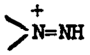
Tetrahedron Letters No.29, pp. 1955-1960, 1964. Pergamon Press Ltd.
Printed in Great Britain.

DIAZENIUM IONS

D. M. Lemal, C. D. Underbrink and T. W. Rave
Department of Chemistry, University of Wisconsin
1112 W. Johnson Street, Madison, Wisconsin 53706

(Received 1 June 1964)

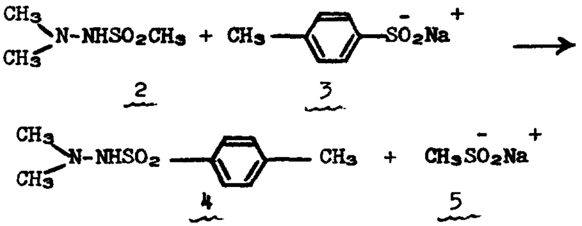
SEVERAL years ago Mc Bride and his coworkers established the existence of a new kind of cation, which they termed a diazenium ion (1).[1] Dialkyldiazenium ions were generated by



1

oxidation of the corresponding hydrazines in mineral acid. Whereas half-lives in this medium were measurable in hours, neutralization immediately destroyed the cations. We wish to record experiments which demonstrate that diazenium ions can conveniently be produced and investigated even in neutral and basic media.

Within seconds of mixing an aqueous solution of 1,1-dimethyl-2-methanesulfonylhydrazine (2) with one containing

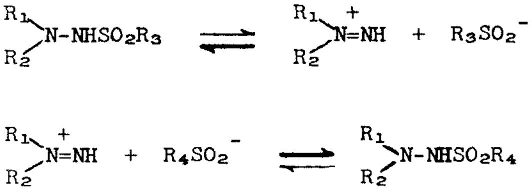


excess sodium *p*-toluenesulfinate (3), 1,1-dimethyl-2-*p*-toluenesulfonylhydrazine (4) crystallizes in near-quantitative yield. When solvent and reactants are so chosen that all species remain in solution, the very general exchange equilibrium represented by Equation I is established.

$$R_1R_2N\text{-}NHSO_2R_3 + R_4SO_2^-M^+ \rightleftharpoons R_1R_2N\text{-}NHSO_2R_4 + R_3SO_2^-M^+$$

Eq. I

Nuclear magnetic resonance spectroscopy has made it possible to measure rate of approach to equilibrium as well as equilibrium composition by virtue of the fact that substantial proton chemical shifts in R_3 accompany the change from sulfonylhydrazine to sulfinate ion in many cases (analogously for R_4). In methanol, for example, the signal for sodium methanesulfinate (5) appears 0.78 ppm upfield from the corresponding resonance for 2. By the n.m.r. technique it was found that exchange reactions of the above type are dramatically accelerated by increasing solvent polarity. Moreover, initial exchange rates are not enhanced by increasing the concentration of metal sulfinate. These observations are accommodated by the hypothesis that ionization of the sulfonylhydrazine to a diazenium and a sulfinate ion is rate-determining and that rapid anion interchange follows (Equation II).[2]



$$R_1R_2N\text{-}NHSO_2R_3 \rightleftharpoons R_1R_2\overset{+}{N}{=}NH + R_3SO_2^-$$

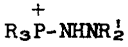
$$R_1R_2\overset{+}{N}{=}NH + R_4SO_2^- \rightleftharpoons R_1R_2N\text{-}NHSO_2R_4$$

Eq. II

Choice of substituents for the sulfonylhydrazine affects exchange rates in the manner predicted by the ionization mechanism. The stability of a diazenium ion should depend heavily upon the basicity of the substituted nitrogen atom;[3] thus it is expected that replacement of N-alkyl by N-aryl groups in a sulfonylhydrazine would sharply decrease ionization rates. In experiments conducted at 33° in 80% pyridine/water containing sodium benzenesulfinate, the initial exchange rate for **2** was too fast to measure accurately by the present n.m.r. method. Substitution of a phenyl for one of the N-methyls resulted in a several hundredfold decrease in initial rate. No exchange whatever was observed for 1,1-diphenyl-2-methanesulfonylhydrazine after several days. As anticipated, increase in the electron-withdrawing character of the substituent on sulfur in a sulfonylhydrazine accelerates initial exchange rates and drives exchange equilibria toward the right.

A variety of nucleophilic agents was introduced into aqueous methanolic solutions of 1,1-dimethyl-2-*p*-toluenesulfonylhydrazine (4) in the hope of intercepting the dimethyldiazenium ion. Bisulfite was found to compete effectively with sulfinate for dimethyldiazenium ions, yielding the hydrazinosulfonic acid $(CH_3)_2\overset{+}{N}HNHSO_3^{-}$. Interestingly, excellent nucleophiles such as thiosulfate, thiocyanate, azide and cyanate ion had no perceptible effect upon the n.m.r. spectra of solutions **4**. Very likely these nucleophiles also combine reversibly with the diazenium ion, but the exchange equilibrium strongly favors the sulfonylhydrazine with its partial double bond character between nitrogen and sulfur.

Such reasoning led to trapping attempts with tertiary phosphines, as the resulting phosphonium salts should be characterized by high bond orders between nitrogen and phosphorus whether 6 or 7 be the stabler tautomeric form. Triphenylphosphine reacted slowly with 4 in aqueous acetone but no adduct

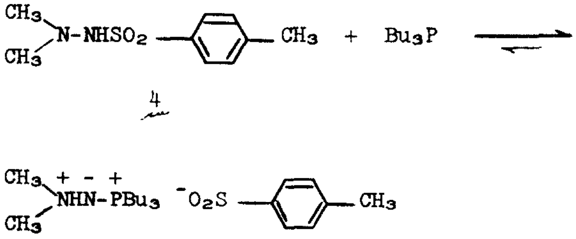

$\overset{+}{R_3P}\text{-}NHNR'_2$

6


$\left\{ R_3\overset{+}{P}\text{-}\overset{-}{N}\text{-}\overset{+}{N}HR'_2 \longleftrightarrow R_3P{=}N\text{-}\overset{+}{N}HR'_2 \right\}$

7

could be isolated. Instead triphenylphosphine oxide was obtained, implying that the desired phosphonium salt had formed and then hydrolyzed. Powerfully nucleophilic tri-*n*-butylphosphine replaced the *p*-toluenesulfonyl group of 4 with great speed in methanol; the equilibrium favored the salt 8 (representation of 8 as the tripolar tautomer is somewhat arbitrary). Aqueous base rapidly hydrolyzed 8, giving 1,1-dimethylhydrazine in 80% yield. When 2 and sodium benzene-


4

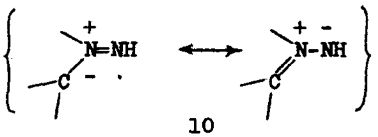
8

sulfinate are combined in strong aqueous base, exchange does *not* occur readily at room temperature. Hence dissociation of the *anion* of 2 into a diazene (9, diazenium ion conjugate base) and a sulfinate ion requires a substantially higher free energy of activation than ionization of 2. Solutions of


$\left\{ >\overset{+}{N}{=}\overset{-}{N} \longleftrightarrow >N\text{-}N \right\}$

9

2 in concentrated aqueous alkali are stable for many hours, as are solutions in water alone. *Nevertheless, when a moderate amount of sodium hydroxide (e.g. 0.5-1 equivalent) is present rapid decomposition ensues.*[4] The peculiar dependence of decomposition rate upon alkali concentration indicates that both the weakly acidic sulfonylhydrazine (not its salt) and base must be present for reaction to proceed fast in the cold. Clearly the initial intermediate is again the *diazenium ion*, which is subsequently attacked by base. Proton loss from a diazenium ion may occur either from nitrogen (probably reversibly) or from an α-carbon, giving the diazene[1] or a 1,3-dipolar species (10),[5] respectively.



10

Major pathways for the base-catalyzed decomposition of 1,1-disubstituted-2-sulfonylhydrazines include fragmentation with twofold carbon-nitrogen cleavage and tetrazene, cyclic dimer and hydrazone formation (depending upon the nature of the substituents and upon reaction conditions).[5-8] Fragmentation and tetrazene production are traceable to the diazene intermediate;[6] cyclic dimer and probably also hydrazone formation are attributable to its 1,3-dipolar tautomer.[5,9]

Acknowledgment.--The authors wish to thank the National Science Foundation, the National Institutes of Health and the donors of the Petroleum Research Fund of the American Chemical Society for generous financial support.

BIBLIOGRAPHY

1. W. R. McBride and H. W. Kruse, J. Am. Chem. Soc., **79**, 572 (1957); W. H. Urry, H. W. Kruse, and W. R. McBride, ibid., **79**, 6568 (1957); W. R. McBride and E. M. Bens, ibid., **81**, 5546 (1959).

2. S. Wawzonek and W. McKillip J. Org. Chem., **27**, 3946 (1962) studied the decomposition of sulfonylhydrazines in concentrated mineral acids at elevated temperatures and interpreted their results in terms of diazenium ion intermediates.

3. In all of our experiments concentrations of diazenium ions were too low to be detected directly by n.m.r.

4. Although other sulfonylhydrazines are less stable than **2** in strong alkali, the conclusion that decomposition of a given 1,1-dialkyl-2-sulfonylhydrazine is faster in dilute than in concentrated base appears to be general.

5. D. M. Lemal, F. Menger and E. Coats, J. Am. Chem. Soc., in press; D. M. Lemal and T. W. Rave, to be published.

6. L. A. Carpino, Chem. and Ind., 172 (1957); J. Am. Chem. Soc., **79**, 4427 (1957); ibid., **84**, 2196 (1962); ibid., **85**, 2144 (1963); R. L. Hinman and K. L. Hamm, ibid., **81**, 3294 (1959); W. Baker, J. F. W. Mc Omie and D. R. Preston, Chem. and Ind., 1305 (1960); J. Chem. Soc., 2971 (1961); D. M. Lemal, T. W. Rave and S. D. McGregor, J. Am. Chem. Soc., **85**, 1944 (1963).

7. P. Carter and T. S. Stevens, J. Chem. Soc., 1743 (1961).

8. W. H. Urry and C. Ikoku, Abstracts of the 146th National Meeting of the American Chemical Society, Denver, Colorado, Jan. 1964, p. 25c.

9. Urry has suggested, however, that the common conjugate base of the two intermediates is responsible for hydrazone formation (ref. 8).