work[6,7] and the data here. In particular, at low temperature the reaction proceeds with a high degree of stereospecificity indicating that the stereochemistry of the starting dibromide is being relatively faithfully translated into the stereochemistry of the product. Considering that bromide is a much better leaving group than dialkyl sulfide,[8] the yields of cyclopropane and the degree of stereospecificity should be higher (or at least comparable) in the bromide cases than in the case of the thietanonium salts.[9] The opposite is observed. Furthermore, the isomer ratio for the thietanonium reactions is practically independent of temperature in our operating range, whereas for the dibromide reaction there is such a dependence. This observation is the opposite of that anticipated for mechanism C. Finally, reaction of 1,2,2,4-tetramethyl-1-thiacyclobutonium fluoroborate with *n*-butyllithium under the same conditions as for III and IV produces 1,2,2-trimethylcyclopropane in yields of 20–30%. The undiminished yields compared to the dimethyl case also suggests the unlikelihood of a displacement mechanism (*i.e.*, C).

Although the above data strongly suggest that mechanism C can be eliminated, it does not allow a distinction to be made between mechanisms A and B. Geometrically, mechanism A seems less likely than B.

Acknowledgment. We wish to express our gratitude to the National Science Foundation for generous support of our program.

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(6) (a) R. L. Letsinger, *J. Am. Chem. Soc.*, **72**, 4842 (1950); (b) H. O. House and R. S. Ro, *ibid.*, **80**, 182 (1958), and references therein.

(7) B. M. Trost and S. Ziman, *Chem. Commun.*, 181 (1969).

(8) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 182–185.

(9) The stereochemistry of cyclopropane formation from the dibromide requires a double inversion process for this 1,3 elimination. Such has been found for a modification of the Ramberg–Bäcklund reaction. See F. G. Bordwell, B. B. Jarvis, and P. W. R. Corfield, *J. Am. Chem. Soc.*, **90**, 5298 (1968).

(10) Alfred P. Sloan Foundation Fellow.

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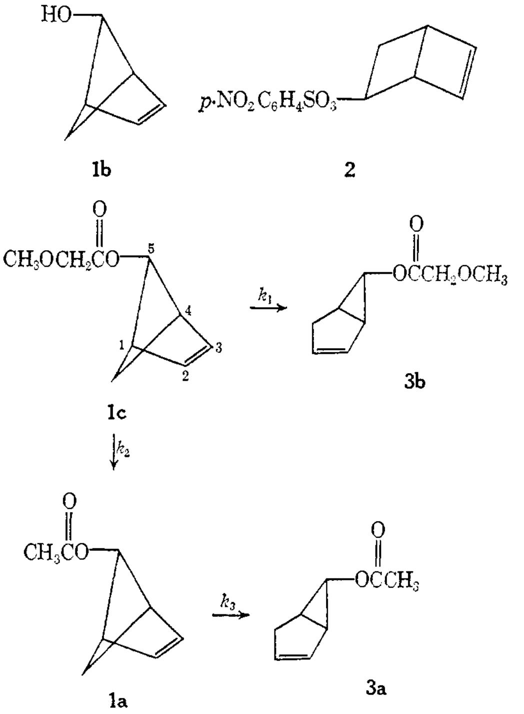
Solvolysis and Thermolysis of *exo*-Bicyclo[2.1.1]hex-2-en-5-ol Derivatives

Sir:

Current interest[1] in the bicyclo[2.1.1]hex-2-ene system has arisen largely from the obvious curiosity on the solvolytic behavior of C-5 derivatives of this system. Our synthesis recently reported[2] has been designed particularly to solve this problem and has provided *exo*-bicyclo[2.1.1]hex-2-en-5-yl acetate (**1a**). We wish to report herein the solvolysis of esters of the alcohol **1b** and, further, the stereochemistry of thermal rearrangement of this system.

Solvolysis of bicyclo[2.2.0]hexenyl *p*-nitrobenzenesulfonate (2) in methoxyacetic acid containing 2 equiv of sodium methoxyacetate proceeded in a manner similar to acetolysis of 2 and provided a methoxyacetate (**1c**) (half-life, *ca.* 2.5 hr at 80°).[3] An nmr spectrum ($CDCl_3$) of **1c** was very similar to that of **1a** except for the signals due to the methoxyacetoxy group.[4] The course of acetolysis of **1c** (0.3 *M* solution) was followed by glpc (F & M 5750) analysis (using *cis*-decalin as an internal standard) of no less than ten sealed ampoules immersed in a constant-temperature bath. Compound **1c** underwent two parallel first-order reactions to provide **1a** and **3b**, and a proof for the structure of **3b** is described later (Scheme I). The rate (k_2) of formation of **1a** was determined to be $(3.65 \pm 0.14) \times 10^{-5}$ sec^{-1} at 75.5°, $(2.66 \pm 0.10) \times 10^{-4}$ sec^{-1} at 96.0°, $\Delta H^{\ddagger} = 24$ kcal/mol, $\Delta S^{\ddagger} = -10$ eu, and $k = 9 \times 10^{-8}$ sec^{-1} at 25°.[5] The ratio of k_2/k_3 was 3 to 5 in this temperature range and during the acetolysis formation of **3a** was evident (*vide infra*). Norbornadien-7-yl methoxyacetate (**4**) was prepared for comparison, and the acetolysis of **4** provided the following kinetic parameters (quantitative conversion to the corresponding acetate): $k = (1.12 \pm 0.03) \times 10^{-5}$ sec^{-1} at 75.5°, $(8.70 \pm 0.22) \times 10^{-5}$ sec^{-1} at 96.0°, $\Delta H^{\ddagger} = 25$ kcal/mol, $\Delta S^{\ddagger} = -10$ eu, and $k = 2 \times 10^{-8}$ sec^{-1} at 25.0°.[5] Therefore the acetolysis rate of **1c** is estimated to be approximately five times as large as that of **4** at 25°.

Scheme I



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(1) (a) J. Meinwald and F. Uno, *J. Am. Chem. Soc.*, **90**, 800 (1968); (b) F. T. Bond and L. Scerbo, *Tetrahedron Letters*, 2789 (1968); (c) K. B. Wiberg and R. W. Ubersax, *ibid.*, 3063 (1968); (d) Y. Hata and H. Tanida, *J. Am. Chem. Soc.*, **91**, 1170 (1969).

(2) S. Masamune, E. N. Cain, R. Vukov, S. Takada, and N. Nakatsuka, *Chem. Commun.*, 243 (1969).

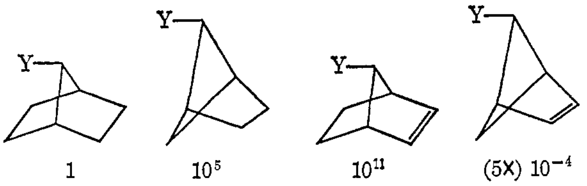
(3) Although we have not attempted exhaustively to prepare **1b** from **1a** a preliminary result indicated that **1b** was extremely unstable. Formation of Δ^3-cyclopentenecarboxaldehyde was evident in several such attempts. Solvolysis of acetate **1a** in acetic acid-d_1 was found to proceed slowly compared to thermolysis of **1a** to provide 3a (see text) and we were unable to obtain kinetic data for this acetate exchange reaction. Since methoxyacetic acid is a stronger acid ($pK_a = 3.52$), we expected that acetolysis of **1c** would proceed faster than that of **1a** while rates of thermolysis of the two compounds (**1a** and **1c**) would be in the same order of magnitude.

(4) τ 3.25 (t, 2 H), 5.10 (d, 1 H, $J = 6.8$ Hz), 5.91 (s, 2 H), 6.52 (s, 3 H), 6.73 (m, 1 H), 7.34 (q, 2 H), and 7.67 (dd, 1 H, $J = 6.8, 5.7$).

(5) The rate of decrease of **1c** ($k_1 + k_2$) was 4.03×10^{-5} at 75.5°, 3.17×10^{-4} at 96.0° and k_1 (rate of formation of **3b**) was 3.81×10^{-6} sec^{-1} at 75.5°, sec^{-1} 5.07×10^{-5} sec^{-1} at 96.0°. Direct determination of k_2 involved the measurement of two glpc peaks (the detector sensitivity to **1a** was different from that to 3a), thus increasing the magnitude of error. Therefore, the difference between the decrease of **1c** and k_1 was recorded for k_2.

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]

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

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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.

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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 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).