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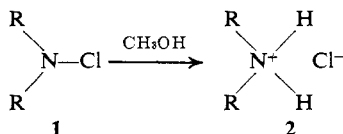
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The Discrete Existence of Singlet and Triplet Nitrenium Ions¹

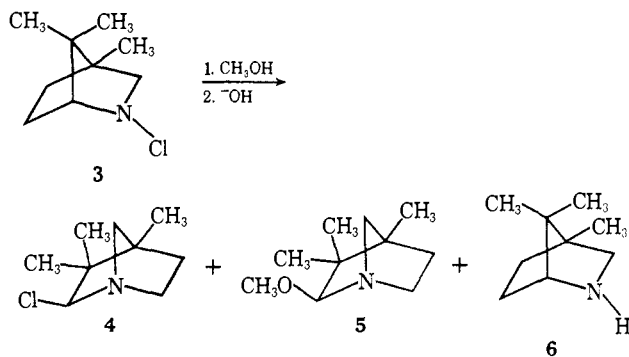
Sir:

Although the principles of nitrenium ion (divalent electron-deficient nitrogen) theory have proven invaluable in predicting the reaction products which result from the heterolytic cleavage of the N-X bond,² no evidence existed to indicate whether a nitrenium ion could have a discrete existence. We wish to present preliminary findings which not only show that divalent electron-deficient nitrogen species are true intermediates, but also indicate that *nitrenium ions exist in both singlet and triplet spin states*.

When N-chloramines (1) are solvolytically ionized, small amounts of secondary amine salts (2) are often observed among the reaction products.^{1b} For instance,



in the methanolysis of 4,7,7-trimethyl-2-chloro-2-azabicyclo[2.2.1]heptane (3) we found 59% 4, 20% 5, and 7% 6. Although the formation of 4 and 5 was to be expected on the basis of nitrenium ion theory, the presence of 6 appeared to be anomalous because 6 is not the type of product expected from a positively charged species.^{1b}

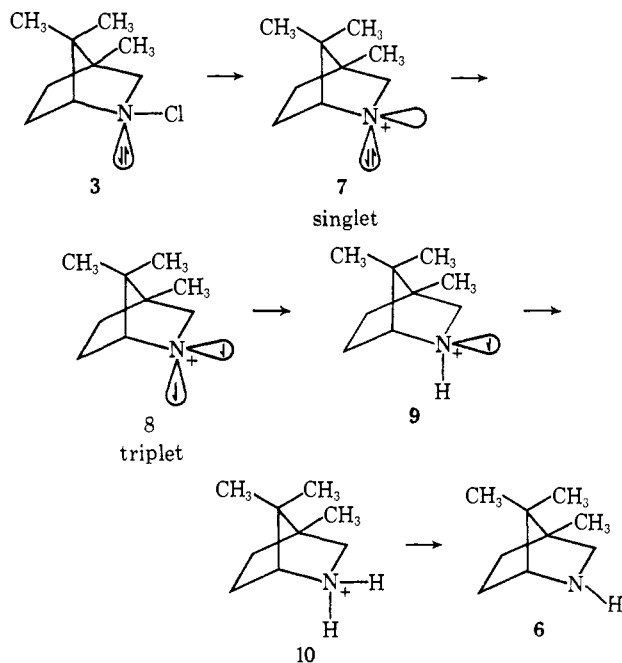


However, an important factor which requires consideration is that the nitrenium ion differs from most positive ions of interest to the organic chemist in that it possesses a nonbonding pair of electrons. Thus an attractive

(1) Paper IX in a series on the chemistry of nitrenium ions. For the preceding papers see (a) P. G. Gassman and A. Carrasquillo, *Chem. Commun.*, 495 (1969); (b) P. G. Gassman and R. L. Cryberg, *J. Am. Chem. Soc.*, **91**, 2047 (1969).

(2) P. G. Gassman and D. K. Dygos, *ibid.*, **91**, 1543 (1969); P. G. Gassman, G. Campbell, and R. Frederick, *ibid.*, **90**, 7377 (1968), and references contained therein.

rationale for the formation of 6 would involve initial ionization of 3 to give 7³ which by virtue of its mode of generation would be in the singlet state. Spin inversion could then occur, converting 7 into the triplet species 8. This triplet might be expected to behave more like a



nitrogen cation radical than like a carbonium ion or singlet nitrenium ion. Since nitrogen cation radicals are excellent hydrogen abstractors⁴ and methanol is a good source of hydrogen atoms, 8 would be expected to react with methanol to yield 9. A second hydrogen abstraction from methanol by 9 would yield 10 which on neutralization with base would give 6.

In order to test the validity of this hypothesis we investigated the effect of heavy atom solvents on the product composition observed in the methanolysis of 3. Since heavy atoms are known to enhance the probability of singlet to triplet inversion through coupling of spin and orbital angular momenta,^{5,6} the amount of 6 should increase in the presence of heavy atoms if our hypothesis is correct. Table I presents the results of our investigation. As shown in Table I the presence of heavy atoms has a very dramatic effect on the product ratios. A comparison of the products from methanol-bromoform and pure methanol showed that the presence of bromoform resulted in a 500-fold change in product ratio! Smaller effects were noted for chloroform (180-fold change) and carbon tetrachloride (50-fold change). *p*-Dibromobenzene also showed a very significant heavy atom effect when the relative percentage of heavy atoms present in the methanol-*p*-dibromobenzene solvent was taken into consideration.

The change in product ratios cannot be attributed to an effect of solvent polarity since methanol-hexane, the least polar solvent mixture, gave a product mixture very

(3) The filled and empty orbitals in structures 3, 7, 8, and 9 are not intended to imply any stereochemical relationships.

(4) Nitrogen cation radicals are considered to be the reactive hydrogen-abstracting intermediates in the Hofmann-Löffler-Freytag reaction: M. Wolff, *Chem. Rev.*, **63**, 55 (1963).

(5) C. D. Dijkgraaf and G. J. Hoijtink, *Tetrahedron Suppl.*, **2**, 179 (1963). See also J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," John Wiley & Sons, Inc., New York, N. Y., 1963, pp 294-300.

(6) A. G. Anastassiou, *J. Am. Chem. Soc.*, **88**, 2322 (1966).

similar to that observed in the most polar medium, pure methanol. The slight decrease in singlet to triplet product ratio in going from pure methanol to methanol-hexane may be indicative of a very small dilution effect.⁷

The results listed in Table I provide convincing evidence that the precursor of **2** in the solvolysis of **1** is a triplet nitrenium ion. In order to form a triplet nitre-

Table I. Product Yields^a in the Solvolysis of 4,7,7-Trimethyl-2-chloro-2-azabicyclo[2.2.1]heptane (**3**)

Solvent	% yield			Total % yield	% yield of singlet products	
	4	5	6		(4 + 5)	triplet products
CH ₃ OH-C ₆ H ₁₄ ^b	56	10	8	74	66	8.2
CH ₃ OH-CCl ₄ ^b	13	<1	59	73	13	0.22
CH ₃ OH- <i>p</i> -Br ₂ C ₆ H ₄ ^c	33	10	25	68	43	1.7
CH ₃ OH-CHCl ₃ ^b	4	<1	63	68	4	0.064
CH ₃ OH-CHBr ₃ ^b	1	<<1	45	46	1	0.022
CH ₃ OH-CH ₃ OH	59	20	7	86	79	11.3

^a Yields were determined by vpc using *N,N*-dimethylaniline as an internal standard. Yields were reproducible within the limits of analysis by vpc ($\pm 2\%$) with the exception of the CH₃OH-CHBr₃ runs in which the per cent of **6** varied by $\pm 3\%$. ^b Solvent mixtures were 1:1 by volume. ^c The solvent was prepared by mixing methanol and *p*-dibromobenzene on a 1 ml to 1 g basis.

nium ion from **1**, a heterolytic cleavage of the N-Cl bond of **1** must have occurred to produce a singlet nitrenium ion, which was then converted into the triplet nitrenium ion by spin inversion.⁸ Thus, the heavy atom effects discussed in this communication provide the first attestation of the discrete existence of two new ions, the singlet nitrenium ion and the triplet nitrenium ion.

We are currently investigating the spectroscopic and chemical properties of both singlet and triplet nitrenium ions.

Acknowledgment. We wish to thank the National Cancer Institute of the Public Health Service for Grant CA-07110 which supported this research.

(7) Upon dilution, collision with an inert solvent can result in collisional deactivation of the higher energy species to a less energetic state. For examples of such dilution effects see W. Lwowski and J. S. McConaghy, Jr., *J. Am. Chem. Soc.*, **87**, 5490 (1965); E. Ciganek, *ibid.*, **88**, 1979 (1966); M. Jones, Jr., and K. R. Rettig, *ibid.*, **87**, 4013 (1965).

(8) A casual evaluation of our data might tempt one to suggest that the results discussed in this communication could be explained by the homolytic cleavage of **3** to give a chlorine radical and a nitrogen radical. In the presence of chloroform and bromoform the nitrogen radical could be postulated to abstract a hydrogen atom to give **6**, and a radical chain reaction could then ensue. However, the fact that we observe the same qualitative results in carbon tetrachloride, which cannot serve as a hydrogen source, as we do in chloroform and bromoform rules out any explanation involving initial homolytic cleavage of the N-Cl bond of **3**. An alternate explanation would involve initial homolytic cleavage of the heavy atom solvent followed by abstraction of the chlorine from **3**. Since it is inconceivable that dibromobenzene could undergo such spontaneous homolytic cleavage under the reaction conditions, this possibility is also eliminated.

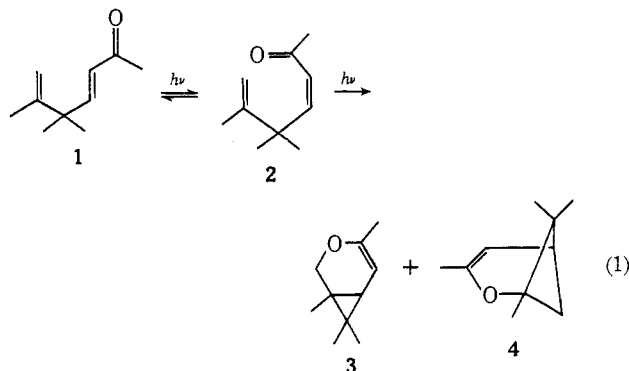
(9) Alfred P. Sloan Foundation Research Fellow, 1967-1969.

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Competing Pathways in the Photochemistry of a 2,5-Pentadienone¹

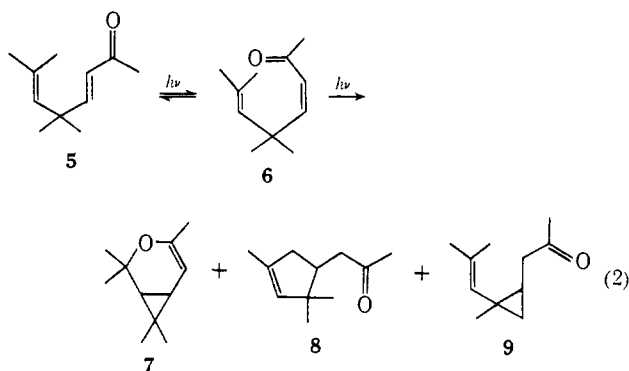
Sir:

We recently reported a novel photochemical 4 + 2 cycloaddition reaction in which the acyclic dienone **1** was transformed, *via* its *cis* isomer **2**, into the dihydropyrans **3** and **4** (eq 1).² We have now found that this



is a rather general reaction of 2,5-dienones, and the details of this work will be reported elsewhere.³ An especially interesting example, however, is provided by 5,5,7-trimethylocta-3,6-dien-2-one (**5**) which, after conversion to its *cis* isomer **6**, shows both the photochemical cycloaddition characteristic of **2** and a pair of hydrogen-abstraction reactions, one of which we have demonstrated to involve a nine-membered-ring transition state.

trans-Dienone **5**⁴ is readily prepared by condensation of 2,2,4-trimethylpent-3-enal⁵ with acetone in the presence of sodium methoxide. Its stereochemistry is clear from its nmr spectrum, which shows a 16.5-cps coupling constant between the α - and β -olefinic protons.⁶ Irradiation of a 1% solution of **5** in 30-50° petroleum ether using a 450-W Hanovia lamp through a Pyrex filter results in relatively rapid equilibration (0.5 hr) with the *cis* isomer **6**.⁴ Further irradiation (*ca.*



(1) The partial support of this research by National Institutes of Health Grants GM-00834 and GM-14662 is acknowledged with pleasure.

(2) R. A. Scheider and J. Meinwald, *J. Amer. Chem. Soc.*, **89**, 2023 (1967).

(3) See J. Meinwald, Abstracts, 21st National Symposium on Organic Chemistry, Salt Lake City, Utah, June 15-19, 1969, pp 61-70.

(4) Each new compound described gave satisfactory elemental analyses, as well as infrared and nmr spectra compatible with the assigned structures.

(5) R. H. Hasek, R. C. Clark, and J. H. Chaudet, *J. Org. Chem.*, **26**, 3130 (1961).

(6) I. Fleming and D. H. Williams, "Spectroscopic Methods in Organic Chemistry," McGraw-Hill Publishing Co. Ltd., London, 1966, p 106.