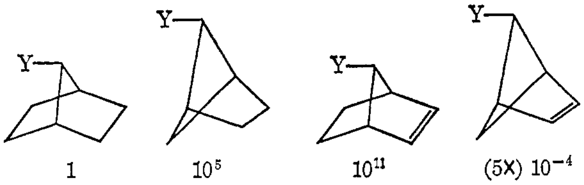
Formation of a cation of **1a** in fluorosulfuric acid has already been described.[2] Chart I shows approximate relative solvolysis rates of some representative esters at 25°.[6] Presumably the most meaningful comparison would be that of the bicyclo[2.1.1]hexene and norbornene systems because of the same solvolytic behavior of the two systems. We have observed a rate acceleration of 5×10^3 with the former system, despite the fact the angle (C_1–C_5–C_4) of **1c** is undoubtedly smaller than that (C_1–C_7–C_4) of norbornene.[7] Further comments will be offered in a future publication.

Chart I. Relative Rates of Solvolysis of Some Model Compounds.



Compound **1a** in *n*-dodecane readily and quantitatively isomerized to **3a**[1b] and during the entire course of reaction (10 half-lives) no other products, including the *endo* isomer of **3a**, were detected The isomerization was first order and provided the following kinetic parameters: $k = (3.39 \pm 0.10) \times 10^{-5}$ sec^{-1} at 85.1°, $(2.78 \pm 0.07) \times 10^{-4}$ sec^{-1} at 105.1°, $\Delta H^{\ddagger} = 27.5$ kcal/mol, $\Delta S^{\ddagger} = -2$ eu.[8] Therefore, **3a** formed in the acetolysis of **1c** or **2**[2] through a unimolecular thermal rearrangement of **1a**. An nmr spectrum (100 MHz, $CDCl_3$) of **3a** showed signals at τ 4.2 (m, 1 H), 4.5 (m, 1 H), 6.67 (broad s, $W_{1/2}$ = 3.5 Hz, 1 H), 7.5 (m, 2 H), 7.9 (m, 1 H), 8.00 (s, 3 H), and 8.25 (m, 1 H).[9] Catalytic hydrogenation of **3a** in methyl acetate with the Adams catalyst provided the corresponding acetate (**5a**) which was in turn converted into a hydroxy compound (**5b**)[9] (*p*-nitrobenzoate (**5c**), mp 86.5–87.5°). These three compounds (**5a**, **b**, **c**) were identical in every respect with the respective authentic samples prepared from *exo*-bicyclo[3.1.0]hex-2-ene-6-carboxylic acid.[10] Therefore, the acetoxy group of **3a** must be *exo* oriented. The structure of **3b** was determined in a similar manner.

The thermolysis of **1a** is interpreted to be a suprafacial [1,3] sigmatropic rearrangement which proceeds with inversion of configuration in the migrating group.[11] Although **3a** is thermodynamically more stable than its epimer, it is unlikely that the steric and electronic factor of the acetoxy group is decisive in controlling the stereochemistry of the product. Bicyclo[2.1.1]hexene contains a large strain energy and its thermal reaction is the reverse process of a well-known vinylcyclopropane–cyclopentene rearrangement. Willcott and Cargle in their investigation on the thermolysis of specifically deuterated vinylcyclopropane have demonstrated that the loss of stereospecificity at the deuterium labeled site in the cyclopropane ring is at least five times as fast as its conversion to cyclopentene.[12] They have interpreted these results on the basis of the trimethylene diradical model. The present stereospecific conversion of **1a** into **3a** indicates that a diradical does not intervene in this particular reaction coordinate, as this interpretation is obviously predicted from the conservation of orbital symmetry.[13]

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(6) K. B. Wiberg and R. Fenglio, *Tetrahedron Letters*, 1273 (1963); S. Winstein and C. Ordronneau, *J. Am. Chem. Soc.*, **82**, 2084 (1960); S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *ibid.*, **77**, 4183 (1955). The hydrolysis rate of *anti*-7-chloronorbornene in 80% aqueous acetone was compared with that of 7-chloronorbornadiene. The relative rate of a given pair of *p*-toluenesulfonates is assumed to be the same as that of the chlorides and methoxyacetates.

(7) P. D. Bartlett and W. P. Giddings, *ibid.*, **82**, 1240 (1960).

(8) The rate of this thermal isomerization of **1a** in acetic acid was $k = (4.25 \pm 0.11) \times 10^{-5}$ sec^{-1} at 90.4°, $(3.60 \pm 0.10) \times 10^{-4}$ sec^{-1} at 110.0°, $\Delta H^{\ddagger} = 29$ kcal/mol, $\Delta S^{\ddagger} = 2$ eu. The thermolysis proceeded approximately 1.5 times faster in dodecane than in acetic acid.

(9) U. Schöllkopf, J. Paust, A. Al-Azrak, and H. Schumacher, *Chem. Ber.*, **99**, 3391 (1966).

(10) J. Meinwald, S. S. Labana, and M. S. Chada, *J. Am. Chem. Soc.*, **85**, 582 (1963). This acid was converted into the corresponding methyl ketone which was treated with peroxytrifluoroacetic acid.

(11) J. A. Berson and G. L. Nelson, *ibid.*, **89**, 5503 (1967).

(12) M. R. Willcott and V. H. Cargle, *ibid.*, **89** 723 (1967), and references cited therein.

(13) NOTE ADDED IN PROOF. We have prepared the *endo* isomer of **3a** which was found to be stable under the present thermolys conditions. In contrast to the reported sigmatropic rearrangement[11] the thermolysis of **1a** is free from any observable side or consecutive reactions throughout the reaction, and for the first time kinetic parameters are measured for a rearrangement of this type. In reply to our letter attached to this manuscript, Professor Bond informed us (May 6, 1969) that he observed similar results in a different system.

A Novel Oxidative Fragmentation.
The Formation of Benzyl Azide from the Reaction of 1,1,4,4-Tetrabenzyltetrazene with Lead Tetraacetate

Sir:

During the course of our investigation of the chemistry of N-nitrenes (>NN)[1] we have discovered a novel reaction which we report briefly at this time.

Lead tetraacetate has been shown to be an effective oxidizing agent for various nitrogen-containing functional groups.[2] Very recently, Rees and his group[3] have oxidized 1,1-disubstituted hydrazines with $Pb(OAc)_4$ and obtained evidence of the intermediacy of N-nitrenes.

As a part of our general interest in the chemistry of N-nitrenes, the oxidation of N,N-dibenzylhydrazine (I) with lead tetraacetate was investigated. Although reaction occurred readily in benzene, very little nitrogen evolution was observed. The presence of benzaldehyde (bands at 2730 and 1705 cm^{-1}) and of benzyl azide (band at 2000 cm^{-1}) was confirmed by their isolation and unequivocal characterization. Traces of bibenzyl were also detected. No attempt was made to identify the minor components of the reaction mixture.

Evidently, since benzyl azide has *three* nitrogens, the third nitrogen had to be provided by a second molecule of the starting hydrazine. The most likely intermediate

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(1) This is the eighth in a series of papers related to the chemistry of diazene derivatives. For previous papers see N. Koga, G. Koga, and J.-P. Anselme, *Can. J. Chem.*, **47**, 1143 (1969).

(2) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," John Wiley & Sons, Inc., New York, N. Y., 1967, p 537; R. Criegee in "Oxidation in Organic Chemistry, Part A," K. B. Wiberg, Ed., Academic Press, New York, N. Y., 1965, p 353; R. N. Butler, *Chem. Ind.* (London), 437 (1968).

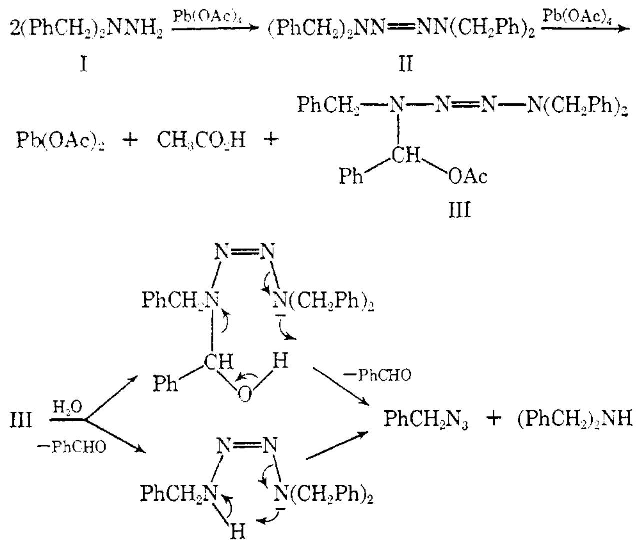
(3) R. S. Atkinson and C. W. Rees, *J. Chem. Soc.*, 772 (1969); C. W. Rees, *et al.*, *Chem. Commun.*, 146, 147 (1969).

capable of accounting for our reaction is the corresponding tetrazene (II). Indeed, the slow addition of a benzene solution of II to a suspension of 1 equiv of $Pb(OAc)_4$ in benzene at 5–10° resulted in a slightly exothermic reaction until about half-way through the addition of the tetrazene solution. After all the tetrazene solution had been added, a second equivalent of $Pb(OAc)_4$ was added in small portions. The yield of lead diacetate was quantitative. The solution was washed with an aqueous solution of sodium bicarbonate and chromatographed on alumina.[4] A 64% yield of benzyl azide and a 20–25% yield of benzaldehyde were obtained. Other products isolated were dibenzylamine (10%) and benzyl alcohol (13%); benzyl acetate was also identified as a very minor component.

When the ratio of $Pb(OAc)_4$ to tetrazene was decreased to 1:1 and the reaction mixture treated as previously, only traces of benzaldehyde (less than 5%) were obtained; instead benzyl alcohol was isolated in 34% yield.[5] Benzyl azide was obtained in 76% yield and dibenzylamine was formed in 63% yield. Infrared examination of the yellowish oil *before* chromatography indicated that only small amounts of the products isolated were present at that time; furthermore the component which appeared to be present in the largest quantity, benzaldehyde, was isolated in less than 5% yield *after* chromatography. The oil upon standing at room temperature for 2 days was slowly converted to the products as shown by the examination of the infrared spectrum. Evidently, the oil contained an intermediate which underwent decomposition to benzyl azide and dibenzylamine on standing. It was later discovered that, when pure benzaldehyde was passed through the column, only 16% of it was recovered and a 37% yield of benzyl alcohol was obtained.[6] Thus, benzaldehyde and *not* benzyl alcohol is the main product of the reaction and would amount to 75% yield.[6] On the basis of the information at hand, the mechanism given in Scheme I may be viewed for the reaction. The net stoichiometry of the reaction would then be

$$(PhCH_2)_2NN{=}NN(CH_2Ph)_2 + Pb(OAc)_4 + (H_2O) \longrightarrow PhCH_2N_3 + (PhCH_2)_2NH + PhCHO + Pb(OAc)_2 + 2CH_3CO_2H$$

Scheme I



We are deferring any detailed discussion of this reaction at this time. The scope and the extension of this novel oxidative fragmentation reaction are being currently investigated in our laboratories.

Acknowledgment. The generous support of this work by the National Institutes of Health under Grant GM-13689-03 is hereby acknowledged with deep appreciation.

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[4] Fisher Scientific Co., alumina A-540.

[5] The yields given for the reaction run with 1 equiv of lead tetraacetate are all corrected for recovered tetrazene (8%).

[6] Presumably the column promoted a Cannizzaro-type rearrangement. Benzoic acid probably remained in the column.

[7] To whom all inquiries should be addressed. Fellow of the Alfred P. Sloan Foundation.

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The Structure of α-Ferrocenylcarbonium Ions[1]

Sir:

The extraordinary stability of α-metallocenylcarbonium ions as well as the great stereoselectivity of their reactions[2] has given rise to considerable speculation regarding the structural and electronic factors responsible for these properties.[3] It has been suggested[3a] that the cation is stabilized in part by direct interaction of the metal atom with the carbonium ion center, and that as a consequence the metal atom is displaced in the cation toward the α-carbon atom, as depicted in structure **1**.[4] These suggestions have however been questioned.[3b]

The nmr spectra of a series of α-ferrocenylcarbonium ions have recently been interpreted as providing evidence for such a molecular distortion.[5] Thus, while

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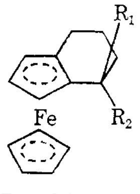
[1] Presented in part at the annual meeting of The Chemical Society, Dublin, Ireland, April 1968.

[2] These properties are well illustrated by the reactions of the epimeric acetates (i and ii) both of which undergo solvolysis by uncatalyzed ionization to give the *exo* alcohol (iii) exclusively. The *exo* acetate solvolyzes more rapidly than the *endo* isomer by a factor of 2500 and more rapidly than triphenylcarbinyl acetate by a factor of 28. (a) E. A. Hill and J. H. Richards, *J. Am. Chem. Soc.*, **83**, 4216 (1961); (b) D. S. Trifan and R. Bacskai, *Tetrahedron Letters*, 1 (1960).



i, $R_1 = OAc$; $R_2 = H$
ii, $R_1 = H$; $R_2 = OAc$
iii, $R_1 = OH$; $R_2 = H$

[3] (a) E. A. Hill and J. H. Richards, *J. Am. Chem. Soc.*, **83**, 3840 (1961), and ref 2a; (b) J. C. Ware and T. G. Traylor, *Tetrahedron Letters*, 1295 (1965); T. T. Tidwell and T. G. Traylor, *J. Am. Chem. Soc.*, **88**, 3442 (1966); **89**, 2304 (1967); J. D. Fitzpatrick, L. Watts, and R. Pettit, *Tetrahedron Letters*, 1299 (1966); M. Rosenblum and F. W. Abbate, Advances in Chemistry Series, No. 62, American Chemical Society, Washington, D. C., 1966, p 532.

[4] The magnitude of the shift required to account qualitatively for the nmr spectra of these carbonium ions has been estimated to be about 1 Å: M. I. Levenberg, Ph.D. thesis, California Institute of Technology, 1965.

[5] M. Cais, J. J. Dannenberg, A. Eisenstadt, M. I. Levenberg, and J. H. Richards, *Tetrahedron Letters*, 1965 (1966).