Table I. Cationized Species in the SIMS Spectrum of *p*-Aminobenzoic Acid and LiCl on Ag[a]

m/e	Rel intensity, %	Ion
137	12	M^+
143, *144*	12	$(M + Li)^+$
149, *150*, 151	35	$(M - 1 + 2Li)^+$
155, *156*, 157, 158	5	$(M - 2 + 3Li)^+$
199, 201	2	$(Ag + 92)^+$
213, *214*, 216, 218	1	Ag_2^+ and $(Ag + Li + 91/92)^+$
226, 228	0, 8	$(Ag + 119)^+$
244, 246	1	$(Ag + M)^+$

[a] Intensities are expressed relative to *m/e* 120. Lithiation of lower mass fragments did not occur to an appreciable extent. The italicized ion is the most abundant in each cluster.

to the substitution of successive hydrogen atoms by lithium.

Our results are most simply interpreted in terms of an ionization mechanism in which the major primary ion is (M + cation)$^+$. The organometallic ions falling below the cationized molecule in mass are believed to have the cationized molecule as their precursor. Evidence for this view was obtained by preparing the protonated molecule by chemical ionization (CI) and observing its fragmentation pattern.[10] The fragmentation pattern observed for $(M + Ag)^+$ in SIMS is similar to that of $(M + H)^+$ in CI.[11]

It now seems possible that, through cationization, SIMS may find a role in the analysis of labile materials such as compounds of biological origin. The cationization observed here will undoubtedly prove important in extending our understanding of the SIMS mechanism. More important still, these results indicate that there may be common features to all of the ionization methods in which a neutral molecule in the solid state is directly converted into a gas phase ion. Further exploration of this possibility would seem to be of value.[12]

Acknowledgment. This work was supported by the National Science Foundation. We are grateful to W. E. Baitinger, A. T. Shepard, and R. W. Hewitt for assistance with the instrumentation.

References and Notes

(1) SIMS spectra were obtained using instrumentation previously described[2] under conditions of low primary ion flux (Ar^+, 5 keV, 4×10^{-10} to 5×10^{-9} A/cm^2). The organic compound ($\simeq$0.1 mg) was evaporated onto the metal support most generally from ethanol, and experiments were done at 1×10^{-8} Torr or less. The base pressure was $<10^{-9}$ Torr. The absolute ion yield for *m/e* 199 (cf. Figure 1) was 3×10^{-5}, and the sensitivity was estimated by a standard method to be $<10^{-11}$ g (cf. A. Benninghoven, *Surf. Sci.*, **35**, 427 (1973)).

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(3) These ions are $(Ag_2 + 17)^+$, $(Ag_2 + 35)^+$, $(Ag_2 + 37)^+$, and $(Ag_2 + 51)^+$. OH and Cl appear to be implicated in these structures.

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(10) We used the reversed sector MIKE spectrometer for the CI study: J. H. Beynon, R. G. Cooks, J. W. Amy, W. E. Baitinger, and T. Ridley, *Anal. Chem.*, **45**, 1023A (1973).

(11) The methane CI mass spectrum of *p*-aminobenzoic acid shows, in order of abundance, *m/e* 138 $(M + H)^+$, 120 $(M + H - H_2O)^+$, and 94. Collision-induced dissociation of *m/e* 138 showed loss of 1, 18, 45, and 46 amu. The corresponding pattern in SIMS for the argentated ion (*m/e* 244), is the loss of Ag, Ag + 17, and Ag + 45. An analogous pattern in which the silver is retained is represented by the losses of 18 and 45 from *m/e* 244.

(12) Since submission of this manuscript, we have observed, under strictly static SIMS conditions, the argentation of hexamethylbenzene and *o*-phenylenediamine. We have also observed the metalation of several involatile polycyclic heteroaromatics.

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Ring-Strain-Promoted 1,2-Carbanionic Rearrangements

Sir:

Unequivocal examples of concerted all-carbon 1,2-anionic rearrangements involving migration of sp^3-hybridized carbon are unknown.[1] There appear to be two primary reasons for this: (1) orbital symmetry considerations[2] predict sterically unlikely suprafacial-inversion or antarafacial-retention pathways, and (2) as Zimmerman[2a,3] and Phelan, Jaffé, and Orchin[4] have pointed out, the energetics of the reaction are unfavorable (relative to the analogous carbocationic and free radical processes) owing to the necessity of accommodating four electrons in one bonding and two antibonding molecular orbitals at the transition state.

It occurred to us that the energetic disadvantage inherent in the migration of saturated carbon to an anionic center could be overcome at least in part by designing a system in which relief of ring strain provides the driving force for rearrangement while at the same time the starting and final carbanions maintain equal degrees of resonance stabilization or better.

An ideal preliminary substrate for such a study appeared to be diketone **1a** (Scheme I) which is readily available in gram quantities via irradiation of the duroquinone-2,3-dimethylbutadiene Diels-Alder adduct.[5] The present communication reports on the base-catalyzed rearrangement of **1a** and on labeling studies which establish the overall 1,2 nature of the process.

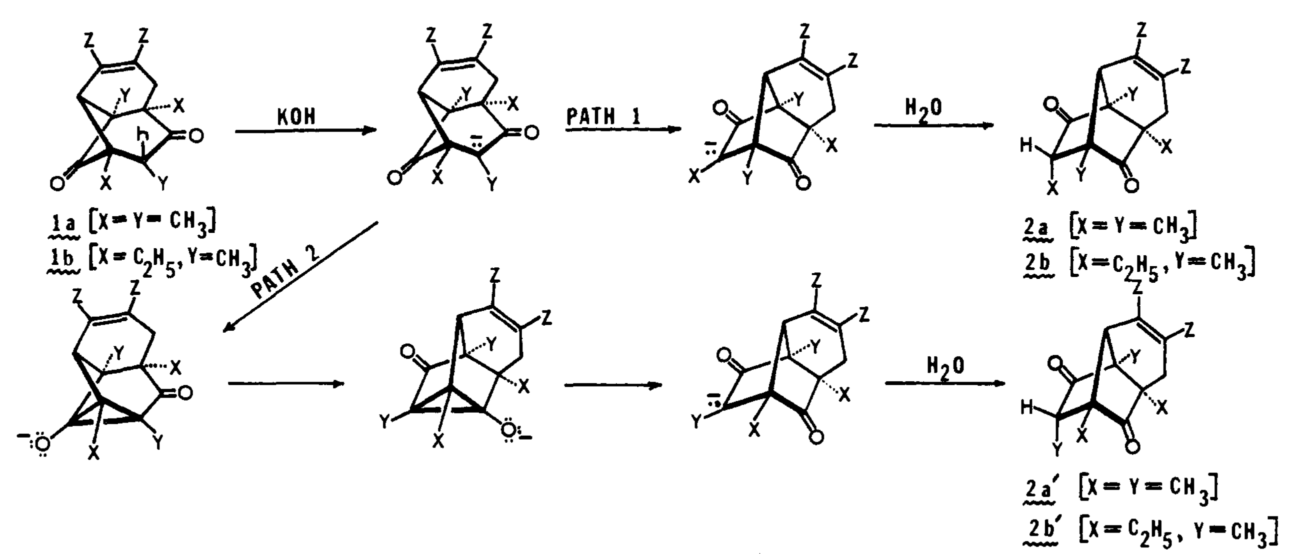
Refluxing a 40% aqueous dioxane solution of cyclobutanone **1a** (0.03 M) in the presence of 0.04 M potassium hydroxide for 24 h afforded the known [5,6] diketone **2a** in essentially quantiative yield. Two label-specific general mechanistic possibilities present themselves for this reaction: path 1, a 1,2-shift process of an as yet unspecified nature yielding **2a**, and path 2, a double homoenolate anion rearrangement[7] affording **2a′**. Since for **1a** products **2a** and **2a′** are identical, no conclusion can be drawn concerning the relative importance of paths 1 and 2.

We therefore turned our attention to the synthesis of a substrate in which X $\neq$ Y selecting the case X = C_2H_5; Y = CH_3. Cyclobutanone **1b** with the required labeling pattern was available in modest quantities from irradiation of the Diels-Alder adduct between 2,3-dimethylbutadiene and 2,5-dimethyl-3,6-diethyl-*p*-benzoquinone.[8] That the photoproduct was actually **1b** and not its "opposite" was established by NMR which clearly showed the acidic methine hydrogen as a quartet (J = 7.5 Hz) at δ 2.50.

Treatment of **1b** with potassium hydroxide in aqueous dioxane as before afforded exclusively diketone **2b**. This was established unambiguously by NMR shift reagent studies which showed a clean and successively downfield-shifted one-proton triplet (J = 7 Hz) upon addition of increasing concentrations of EuFOD.[9]

The labeling study thus indicates the exclusive occurrence of a 1,2-shift process (path 1). At present, three mechanistic possibilities for this process come to mind.

Scheme I^a

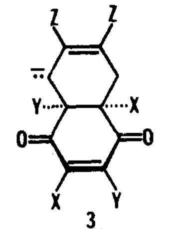


^{a}Z = CH_3 unless otherwise specified.

A. A Nonconcerted 1,2 Shift via Either Carbanion 3 or Diradical Anion 4. This mechanism has analogy in the rearrangement of certain 1-lithio-2,2-diaryl-4-pentenyl compounds which, in addition to [2,3]-sigmatropic rearrangements, undergo 1,2-allyl shifts via dissociation-recombination pathways.[10] To test for the possible involvement of **4**, CIDNP experiments were carried out. Under conditions such that the rearrangement was complete in ~1 h, no enhanced absorption or emission resonances were observed. The intermediacy of carbanion **3** also seems contraindicated by its expected but unobserved protonation in the aqueous medium.

B. A Concerted 1,2-Anionic Shift. The conversion of **1** to **2** (necessarily suprafacial with retention) is forbidden by application of the conventional Zimmerman[2a] or Woodward-Hoffman[2b] orbital symmetry methodologies. Epiotis,[2c] however, has shown that the sigmatropic stereochemical selection rules may be reversed for certain reactions involving polar (AX) transition states. Included in this category are 1,2-anionic shifts. The present reaction, formally involving the migration of an allyl carbanion across the carbon atoms of an electron-deficient ene-1,4-dione double bond, may well fulfill this requirement.

C. Successive [2,3]- and [1,3]-Sigmatropic Rearrangements. The intriguing possibility exists that initial rearrangement of the enolate of **1** gives **5** via an allowed and well-precedented[10] [2,3]-sigmatropic shift and that **5** then rearranges to **2** through a secondary (formal) [1,3]-sigmatropic shift. This is supported by the fact that generation of **5** (X = Y = H; Z = CH_3) under the typical basic reaction conditions gives nearly quantitative yields of **2** (X = Y = H; Z = CH_3).[11] This reaction, which is concertedly disallowed,[2b] does not occur under otherwise identical conditions in the absence of base. More drastic neutral conditions (200 °C, sealed tube) do bring about this transformation, however.[5] Also consistent with mechanism C is the observation that, while **1** (X = Y = CH_3; Z = H) rearranges smoothly to **2** (X = Y = CH_3; Z = H), the corresponding dihydro compound **6**, which is of course incapable of [2,3] rearrangement, is inert.[12]



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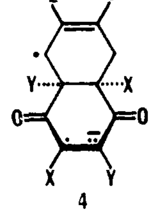

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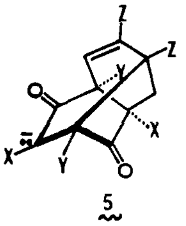

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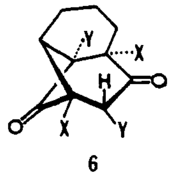

6

Further work to attempt to distinguish between mechanisms A, B, and C is in progress.

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(8) The required 2,5-dimethyl-3,6-diethyl-*p*-benzoquinone was prepared by conventional methods, mp 81–82 °C, reported mp (B. Eistert, H. Fink, J. Riedinger, H. G. Hahn, and H. Dürr, *Chem. Ber.*, **102**, 3111 (1969)) 82 °C. Photolysis of the corresponding Diels–Alder adduct with 2,3-dimethylbutadiene, mp 70–71 °C, gave cyclobutanone **1b** (oil) which showed IR (film) 5.67, 5.85 (C=O) μ; NMR (CCl_4) δ 2.50 (q, J = 7.5 Hz, 1 H, acidic CH), 2.25 (br s, 1 H, allylic CH), 2.05–1.84 (m, 2 H, allylic CH_2), 1.72 (br s, 6 H, vinyl CH_3), 1.52–0.93 (m, 13 H, CH_3 and C_2H_5), 0.62 (t, J = 7.5 Hz, 3 H, $-CH_2CH_3$); mass spectrum parent (70 eV) m/e 274. Rearrangement

product **2b** (oil) showed IR (film) 5.74 (C═O) μ; NMR (CCl_4) δ 2.13–1.77 (m, 4 H, CHs and allylic CH_2), 1.70 (br s, 3 H, vinyl CH_3), 1.63 (br s, 3 H, vinyl CH_3), 1.25–0.85 (m, 16 H, CH_3 and C_2H_5); mass spectrum parent (70 eV) *m*/e 274.

(9) Similar shift reagent studies on **2**a gave rise to a clear increasingly downfield-shifted one-proton quartet (*J* = 7 Hz) indicating that, had the rearrangement product from **1b** been **2b′**, it could have been detected.

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(12) Irradiation of the duroquinone–butadiene Diels–Alder adduct, mp 55.0–55.5 °C, in benzene afforded cyclobutanone **1** (X = Y = CH_3; Z = H) in essentially quantiative yield: mp 75.5–76.5 °C; IR (CCl_4) 5.64, 5.82 (C═O) μ; NMR ($CDCl_3$) δ 5.94 (m, 2 H, vinyls), 2.65 (q, *J* = 7.5 Hz, 1 H, acidic CH), 2.30 (m, 1 H, allylic CH), 2.13 (m, 2H, allylic CH_2), 1.22 (s, 3 H, CH_3), 2.23 (s, 3 H, CH_3), 1.11 (d, *J* = 7.5 Hz, 3 H, C-4 CH_3), 1.06 (s, 3 H, CH_3); mass spectrum parent (70 eV) *m*/*e* 218. The rearrangement product **2** (X = Y = CH_3; Z = H), mp 71.5–72.5 °C, showed IR (CCl_4) 5.74 (C═O) μ; NMR ($CDCl_3$) δ 5.81 (m, 2 H, vinyls), 2.39 (d, *J* = 6 Hz, 1 H, allylic CH), 2.20 (q, *J* = 7.5 Hz, 1 H, exchangeable CH), 2.09 (m, 2 H, CH_2), 1.20 (s, 3 H, CH_3), 1.07 (s, 3 H, CH_3), 0.89 (d, *J* = 7.5 Hz, 3 H, *endo*-CH_3), 0.80 (s, 3 H, CH_3); mass spectrum parent (7O eV) *m*/e 218. Catalytic hydrogenation of **1** (X = Y = CH_3; Z = H) afforded compound **6:** mp 46.5–48.5 °C; IR (CCl_4) 5.65 and 5.83 (C═O) μ; NMR ($CDCl_3$) δ 2.86 (q, *J* = 7.5 Hz, 1 H, exchangeable CH), 1.90 (m, 3 H), 1.60 (m, 4 H), 1.16 (s, 6 H, CH_3s), 1.13 (d, *J* = 7.5 Hz, 3 H, C-4 CH_3), 1.05 (s, 3 H, CH_3); mass spectrum parent (70 eV) *m*/e 220.

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A New Series of Antiferromagnets

Sir:

We report here the preparation, characterization, and magnetic behavior of a series of compounds of iron(III), $A_2FeX_5{\cdot}H_2O$, where A is an alkali ion and X is chloride or bromide. Although the materials contain discrete octahedra, they exhibit certain features of lower dimensional magnets at low temperatures, and they all undergo long-range magnetic ordering at easily accessible temperatures. The variation of the critical temperature, T_c, as the constituent ions A and X are changed exhibits the influence of the size and polarizability of the A and X ions, respectively.

The crystals are easily grown by slow evaporation from acidic solution of the appropriate alkali halide and ferric halide. They have been characterized by elemental analysis and crystallographic procedures (precession camera) that lead to the unit cell information presented in Table I.[1] Complete crystal structures of $(NH_4)_2[InCl_5{\cdot}H_2O]$,[2] $(NH_4)_2[FeCl_5{\cdot}H_2O]$,[3] and $K_2[InCl_5{\cdot}H_2O]$[4] have been reported in which discrete octahedral $[MCl_5(H_2O)]^{2-}$ ions are observed. The water molecules are not oriented randomly, but occupy particular corners of the octahedra that lie on the symmetry planes in the cell. All these orthorhombic materials as well as those reported here appear to be isostructural. The indium compounds are well known as hosts for EPR studies of metal ions, including iron.[5] The compound $Cs_2FeCl_5{\cdot}H_2O$ appears to be isostructural with $Cs_2RuCl_5{\cdot}H_2O$.[6]

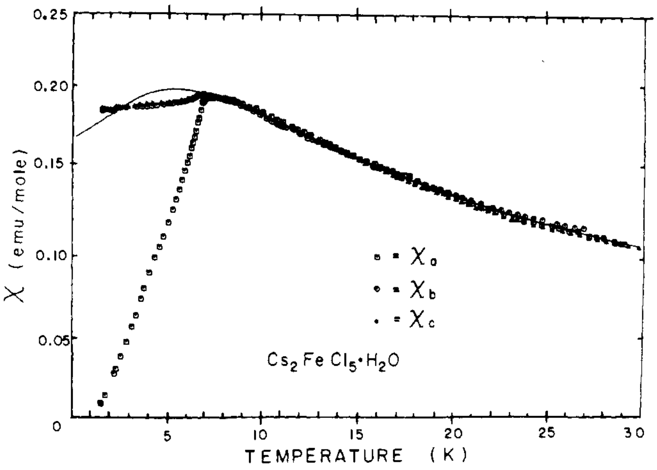

Figure 1. Magnetic susceptibility of $Cs_2FeCl_5{\cdot}H_2O$ along the three crystal axes. Fitted curve is described in the text.

The three orthogonal, isothermal susceptibilities of $Cs_2FeCl_5{\cdot}H_2O$ are illustrated in Figure 1; the data are representative of all those in the series. The results appear to indicate a normal three-dimensional antiferromagnetic ordering, $T_c = 6.43 \pm 0.05$ K, with the *a* axis the preferred axis of spin alignment. Little or no anisotropy is apparent in the data above T_c, suggesting that this could be a Heisenberg model system.[7,8] It is apparent, however, that the magnitude of the susceptibilities throughout the paramagnetic region is too small to be fit in a straightforward fashion; though the data illustrated can in fact be fit by the Curie-Weiss law above 10-12 K, with a reasonable *g* value of 2.08 for $S = {}^5\!/_2$, the derived Weiss constant θ is −14.6 K (antiferromagnetic). This is too large a value to accept as a valid limiting asymptote from the data presented, for the highest temperature accessible to us is 30 K, or only about $2|\theta|$.[9] The zero-field splitting for iron in the $(NH_4)_2[Fe,InCl_5(H_2O)]$ EPR study at 77 K is $D = -1894$ G ~0.25 K, a value too small to influence the susceptibilities in this temperature region. The situation is even worse with $Rb_2FeCl_5{\cdot}H_2O$, where the Curie-Weiss law fit requires $g = 2.4$ and $\theta = -60$ K. The transition temperatures are relatively high for hydrated transition metal halide double salts and provide evidence for extensive exchange interactions.

The crystal structure of the $A_2MX_5{\cdot}H_2O$ compounds suggests that hydrogen bonding may occur between adjacent molecules along the *a* axis in $Cs_2FeCl_5{\cdot}H_2O$, forming a chain in this direction. If it is assumed that the magnetic behavior follows this structural pattern, then a good fit to the data can be obtained. In fact, the curve drawn through the data (Figure 1) is a fit to the equation of Fisher for one-dimensional classical

Table I. Crystallographic and Magnetic Properties of $A_2FeX_5{\cdot}H_2O$

A,X	Cs,Cl	Rb,Cl	Cs,Br	Rb,Br
Space group	*Cmcm*	*Pnma*	*Pnma*	*Pnma*
a, Å	7.4	13.8	14.7	14.2
b, Å	17.4	9.8	10.7	10.4
c, Å	8.0	7.1	7.6	7.4
$\rho_{calcd}(Z = 4)$	3.3	2.9	4.1	3.9
ρ_{obsd}	3.24	2.86	4.02	3.80
$T_c(C_p)$, K	6.57 ± 0.05	10.03 ± 0.05	14.06 ± 0.10[a]	22.90 ± 0.05
$T_c(\chi)$, K	6.43 ± 0.05	10.20 ± 0.08	14.21 ± 0.07	22.91 ± 0.05
J/*k*, K	−0.65	−1.39	−1.6	−2.5
zJ′/*k*, K	−0.46	−1.86	−2.3	−2.5

[a] A second λ anomaly was also observed at 12.92 K.