inequivalence of these hydrogens. This conclusion is quite consistent with the observation of Bovey and Tiers,[4] and it also rationalizes, at least in part, the discrepancy noted by Martin[5] since hydrogen exchange in N-alkyl amides, which are s-trans, does not require rotation, but isomerization of N,N-dialkyl amides does.

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Hydrogen Exchange in Amidinium Ions. Chemically Significant Consequences of Slow Rotation about a Carbon–Nitrogen Single Bond

Sir:

A study of acid-catalyzed hydrogen exchange in amides[1] suggested that there may not be free rotation about the C–N bond of $RCONH_3^+$ during its lifetime. A mechanistic ambiguity precludes a definitive test of this possibility in amides but not in amidinium ions (1). These show[2a] diastereotopic "inside" and "out-

1
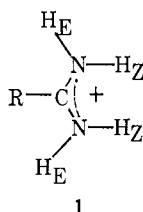
side"[3] N–H resonances in the nmr spectrum. In aqueous sulfuric acid these ions undergo[2b] an acid-catalyzed hydrogen exchange, *via* the dication $RC(NH_3^+)=NH_2^+$ (2). It would appear that the hydrogens of the $-NH_3^+$ group have become equivalent, since rotation about the C–N single bond should be very fast. But since 2 is a very strong acid, proton transfer to H_2O or HSO_4^- would be diffusion controlled,[4] so that its lifetime is only $\sim10^{-11}$ sec. This is uncomfortably close to the estimated time required to convert one conformer of 2 into another. Judging from the isoelectronic species $RC(CH_3)=O$, $R = CH_3$, for which the rate of conformational interconversion[5] is 2×10^{12} sec^{-1}, we might conclude that the rotation is sufficiently rapid. However, hydrogen bonding to solvent or to counterions may increase the barrier to C–N rotation, which then may not be free.

A barrier of only a few kilocalories per mole could lead to a novel conformational effect. Protonation of the lone pair of one of the nitrogens must produce a Boltzmann distribution of the conformers of 2, so that the dominant conformation is close to the most stable

one[6] (3). The labeling must be as indicated, since for-

3   4

mation of 4 would require rotation about the C–N partial double bond of 1, for which the barrier is *ca.* 20 kcal/mol. If the $-NH_3^+$ group does not rotate before it loses a proton, then the only proton that can be exchanged from 3 is H_E. In order for H_Z to exchange, there must be rotation about the C–N single bond. The transition states for this rotation are the maximum energy conformations 5a and 5b. If rotation

5a   5b
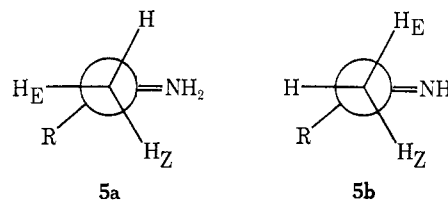
is slow compared to deprotonation, then 5a and 5b are also the transition states for exchange of H_Z, and rotation about the C–N single bond is rate limiting. Even if the rate of rotation is comparable to that of deprotonation, exchange of H_Z is retarded. Only if rotation is rapid would the two hydrogens exchange at the same rate. Thus this conformational effect can be demonstrated by showing that the diastereotopic hydrogens of amidinium ions undergo acid-catalyzed exchange at different rates, despite the equivalence implied by the $-NH_3^+$ group.

Data exist that suggest this result. Neuman and Hammond[2b] observed that for N,N'-dimethylacetamidinium ion, whose dominant configuration is 6, acid-

6   7   8
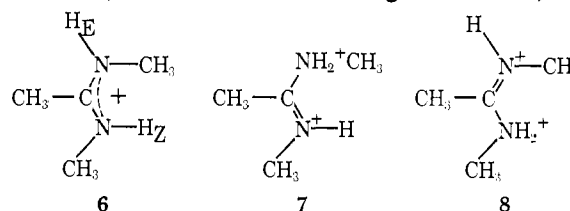
catalyzed exchange of H_E is 6.4 times as fast as that of H_Z. This rate difference was attributed[2b] to a difference in the rates of protonation of the two nitrogens, which are, of course, nonequivalent. However, we would not expect one nitrogen to be 6.4 times as basic as the other, inasmuch as the two conjugate acids, 7 and 8, are isoelectronic to (E)- and (Z)-3-methyl-2-pentene, respectively, for which the E/Z equilibrium constant[7] is only 1.5. We prefer an interpretation based on the above conformational effect. The two nitrogens are protonated at nearly the same rate, such that 7 is formed ~1.5 times as often as 8, but 8 is formed in a conformation unsuitable for hydrogen exchange. Exchange of H_Z is thus slower because it requires rotation about the C–N bond in 8, but exchange of H_E requires no such rotation. Yet these data are not conclusive proof for this effect, since it can be argued that solvation
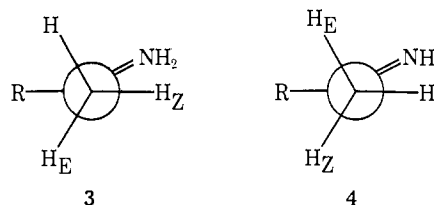
(1) C. L. Perrin, *J. Amer. Chem. Soc.*, 96, 5628 (1974).
(2) (a) G. S. Hammond and R. C. Neuman, Jr., *J. Phys. Chem.*, 67, 1655 (1963); (b) R. C. Neuman, Jr., and G. S. Hammond, *ibid.*, 67, 1659 (1963).
(3) For the E/Z specification, see J. E. Blackwood, *et al.*, *J. Amer. Chem. Soc.*, 90, 509 (1968).
(4) M. Eigen, *Angew. Chem., Int. Ed. Engl.*, 3, 1 (1964).
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(6) J. P. Lowe, *Progr. Phys. Org. Chem.*, 6, 1 (1968).
(7) F. D. Rossini, *et al.*, Selected Values of Properties of Hydrocarbons, *Nat. Bur. Stand. (U.S.)*, No. 461, 162 (1947).
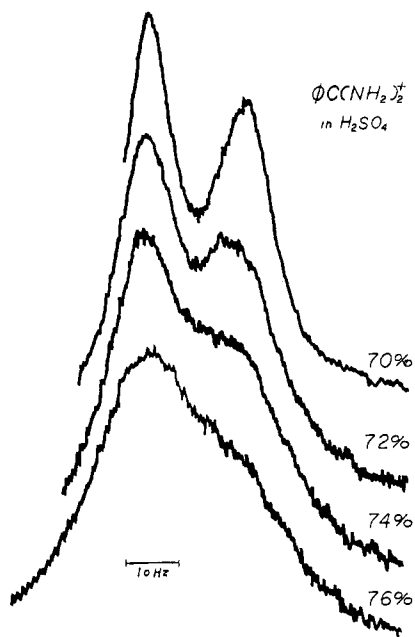
Figure 1. A 220-MHz pmr spectrum of the N–H resonances of 0.5 M PhC(NH$_2$)$_2$$^+$ in aqueous H$_2$SO$_4$ at 20°.

effects that increase the stability of 7 are responsible for the 6.4–fold rate difference.

Unsubstituted amidinium ions provide unambiguous proof. In 20% aqueous H$_2$SO$_4$, benzamidinium ion (1, R = Ph) shows two broad (width 12 Hz) N–H resonances downfield of the phenyl and solvent resonances. By analogy to amides,[8] the low-field resonance may be attributed to H$_E$. With increasing H$_2$SO$_4$ content, these peaks shift upfield without broadening, and the low-field peak shifts more rapidly. From 30 to 65% H$_2$SO$_4$ the N–H peaks are obscured under phenyl or solvent resonances. In 70% H$_2$SO$_4$ the two peaks are again observable. The one at higher field is slightly broader (Figure 1). With increasing H$_2$SO$_4$ content both peaks undergo further broadening, with the one at higher field always distinctly broader (Figure 1).

This observation demonstrates that the diastereotopic hydrogens of benzamidinium ion undergo acid-catalyzed exchange at different rates and that the hydrogens of the –NH$_3$$^+$ *group do not become equivalent.* From the extent of the broadening, the rate ratio is calculated to be 3:1, corresponding to a barrier height of ~3 kcal/mol. We cannot be certain that H$_E$ is the faster to exchange, as the above argument suggests, but this is consistent with the behavior of the chemical shifts and also with the exchange rates in the N,N'-dimethyl analog.[2b] We therefore conclude that there is a chemically significant barrier to rotation about the C–N single bond of RC(NH$_3$$^+$)=NH$_2$$^+$, which is produced in a conformation (3) that requires that the "outside" hydrogen exchange faster than the "inside" one. We have thus demonstrated a novel conformational effect that is, to our knowledge, entirely without precedent.

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Crown Ethers in Carbene Chemistry. The Generation of Free Phenylhalocarbenes

Sir:

A basic uncertainty accompanying carbene generation by base-induced α-elimination has heretofore been the "freeness" of the carbenic species. With haloorganic progenitors, carbenoids were often encountered.[1] Our interest in carbenic reactivity[4] led us to determine the selectivity toward alkenes of phenylbromocarbene (1a)[5,6] and phenylchlorocarbene (1b),[7] generated either by treatment of the requisite benzal halides (2) with potassium *tert*-butoxide[5,7] or by photolysis of the corresponding phenylhalodiazirines (3)[6,7]; see eq 1,

a, X = Br; b, X = Cl
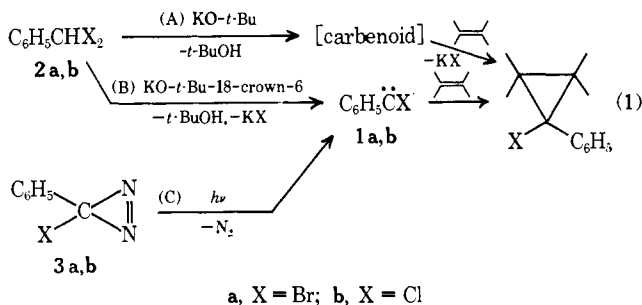
paths A and C, respectively.

The selectivities of the base- and light-generated "carbenes" were clearly different, as is shown in Table I (columns a and b). A conventional explanation was offered. The photolytic intermediate was a free carbene, whereas the base-generated intermediate was a carbenoid—either a phenylhalocarbene–potassium halide complex or a phenylhalocarbene–potassium *tert*-butoxide[8] complex. If this explanation is correct, then it should be possible to generate free phenylhalocarbenes by the base-induced α-elimination reaction, provided that the potassium cation or the solid KO-*t*-Bu can be rendered unavailable for complexation with the carbene.

Crown ethers[10] complex various cations, and K$^+$ is particularly well complexed by the 18-crown-6 ethers.[10,11] In their presence, KMnO$_4$[12] and KF[13] become useful reagents in organic solvents; KO-*t*-Bu can be solubilized, and its dissociation and reactivity are enhanced.[14] We therefore examined the olefin

(1) The noun "carbenoid" defines an intermediate "which exhibit(s) reactions qualitatively similar to those of carbenes without necessarily being (a) free divalent carbon species." [2,3]
(2) G. L. Closs and R. A. Moss, J. Amer. Chem. Soc., 86, 4042 (1964).
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(8) Potassium tert-butoxide is associated in nonpolar solvents.[9] Moreover, the benzal halide–potassium tert-butoxide–alkene reaction mixtures were heterogeneous.[5]
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(13) C. L. Liotta and H. P. Harris, J. Amer. Chem. Soc., 96, 2250 (1974).
(14) J. N. Roitman and D. J. Cram, J. Amer. Chem. Soc., 93, 2231 (1971); M. J. Maskornick, Tetrahedron Lett., 1797 (1972); R. A. Bartsch, G. M. Pruss, R. L. Buswell, and R. A. Bushaw, ibid., 2621 (1972); R. A. Bartsch and K. E. Wiegers, ibid., 3819 (1972).