nances. This method also allows the measurement of T_1 as well as T_2 of these otherwise obscured lines by the method of Freeman and Hill.[4] We have, for example, recently determined the T_1's and the line widths of both the choline and terminal methyls of egg lecithin bilayers.[5] Hopefully, further applications can be made to nmr studies of liquid-crystalline and gel-like samples in general.

Acknowledgment. This work was supported in part by Grant GM 14523-05 from the National Institute of General Medical Sciences, U. S. Public Health Service, and by Grant GP-8540 from the National Science Foundation.

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(4) R. Freeman and H. D. W. Hill, *J. Chem. Phys.*, **54**, 3367 (1971).

(5) G. W. Feigenson, C. H. A. Seiter, and S. I. Chan, *J. Amer. Chem. Soc.*, submitted for publication.

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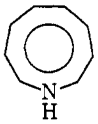
Alkali Metal Azonides. Acidity of 1*H*-Azonine

Sir:

Recently we described the preparation of 1*H*-azonine[1] and a variety of N-substituted derivatives[2] by the low-temperature alcoholysis of *N*-carbethoxyazonine followed by appropriate quenching, and indicated that the overall conversion is best reasoned by the initial generation of the azonide system, *i.e.*, **2**.[2] Presently, we describe the isolation and spectral characterization of various alkali metal azonides and also record information relating to the acidity of 1*H*-azonine (**1**).



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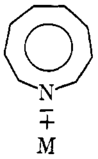

2a, M = Li
b, M = Na
c, M = K
d, M = Rb
e, M = Cs

The azonides shown in **2b**–**2e** were prepared in good yield (>80%) on treatment of *N*-carbethoxyazonine with a slight deficiency of the appropriate metal *tert*-butoxide in tetrahydrofuran at *ca.* −20°, while lithium azonide (**2a**) was generated in the same medium on the reaction of 1*H*-azonine with *n*-butyllithium at *ca.* −30°; 61% yield. In each case, **2** was isolated pure as a white hygroscopic solid, the relative sensitivity to water increasing in the order **2e** → **2a** and invariably resulting in the formation of the common conjugate acid, *i.e.*, **1**, on exposure to air. In their thermal behavior the azonides are strongly reminiscent of 1*H*-azonine in that they are inert to prolonged heating. For example, each member shown in **2** was recovered quantitatively (nmr) after being heated neat for 2 days at *ca.* 100° *in vacuo* (*ca.* 0.005 mm). The nmr spectra of the azonides are well exemplified by that of **2d** shown in Figure 1, with the low-field resonance invariably possessing one-third the area of the high-field signal. We note that these spectra differ substantially from those of all other heteronins[2] in two respects, (1) the appearance of the α pair of hydrogens at exceedingly low fields (τ 1.30–1.50) and (2) the essential coincidence of the β, γ, and δ resonances (τ 3.40–3.51). The first phenomenon obviously arises from the deshielding influence that the positive gegenion exerts on the most closely located protons, while the second, *i.e.*, the coincidence of resonances, is no doubt due to the more extensively delocalized frame of the azonide compared to 1*H*-azonine, owing to the greater availability of the nitrogen lone pair for overall contribution into the "π" system. Further, the assignment in each case of the low-field resonance to the α hydrogen pair receives strong support from the nmr characteristics of **2a**–**2d** in a less ionizing solvent such as acetone.[3] In this medium, unlike DMSO, the position of the low-field signals was found to be a sensitive function of gegenion size, an increase in the alkali metal ionic radius invariably leading to a shift of this resonance to lower fields. Specifically, the nmr characteristics of **2** in acetone are as follows: for M = Li, τ 2.40 (2 H), 3.30 (6 H); for M = Na, τ 1.74 (2 H), 3.20 (6 H); for M = K, τ 1.36 (2 H), 3.37 (6 H); for M = Rb, τ 1.30 (2 H), 3.30 (6 H). Obviously the nmr spectra of the azonides are largely those of solvent-separated species in DMSO and of tight ion pairs in acetone.

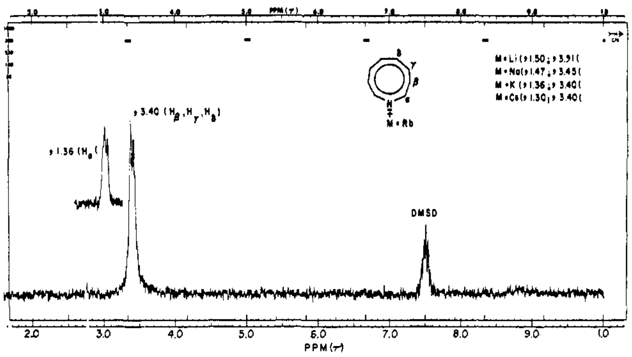

Figure 1. Nmr spectral characteristics of azonides **2a**–**2e** in DSMO-d_6.

The azonide system closely resembles its conjugate acid **1** in its uv spectral characteristics, *e.g.*, for **2c**, $\lambda_{\max}^{\mathrm{THF}}$ 339 nm (sh) (ϵ 3900), 330 (4500), and <280 (>10,000).[4] Significantly, the position of the low-energy absorptions is, for reasons detailed earlier,[2] indicative of a planar geometry.

Acidity measurements relating to the N–H function of π-excessive heterocycles provide yet another means

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(1) A. G. Anastassiou and J. H. Gebrian, *Tetrahedron Lett.*, 825 (1970).

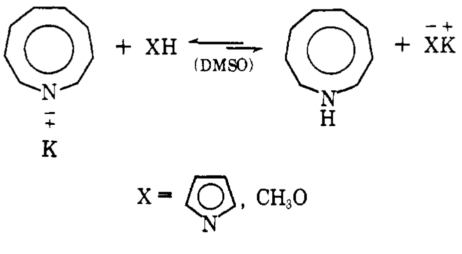
(2) A. G. Anastassiou, S. W. Eachus, R. P. Cellura, and J. H. Gebrian, *J. Chem. Soc. D*, 1133 (1970).

(3) We were unable to record the nmr spectrum of **2e** in acetone-d_6 because of insufficient solubility.

(4) While this band represents the strongest absorption in the spectrum of **2c** its position and intensity could not be accurately assessed owing to the fact that the high dilution necessary here invariably leads to the generation of some 1*H*-azonine ($\lambda_{\max}^{\mathrm{THF}}$ 342 nm (sh) (ϵ 1400), 327 (sh) (2200), 298 (3450), and 234 (24,800)).

of classifying such systems in terms of overall π delocalization. The rationale here is, of course, that N–H acidity is a sensitive function of overall electron density on nitrogen which, in turn, is heavily controlled by the extent to which the lone pair is delocalized into the π system, *i.e.*, an increase in overall delocalization ought to manifest itself in a corresponding enhancement in N–H acidity. In the present instance the availability of both 1*H*-azonine and its conjugate base **2** allowed for a direct comparison between this system and certain key substances of known acidity. Thus, codissolution in DMSO-d_6 of known quantities of potassium azonide (**2c**) and pyrrole led to such a reduction in the amount of **2c** (nmr) as to require 1*H*-azonine (**1**) to be *ca.* 1.8 pK_a units *more* acidic than pyrrole.[5a] Hence, to the extent that electron delocalization is chiefly responsible for the difference in acidity, the π system of azonine appears to be more extensively delocalized than that of pyrrole. Furthermore, an analogous comparison between 1*H*-azonine and methanol has established **1** as more acidic than the alcohol by *ca.* 0.8 pK_a unit.[5b] In light of these findings and to the extent that pK_a differences between two related substances remain reasonably constant in the various media, we estimate the pK_a (Et_2O) of 1*H*-azonine to be *ca.* 15.5.[6]

Scheme I



In brief summary, we note that the data recorded presently serve to unambiguously classify the azonide system as planar (uv) and aromatic (nmr, thermal stability) and to further consolidate our case for a decidedly aromatic 1*H*-azonine.[1,2,9,10]

Acknowledgment. We are very grateful to the National Science Foundation for support of this work under Grant No. GP 26347. We also wish to thank Professor C. D. Ritchie for helpful discussions relating to the solvation of the metal azonides.

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(5) (a) This quantity was obtained as the average of the values observed from three separate runs (ΔpK_a = 1.6, 1.8, and 2.0) in which the relative molar proportions of **2c** and pyrrole were varied from *ca.* 1:2 to 1:6, respectively. Attempts to establish the equilibrium shown in Scheme I through admixture of known quantities of 1*H*-azonine and potassium pyrrolide invariably led to irreproducible results owing to the pronounced sensitivity of **1** to air. (b) This estimate was obtained by averaging the values obtained from two separate runs (ΔpK_a = 1.0 and 0.7) with the relative molar proportions of **2c** and methanol set at *ca.* 1:1 and 1:3, respectively.

(6) For pyrrole[7] pK_a(ether) = 17.5 and for methanol[8] pK_a(ether) = 16.0.

(7) G. Yagil, *Tetrahedron*, **23**, 2855 (1967).

(8) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N.Y., 1965, p 4.

(9) A. G. Anastassiou and H. Yamamoto, *J. Chem. Soc.*, in press.

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A Possible Intermediate in the Tungsten-Catalyzed Olefin Metathesis Reaction

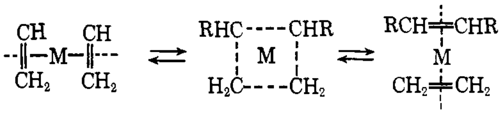
Sir:

Metathesis[1] catalysts promote a reaction in which the carbon–carbon double bonds of two olefins are broken and then remade with the fragments scrambled. A

$$2R_1CH{=}CHR_2 \rightleftarrows R_1CH{=}CHR_1 + R_2CHCHR_2$$

variety of heterogeneous and homogeneous transition[2] metal complexes have been prepared which catalyze this reaction. The most useful catalysts contain either tungsten or molybdenum complexes absorbed on a solid support or as coordination compounds in combination with selected organometallic derivatives.[3]

The mechanism for the reaction has been formulated as a (2 + 2) cycloaddition of the two olefins in the coordination sphere of the metal to form a "quasicyclobutane"[4] intermediate which can decompose by a retro (2 + 2) cycloaddition with a change in the symmetry plane.



Symmetry correlation diagrams can be drawn which show that the (2 + 2) cycloaddition, a reaction that is not allowed thermally, becomes "allowed" due to the admixture of the metal d orbitals of the proper symmetry with the olefin π orbitals.[5,6]

Katz[7] and Eaton[8] have recently investigated the rhodium-catalyzed rearrangement of strained carbocyclic ring systems. They have demonstrated that these reactions involve a metal–carbon σ-bonded intermediate instead of a direct metal-catalyzed electrocyclic rearrangement.

We now have evidence that a carbon–metal σ-bonded species is a possible intermediate in the tungsten-catalyzed olefin metathesis reaction.

A mechanism for the reaction, based on the intermediates demonstrated by Eaton and Katz, can be formulated as follows: (a) a rearrangement of the complexed olefins to a metallocyclic intermediate followed by (b) a rearrangement of the metallocycle and (c) reversal of step a. The rearrangement of A into B may involve a symmetrical intermediate.

To test this alternate mechanism, a procedure was developed for the production of metallocyclic intermediates under conditions used in the metathesis reaction. Wang and Menapace[9] found that a metathesis catalyst could be formed by the reduction of tungsten hexachloride with 2 equiv of butyllithium. The following mechanism was suggested for the formation of tungsten

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(1) N. Calderon, paper presented at the XXIIIrd IUPAC Meeting, Boston, Mass., Aug 1971, paper 559 and references therein.

(2) G. C. Bailey, *Catal. Rev.*, **3**, 37 (1969).

(3) (a) N. Calderon, H. Y. Chen, and K. W. Scott, *Tetrahedron Lett.*, 3327 (1967); (b) W. B. Hughes, *J. Chem. Soc. D*, 431 (1969).

(4) C. P. C. Bradshaw, E. J. Howman, and L. Turner, *J. Catal.*, **7**, 269 (1967).

(5) F. D. Mango and J. H. Schachtschneider, *J. Amer. Chem. Soc.*, **89**, 2484 (1967).

(6) G. S. Lewandos and R. Pettit, *Tetrahedron Lett.*, 780 (1971).

(7) T. Katz and S. Cerefice, *J. Amer. Chem. Soc.*, **91**, 6520 (1969).

(8) L. Cassar, P. E. Eaton, and J. Halpern, *ibid.*, **92**, 3515 (1970).

(9) J. L. Wang and H. R. Menapace, *J. Org. Chem.*, **33**, 3794 (1968).