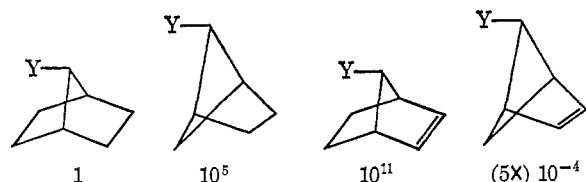


Formation of a cation of **1a** in fluorosulfuric acid has already been described.² Chart I shows approximate

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



relative solvolysis rates of some representative esters at 25°. 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 (C₁-C₅-C₄) of **1c** is undoubtedly smaller than that (C₁-C₇-C₄) of norbornene.⁷ Further comments will be offered in a future publication.

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: $k = (3.39 \pm 0.10) \times 10^{-5} \text{ sec}^{-1}$ at 85.1°, $(2.78 \pm 0.07) \times 10^{-4} \text{ sec}^{-1}$ at 105.1°, $\Delta H^\ddagger = 27.5 \text{ kcal/mol}$, $\Delta S^\ddagger = -2 \text{ eu}$.⁸ Therefore, **3a** formed in the acetolysis of **1c** or **2**² through a unimolecular thermal rearrangement of **1a**. An nmr spectrum (100 MHz, CDCl₃) of **3a** showed signals at τ 4.2 (m, 1 H), 4.5 (m, 1 H), 6.67 (broad s, $W_{1/2} = 3.5 \text{ Hz}$, 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

(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 $k = (4.25 \pm 0.11) \times 10^{-5} \text{ sec}^{-1}$ at 90.4°, $(3.60 \pm 0.10) \times 10^{-4} \text{ sec}^{-1}$ at 110.0°, $\Delta H^\ddagger = 29 \text{ kcal/mol}$, $\Delta S^\ddagger = 2 \text{ eu}$. 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).

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

Acknowledgment. The authors are grateful to the National Research Council of Canada and the donors of the Petroleum Research Fund for financial support.

(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 thermolysis conditions. In contrast to the reported sigmatropic rearrangement¹¹ 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.

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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 group³ 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

(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).

