumptions would result in an incorrect measure of the acidity of one or both of the isomeric 2-butenes.[14] In this instance we would not have expected the consistent results illustrated in Chart I, i.e., that the acidity of each alkene, independently determined relative to each of two standards (water and propene) would, within our experimental error, be the same.

Decomposition of eq 1 into its component processes (eq 2 and 3) reveals that it is the difference in free energies of the neutral 2-butenes which provides the driving force. ($\Delta G° = -0.7$ kcal/mol[6] for eq 2 and $\Delta G° = +0.2$ kcal/mol for eq 3)



(2)

(3)

In fact, it appears that *in the gas phase, the cis isomer of the 1-methylallyl anion is less stable than the trans,*[15] although the free energy preference here is not as great as that for the neutral alkenes. It might be argued that, in comparison to the corresponding neutral olefins, the cis form of the 1-methylallyl anion is stabilized relative to the trans. Whether this small difference is simply a consequence of the reduction of vicinal H-H repulsions in *cis*-2-butene as a result of removal of a proton or of stabilization inherent to the anion in its cis geometry[17] remains a matter for discussion.

The above caveats notwithstanding, what our experiments indicate, however, is that the preference for cis skeletal arrangements in the case of 1-methylallyl organometallics is not to be ascribed to the free anions. Rather it appears to arise because of differences in interaction energies among the allylic skeleton, the metal, and the solvent. Our data also suggest that the relative (cis vs. trans) stabilities of the organometallic compounds involving the most electropositive metals (e.g., potassium and cesium) do not mirror those of the free anions more closely than those of compounds involving the less electropositive metals (e.g., lithium and sodium).

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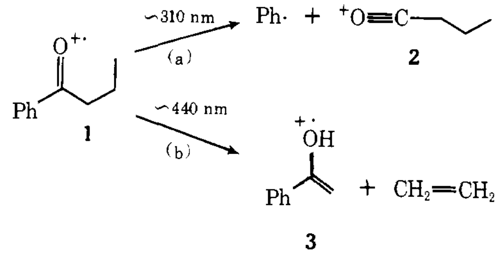
Photodissociation of Butyrophenone Cation. Ionic Analogues of Norrish Type I and II Reactions

Sir:

The Norrish type I and II reactions of ketones are probably the most widely studied of photochemical processes.[1] We wish to report that the analogous reactions can be induced in molecular ions[2,3] and that these reactions occur from specific excited states. Thus, butyrophenone cation **1** undergoes both photochemical α-cleavage (a) and elimination of ethylene (b), eq 1.



(1)

Relevant data[2] are presented in Figure 1, which indicates the total photoinduced disappearance of **1** as well as the appearance of **2** and **3**. The disappearance and total appearance spectra are not strictly congruent, since they have not been corrected for differences in ion trapping times and other mass effects. In addition, some photodecomposition of products also occurs.[4] The possibility that both processes (a) and (b) arise from a common electronic state is essentially excluded by the data which show a sharp transition from (b) to (a) at about 3.3 eV. A possible broad distribution of initial energy states (vibrational or electronic) would also be unlikely to give these results, particularly since the photodissociation spectrum of **1** is independent of electron energy from 12 to 19 eV.

The photochemical onsets of (a) and (b) are well above the appearance potentials (A.P.'s) observed on electron impact.[5] In fact, (a) is energetically feasible at 475 nm although pho-