Whether one can detect an intermediate is then a matter of stability, geometry, rates of pseudorotation, and proton transfer, etc.[2] In the chloride and amide hydrolyses, any intermediate must have entering and leaving groups colinear with phosphorus; the labile P–Cl and P–N^+R_3 bonds which are broken appear to preclude an intermediate with a lifetime sufficient to allow any other geometry. This mechanism is therefore a type of direct displacement although the activated complex could have some stabilization through pentacoordinate character.

It therefore appears that comparison of rates of reaction of **1** with rates of reaction of **3** and/or **4** is *a criterion for mechanism of reaction at phosphorus.* Reaction through an intermediate of sufficient lifetime for pseudorotation can result in rate enhancement when the phosphorus atom is part of a strained ring. Direct displacement results in decreased rates with strained rings such as **1**.

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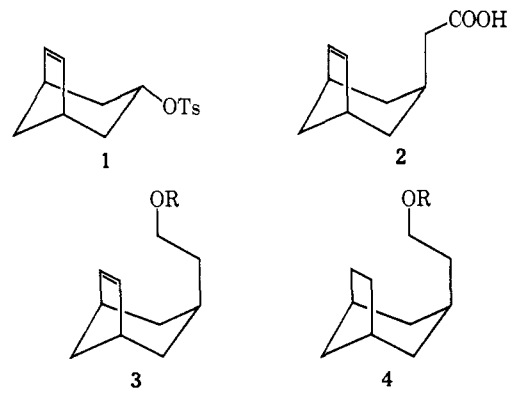
Nature of the Carbonium Ion. III. A π-Route Protoadamantyl Cation

Sir:

We have recently been investigating alternate routes to substituted adamantanes which utilize the favoring energetics of the carbonium ion rearrangements discovered by Schleyer and Donaldson.[1] In contrast to these Lewis acid catalyzed "adamantanizations," our methods involve the less stringent conditions of solvolytic reactions to generate the necessary ions. We now wish to report an example of a solvolytically initiated π-route ring closure[2] which leads preferentially to adamantyl derivatives substituted exclusively in the 2 position. Due to the simplicity of their rearrangements, the carbonium ions generated in this fashion also have the as yet unexploited capability of producing single isomers of polysubstituted adamantyl derivatives, depending only on the substitution pattern of the bicyclic starting material.

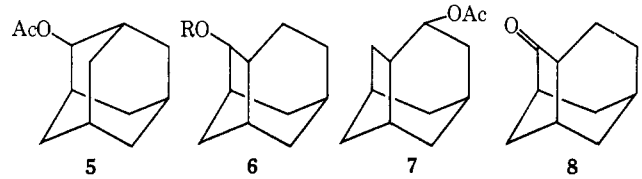
Synthesis of 2-*endo*-(bicyclo[3.2.1]oct-6-en-3-yl)-ethanol (**3a**) was accomplished from the known[3] *exo*-bicyclo[3.2.1]oct-6-en-3-yl *p*-toluenesulfonate (**1**). This was first subjected to malonic ester chain extension giving ultimately the *endo* acid **2**, mp 58.5–60.0°. Lithium aluminum hydride reduction afforded **3a**, bp 71° (0.08 mm), which was obtained in 55% overall yield from **1**. The saturated analog **4a** was synthesized in identical fashion from bicyclo[3.2.1]octan-3-ol.[4] Conversion of **3a** to its *p*-bromobenzenesulfonate



1 2 3 4

a, R = H
b, R = Bs
c, R = Ac

ester **3b** was difficult to accomplish except by cold treatment of the lithium alkoxide of **3a** with *p*-bromobenzenesulfonyl chloride. That this difficulty of synthesis was due to steric hindrance of the alcohol rather than the ease of dissociation of the ester was revealed by the solvolytic rate constants of **3b** in glacial acetic acid with sodium acetate buffer. These were 0.58×10^{-5} sec^{-1} at 60°, 3.8×10^{-5} sec^{-1} at 80°, and 27×10^{-5} sec^{-1} at 100°. From these values $\Delta H^{\ddagger} = 24$ kcal/mol and $\Delta S_{60}^{\ddagger} = -12$ eu. The rate constant for acetolysis of **4b**, mp 68–72° (which afforded only **4c** as a product), was 1.5×10^{-5} sec^{-1} at 100°. Three of the products from the acetolysis of **3b** could be identified as uncyclized acetate **3c**, 2-adamantyl acetate[5] (**5**), and *exo*-4-protoadamantyl acetate[6] (**7**) by comparison with authentic samples. A fourth product was assigned as *exo*-2-protoadamantyl[7] acetate (**6a**) on the basis of the following reaction sequence. The chloro ketone, obtained from **3a** by way of the unsaturated chloride and chloro alcohol,[8] gave 2-protoadamantanone[9] (**8**), mp 245.5–246.0°, upon sodium hydride catalyzed cyclization. Reduction of **8** with sodium in ethanol afforded a mixture of two alcohols, the minor component of which corresponded to **6b** from solvolysis. The major reduction product was identical with the sole product from lithium aluminum hydride re-



5 6 7 8

a, R = Ac
b, R = H

duction of **8**. This was assumed to be the epimeric

(1) For a review, see R. C. Fort, Jr., and P. v. R. Schleyer, *Chem. Rev.*, **64**, 277 (1964).

(2) For summaries of the literature, see (a) J. A. Berson in "Molecular Rearrangements," Part 1, P. de Mayo Ed., Interscience, New York, N. Y., 1963, Chapter 3; (b) P. D. Bartlett, W. S. Trahanovsky, D. A. Bolon, and G. H. Schmid, *J. Amer. Chem. Soc.*, **87**, 1314 (1965); (c) W. S. Johnson, *Accounts Chem. Res.*, **1**, 1 (1968).

(3) N. A. LeBel and R. J. Maxwell, *J. Amer. Chem. Soc.*, **91**, 2307 (1969).

(4) W. Kraus, *Chem. Ber.*, **97**, 2719 (1964).

(5) P. v. R. Schleyer and R. D. Nicholas, *J. Amer. Chem. Soc.*, **83**, 182 (1961).

(6) We are grateful to Professor Schleyer and Dr. D. Lenoir for supplying us with a sample of the corresponding alcohol from which the authentic acetate was prepared.

(7) The tricyclo[4.3.1.$0^{3,8}$]decane carbon skeleton has been given this trivial name by J. E. Baldwin and W. D. Foglesong, *ibid.*, **90**, 4303 (1968).

(8) Alcohol **3a** was treated with triphenylphosphine dichloride and the product subjected to mercuric acetate–tetrahydrofuran–sodium borohydride.

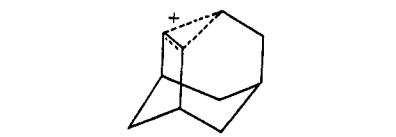
(9) This is the first unequivocal synthesis of 2-protoadamantanone. A comparison of our material with that given this assignment earlier by Whitlock and Siefken[10] was effected by these workers. We are indebted to Professor Whitlock for the report that the samples were identical.

(10) H. W. Whitlock and M. W. Siefken, *ibid.*, **90**, 4929 (1968).

endo alcohol due to the known[11] preference of the reagent for reduction at the least hindered face of most ketones and the identity of the nmr spectrum with that reported by Whitlock and Siefken[10] for this compound. The acetate of the *endo* alcohol was never detected among the products of solvolysis.

The product mixtures from acetolyses of **3b** to seven half-lives were largely (67–83%) composed of 2-adamantyl acetate (**5**). Runs were conducted at various temperatures (40–100°) with and without buffers (sodium acetate, urea), but little variation in product distribution was noted. The actual product composition under conditions identical with the 100° kinetic runs was as follows: **5**, 70%; **3c**, 6%; **6a**, 2%; **7**, 5%; and unidentified acetates,[12] 17%.

The heavy favoring of 2-adamantyl product reflects the ease of obtaining rearrangements to the 2-adamantyl cation **12**.[13] This is not surprising if one considers that the conversion of ions more obviously accessible from **3b** (**9** or **10**) to the adamantyl framework requires only two structural modifications of a fairly common variety for π-route carbonium ions.[14] In addition, the attainment of the extremely stable adamantane skeleton could constitute a prime driving force for these processes to occur. The main questions to be resolved are therefore the extent to which hydride shift and formal 1,2-carbon shift have taken place in the transition state and the nature of the double bond involvement in ionization.



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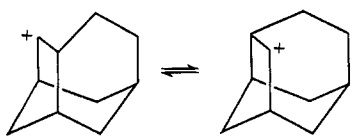

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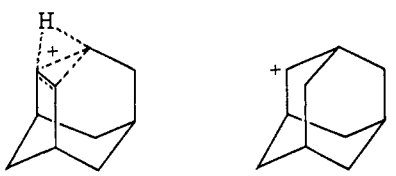

11 **12**

The striking difference in acetolysis rate between the unsaturated *p*-bromobenzenesulfonate **3b** and the saturated ester **4b** (k_{3b}/k_{4b} = 18) is explainable through the possibility of a very favorable pathway for nucleophilic assistance by the π orbital. Substantiating this is the excellent agreement between the rate and product data disclosed by comparing the actually obtained amount of uncyclized acetate **3c** with the prediction of its proportion based on the relative magnitudes of solvent-assisted[15] and π-assisted rates.[16] In fact, the acetolysis of **3b** demonstrates the largest degree of π-orbital influence on ionization and product formation observed for any arylsulfonate with a double bond separated by a *minimum* of four carbon atoms from the site of dissociation. Other reports[2b,17] of acetolyses conducted with this type of arylsulfonate have revealed the effects of direct double bond involvement in rate and products *only* in the case of 3-(3,4-dimethyl-Δ^3-cyclopentenyl)propyl *p*-nitrobenzenesulfonate,[2b] where 58% cyclized products occurred and k_u/k_s = 4.5. In light of the foregoing information, it would seem that the direct attainment of a particularly stable tricyclic carbonium ion from **3b**, as well as a favoring conformational arrangement, renders cyclization a highly favored process.

Differentiation should be made between the delocalized ion **9**, the equilibrating pair of localized ions **10**, and the protonated cyclopropane **11**, as the initially derived species. In the case of **11** the existence of appreciable hydride migration during ionization could be examined for by use of isotopic labeling. Accordingly, acid **2** was reduced with lithium aluminum deuteride and the resultant alcohol converted to **3b**-1,-1-d_2, mp 51.0–51.5°. Acetolysis of this material at 60° afforded the usual mixture of acetates with a rate constant of 0.45×10^{-5} sec^{-1}. The isotope effect was quite instructive since it was too small (k_H/k_D = 1.29 at 60°) for hydrogen bridging to be important in the transition state[14] despite the likelihood of additional stabilization to be gained through partial formation of an adamantyl ion. One may therefore rule out the contribution of the protonated cyclopropane **11** to ionization and conclude that the initially obtained ion from **3b** is *not* adamantyl in structure. For differentiation between **9** and **10** no experimental techniques are available. Recent analyses by Collins and Lietzke[14] of tracer experiments[18] have, however, inferred that the π-route cations derived from 2-(Δ^3-cyclopentenyl)-ethyl *p*-nitrobenzenesulfonate are most easily explained as classical. By analogy, this would indicate the equilibrating enantiomeric ions **10** to be preferred over the bridged species **9**. Regardless of this uncertainty, the products of the reaction must be governed by the competition between the rates of rearrangement by the protoadamantyl ion and the rate of solvent capture. Subsequent studies of solvent and substituent effects, as well as those of the σ-route 2-protoadamantyl ion, should add more information to this area.

Acknowledgment. We are grateful to the National Institutes of Health for generous support of this work (Grant No. AI 09670-01).

(11) See D. S. Noyce and D. B. Denney, *J. Amer. Chem. Soc.*, **72**, 5743 (1950), or C. H. DePuy and P. R. Story, *ibid.*, **82**, 627 (1960), for related examples.

(12) These are not 2- or 4-protoadamantyl or 1-adamantyl derivatives.

(13) The confirmed stabilities of the product acetates to reaction conditions rule out equilibration after solvent capture as a contributing process.

(14) For example, see C. J. Collins and M. H. Lietzke, *J. Amer. Chem. Soc.*, **89**, 6565 (1967).

(15) The observed acetolysis rate of **4b** is assumed to provide an accurate estimate of the solvent assisted rate of **3b**. See ref 16.

(16) For a discussion of this technique, see J. M. Harris, F. L. Schadt, P. v. R. Schleyer, and C. J. Lancelot, *J. Amer. Chem. Soc.*, **91**, 7508 (1969). We are grateful to Professor Schleyer for his suggestions concerning this treatment of our data.

(17) For discussions of the results from solvolyses of 6-heptenyl *p*-nitrobenzenesulfonate, see W. S. Trahanovsky and M. P. Doyle, *Tetrahedron Lett.*, 2155 (1968); W. S. Johnson, *et al.*, *J. Amer. Chem. Soc.*, **86**, 1959 (1964).

(18) C. C. Lee and L. K. M. Lam, *ibid.*, **88**, 2834 (1966).

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