Organic and Biological Chemistry

Stability and Symmetry of the 8,9-Dehydro-2-adamantyl Cation

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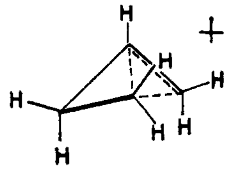
Abstract: 8,9-Dehydro-2-adamantyl 3,5-dinitrobenzoate has been synthesized and solvolyzed in 60% aqueous acetone. The activation parameters obtained were $\Delta H^{\ddagger} = 25.6$ kcal/mol and $\Delta S^{\ddagger}(25°) = -1.6$ eu; the solvolysis product was 8,9-dehydro-2-adamantanol. The 2-deuterio- and 2-tritio-labeled 8,9-dehydro-2-adamantyl 3,5-dinitrobenzoates were solvolyzed to give isotopically scrambled products bearing labels nearly equally at carbons 2, 8, and 9. The structure of the 8,9-dehydro-2-adamantyl cation is discussed in light of these data.

Both the intriguing chemistry characterizing the reactions of cyclopropylcarbinyl, cyclobutyl, and allylcarbinyl systems thought to generate cationic species and the pertinence of these reactions to the continuing debate centered on the definition and detection of nonclassical cationic intermediates have stimulated extensive investigation.[3–12]

Solvolysis of a cyclopropylcarbinyl, cyclobutyl, or allylcarbinyl system is typically unusually fast[13–19] and gives a mixture of cyclopropylcarbinyl, cyclobutyl, and allylcarbinyl products.[13,15,20–22]

Treatment of cyclopropylcarbinyl-α-^{14}C-amine with nitrous acid produced cyclobutanol and cyclopropylcarbinol with an extensive, but not completely equal, distribution of the label among the three methylene groups.[13,21,23,24] The deamination of allylcarbinylamine similarly gives a high but not statistical degree of isotope-position rearrangement.[25]

Possible structures for the ionic intermediates involved in these reactions were considered;[24,26,27] rapidly equilibrating unsymmetrical bicyclobutonium ions (**1**)—12 distinguishable intermediates in all[5]—were held to account for the available experimental data most satisfactorily.[24,26]



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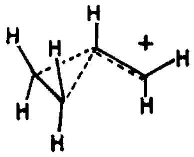

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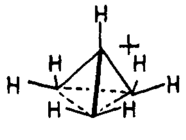

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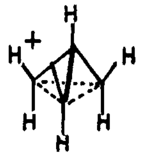

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On the basis of Roberts' experimental work and suggested rationalizations, equilibrating bicyclobutonium ions became widely accepted as the best proposed explanation for the behavior of unsubstituted cyclopropylcarbinyl and cyclobutyl derivatives. Such ions were also proposed in a number of other systems containing the cyclopropylcarbinyl moiety and could be conveniently utilized to explain the rate enhancements observed and the products formed.

More recently, the bisected cyclopropylcarbinyl cation (**2**) has been supported as a preferable representation for substituted cyclopropylcarbinyl cations.[28,29]

The still more symmetrical tricyclobutonium ions **3** and **4** have not attracted sustained backing. The one model, **3**, having six equivalent hydrogens, does have an enticingly plausible molecular orbital scheme;[23,30] but the geometrically more likely form, **4**, is predicted by a variety of approximate theoretical approaches to

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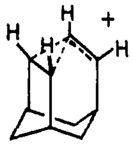
be quite unstable relative to other reasonable alternatives.[31–33]

There is no *a priori* reason to expect a single description to fit all cyclopropylcarbinyl cations, and the recent spate of experimental results obtained with substituted systems may not be directly pertinent to the cyclopropylcarbinyl cation itself—the only system for which positional scrambling of three potentially equivalent carbons has been observed. Yet, unsubstituted cyclopropylcarbinyl is so geometrically ill defined and unconstrained that some unresolved points, such as the possible intervention of the theoretically pleasing tricyclobutonium ion **3** as the transition-state species separating isomeric bicyclobutonium (**1**) or bisected cyclopropylcarbinyl (**2**) cations, may not be unambiguously inferred, hence the interest in generating a cyclopropylcarbinyl cation that would be geometrically defined and of potential C_{3v} symmetry. These design characteristics are nicely fulfilled by the 8,9-dehydro-2-adamantyl cation (**5**).



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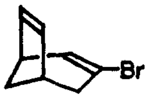
Results

Synthesis of 8,9-Dehydro-2-adamantanone.[34] The readily accessible 3-bromobicyclo[3.2.1]octa-2,6-diene (**6**), obtained through reaction of norbornadiene with dibromocarbene followed by lithium aluminum hydride reduction of the allylic bromine from the initially isolated 3,4-dibromobicyclo[3.2.1]octa-2,6-diene,[35] proved to be a most serviceable entryway into a facile synthetic route to 8,9-dehydro-2-adamantanone. The vinyl bromide **6** gave the corresponding Grignard reagent in tetrahydrofuran[36] which, upon carbonation, afforded 3-carboxybicyclo[3.2.1]octa-2,6-diene (**7**) in 50–60% yield. Selective reduction of the conjugated double bond in the acid **7** with potassium in liquid ammonia and protonation with isopropyl alcohol[37] gave a mixture of the *exo*- and *endo*-3-carboxybicyclo[3.2.1]oct-6-enes (**8** and **9**).



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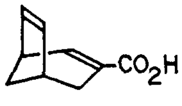

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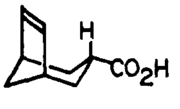

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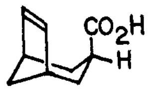

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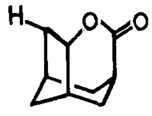

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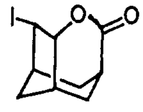

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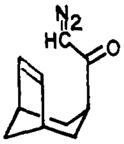
Attempts to separate the isomeric acids and the corresponding esters by tlc and glpc were not successful. Chemical verification of the occurrence of the desired *endo* isomer in the mixture was secured by converting it into the corresponding hydrolactone **10**.[38] The standard iodolactone route[39–41] provided a means of separating the two isomers and estimating the relative amounts of each in the mixture obtained from the reduction; the yield of iodolactone **11** was 60%, while some 35% of *exo* acid was isolated from the reaction mixture.

The sodium salt of the isomerically pure *endo* acid **9** or the mixture of both isomers gave, on treatment with oxalyl chloride followed by diazomethane, the diazomethyl ketone **12**, which decomposed thermally in the presence of cupric sulfate in refluxing tetrahydrofuran[42–48] to give 8,9-dehydro-2-adamantanone (**13**), mp 206.5–207.5°.



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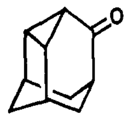

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The yield of purified dehydroadamantanone obtained from the mixture of isomeric acids was 21%. The *endo* acid was converted to the ketone in 27% yield.

As this synthetic sequence was developed, only one serious delay was sustained: initially, conversion of the presumed mixture of acids **8** and **9** to the corresponding acid chlorides was sought through the use of thionyl chloride. The reaction mixture produced had an infrared spectrum containing strong absorptions at 1770 and 1800 cm^{-1}, indicative of acid chloride, and at 1750 cm^{-1}. Subsequent steps gave diazomethyl ketone (2100 and 1645 cm^{-1}) but no dehydroadamantanone. The substance(s) having infrared absorption at 1750 cm^{-1} remained unmodified by the further steps.

Attempted preparation of the acid chlorides of the pure *exo* acid **8** and the pure *endo* acid **9** showed that the material absorbing at 1750 cm^{-1} was formed only from the *endo* isomer. Thus, the acid chloride having the stereochemistry requisite for utilization in the dehydroadamantanone preparation was being diverted by a side reaction—a difficulty overcome by substituting oxalyl chloride for thionyl chloride.

The side products proved to be two ketones of formula $C_9H_{11}OCl$. They were considered to arise from the acid-catalyzed addition of the acyl chloride unit intramolecularly across the double bond,[49] forming the cyclopentanones **14** and **15**.

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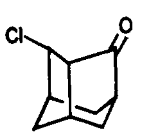

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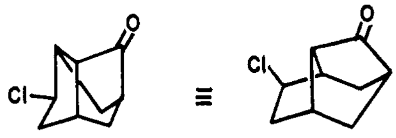

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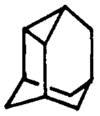
Structural Verification. The material thought to be 8,9-dehydro-2-adamantanone, on the basis of the rational synthetic sequence, analyzed correctly for $C_{10}H_{12}O$; the molecular weight, 148, was confirmed by mass spectrometry. In the nmr spectrum, there were absorptions only in the τ 7.4–8.6 region; the absorption maximum at 1705 cm^{-1} in carbon tetrachloride was appropriate for a conjugated carbonyl function, as was the ultraviolet maximum in chloroform at 376 mμ for the 2,4-dinitrophenylhydrazone derivative.[50]

Attempts to convert dehydroadamantanone by Wolff–Kishner reduction,[51,52] to dehydroadamantane[53] (**16**), or to reach this hydrocarbon by solvolyzing dehydroadamantyl 3,5-dinitrobenzoate in aqueous methanol–sodium borohydride,[54,55] were unsuccessful. Whitlock and Siefken, however, have secured a most helpful structural correlation. "Protoadamantane" (**17**), prepared from 8,9-dehydro-2-adamantanone proved identical with a sample obtained in the course of research further exploring the chemistry of the twistane.[56]



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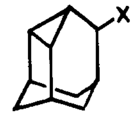
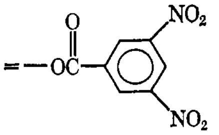
Kinetic Results and Related Synthetic Work.[57] An initial attempt to prepare dehydroadamantanol from the ketone and excess sodium borohydride gave, instead of the alcohol, two products shown by elemental analysis and mass spectrometry to be of formula $C_{11}H_{16}O$ and $C_{10}H_{13}Cl$. Apparently the work-up procedure, in which excess borohydride had been destroyed with hydrochloric acid,[58] was sufficient to convert the highly reactive alcohol **18a** to the corresponding chloride **18b** and methyl ether **18c**. Whether the products were, in fact, the unrearranged dehydroadamantyl derivatives **18b** and **18c** was not demonstrated; the presumption was made on the basis of the solvolytic studies described below and the great similarity in the mass spectral fragmentation patterns of the two products and dehydroadamantanol (**18a**).



18a, X = OH
b, X = Cl
c, X = OCH_3
d, X =



$-OC(=O)C_6H_3(NO_2)_2$

When the reduction was conducted without the hydrochloric acid work-up, the desired alcohol **18a** was obtained without difficulty in 93–95% yield. The molecular weight for $C_{10}H_{14}O$, 150, was confirmed by mass spectrometry. The nmr spectrum showed an unresolved triplet at τ 5.85 ascribed to a $R_2C\mathit{H}OH$ proton. No other absorptions were observed below τ 7.5.

The entire synthetic scheme gave 8,9-dehydro-2-adamantanol in an over-all yield of 1.9%; only 1.5 g of this alcohol was prepared, and small amounts of material were utilized in all the kinetic and isotopic labeling experiments.

Attempts to prepare the tosylate[19,59] of dehydroadamantanol were unsuccessful; in retrospect, it appears likely that even if the tosylate had been prepared, the rate of solvolysis would have been too fast to be measured conveniently. However, 8,9-dehydro-2-adamantyl 3,5-dinitrobenzoate (**18d**) was easily prepared in good yield.[60]

Rate constants for the solvolysis of the dinitrobenzoate **18d** were determined in 60% aqueous acetone at three temperatures. The results are summarized in Table I. From these rate constants, the activation parameters $\Delta H^{\ddagger} = 25.6$ kcal/mol and $\Delta S^{\ddagger} = -1.6$ eu were calculated. The reactions were followed to 80–90% completion by titrating the 3,5-dinitrobenzoic acid formed. Good first-order behavior was observed throughout and infinity titers were always within 8% of the calculated values.

Table I. Rates of Solvolysis of 8,9-Dehydro-2-adamantyl 3,5-Dinitrobenzoate in 60% Aqueous Acetone

Temp, °C	$k \times 10^3$, sec^{-1}
25.00	5.15×10^{-4} [a]
45.02 ± 0.02	$7.73 \pm 0.06 \times 10^{-3}$
	$7.83 \pm 0.10 \times 10^{-3}$
59.97 ± 0.05	$4.54 \pm 0.05 \times 10^{-2}$
	$4.82 \pm 0.12 \times 10^{-2}$
	$4.84 \pm 0.05 \times 10^{-2}$
74.30 ± 0.05	$2.33 \pm 0.04 \times 10^{-1}$
	$2.41 \pm 0.03 \times 10^{-1}$
100.00	3.03[a]

[a] Calculated.

The only solvolysis product detected after a careful investigation of the reaction mixture was the unrearranged alcohol **18a**. It was isolated after glpc collection in yields up to 65%. An isotope dilution experiment in which 2-tritio-8,9-dehydro-2-adamantyl 3,5-dinitrobenzoate was used showed the actual yield of dehydroadamantanol to be approximately 95%.

Labeling Results and Related Synthetic Work. Reduction of dehydroadamantanone with sodium borodeuteride in methanol gave the labeled alcohol, 2-deu-

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(50) Compare ν_{max} 1727 cm^{-1} for 2-adamantanone, the weighted mean of absorptions at 1732.3 and 1722.9 cm^{-1} (P. von R. Schleyer and R. D. Nicholas, *J. Am. Chem. Soc.*, **83**, 182 (1961)), and $\lambda_{max}^{CHCl_3}$ 368 mμ for the 2,4-dinitrophenylhydrazone (W. D. Foglesong, unpublished).

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Table II. Deuterium- and Tritium-Labeling Results for Solvolyses of 2-Deuterio- and 2-Tritio-8,9-dehydro-2-adamantyl 3,5-Dinitrobenzoates in 60% Aqueous Acetone

	Alcohol **18a**			Ketone act., %			Equilibration, %	
Run	Starting act., %[a]	Product act., %	Added 2,4,6-collidine, equiv	From starting alcohol	From equilibrated starting alcohol[b]	From product alcohol	Of alcohol under reacn conditions[c]	Of solvolysis product[d]
1,2-*d*	101	100	0	1	23.5	65	34	97.5
2,2-*t*	107	100	1.4	3	17	60	21	90
1,2-*d*	101		1.8	1	9		12	
3,2-*d*	104	100	4	6	7.5	59	2	88.5

[a] The absolute activities of the starting alcohols were 90% d_1, 10% d_0; 11.9 μCi/mmol; 94% d_1, 6% d_0. [b] From equilibration of the starting alcohol under the solvolysis conditions with 1 equiv of added 3,5-dinitrobenzoic acid and oxidation to the ketone with chromium trioxide. [c] The difference between the activities of the ketones derived from nonequilibrated and equilibrated alcohols divided by 0.667. [d] Activity of ketone derived from solvolysis product divided by 0.667.

terio-8,9-dehydro-2-adamantanol, 90% d_1. Oxidation of this alcohol with chromium trioxide in pyridine produced the ketone, 1% d_1. The corresponding dinitrobenzoate, which showed no $R_2CHOCOR$ absorption in the nmr, was prepared and solvolyzed. The recovered alcohol, 89% d_1, was oxidized to afford dehydroadamantanone, which was 58% d_1. When the starting alcohol, 90% d_1, was placed under the solvolysis conditions in the presence of 1 equiv of 3,5-dinitrobenzoic acid and then oxidized, the resulting ketone was 21% d_1. Thus the alcohol was partially unstable to the reaction conditions, and a part (but only a part) of the scrambling of label observed during the solvolysis could be ascribed to further reaction of the product.

When the labeled dehydroadamantanol, 90% d_1, was placed under the reaction conditions with 1 equiv of 3,5-dinitrobenzoic acid and 1.8 equiv of 2,4,6-collidine,[61] the ketone resulting from oxidation of the recovered alcohol was only 8% d_1.

A different batch of sodium borohydride was used to prepare labeled alcohol, 94% d_1. Oxidation gave ketone, 5.6% d_1. The dinitrobenzoate was solvolyzed in 60% aqueous acetone in the presence of a 4 molar excess of 2,4,6-collidine and the product alcohol, 90% d_1, was oxidized to yield ketone, 53% d_1. Placing the starting alcohol (94% d_1) under the solvolysis conditions in the presence of 4 equiv of 2,4,6-collidine and 1 equiv of 3,5-dinitrobenzoic acid led to recovered alcohol which was 93% d_1. Oxidation of this alcohol led to dehydroadamantanone which was 7% d_1.

The ratios of deuterated to nondeuterated alcohol and ketone in the various samples were determined with an Atlas CH-4 mass spectrometer with a variable-temperature vacuum lock inlet system according to the general procedure described by Biemann.[62] Although the results obtained from the scans at a single electron voltage were almost always in good agreement, peak height ratios measured at a different energy of the bombarding electrons or on a different day were sometimes at variance with the previously secured data. Thus, the peak height ratios appeared to be sensitive to instrumental conditions in some nonreproducible manner. The per cent d_1 values used above and in the construction of Table II below are an average of all the scans of the molecular ion region made for a given sample. The values are probably accurate to within ±3%.

Because of the inaccuracy and uncertainty connected with the mass spectral method used to analyze the deuterium samples, the scrambling experiments were repeated with tritiated samples. The tritium contents could be determined accurately by liquid scintillation counting. Tritium-labeled dehydroadamantanol was prepared with sodium borotritide and, after dilution, had an activity of 11.9 μCi/mmol. Oxidation of this alcohol gave dehydroadamantanone with an activity of 0.39 μCi/mmol. Solvolysis of the corresponding 3,5-dinitrobenzoate in 60% aqueous acetone in the presence of 1.4 equiv of 2,4,6-collidine gave an alcohol with an activity of 11.1 μCi/mmol. Oxidation of this alcohol led to the corresponding ketone, 6.7 μCi/mmol. The starting alcohol (11.9 μCi/mmol) was placed under the solvolysis conditions in the presence of 1 equiv of 3,5-dinitrobenzoic acid and 1.4 equiv of 2,4,6-collidine; the recovered alcohol was oxidized to yield dehydroadamantanone having an activity of 1.90 μCi/mmol. These and the deuterium labeling results are summarized on a per cent basis in Table II.

The 6% of label scrambled in the starting alcohol of run 3 is presumably a consequence of adventitious contact with acidic glassware or other matter.

Discussion and Conclusions

Rates of solvolyses are ordinarily and most easily compared in terms of acetolysis of tosylates at 25°, a consequence, probably, of the pioneering efforts with this choice of substrates and solvent by Winstein and coworkers.[63,64]

The estimation of the acetolysis rate of 8,9-dehydro-2-adamantyl tosylate at 25° was made from the solvolysis rate for the 3,5-dinitrobenzoate in 60% aqueous acetone at 100° and the observed regularity exhibited in the ratios of rate constants for the two sets of solvolytic conditions by systems for which both have been measured (Table III); tosylate acetolyses at 25° are approximately 490 times faster than dinitrobenzoate solvolyses in 60% aqueous acetone at 100°. Thus, the rate of acetolysis of dehydroadamantyl tosylate at 25° was calculated to be 14.7×10^{-1} sec^{-1}.

The most primitive method for estimating the unassisted rate for the solvolysis of dehydroadamantyl tosylate would be to extrapolate from a rate observed for a model compound incapable of comparable charge delocalization. 2-Adamantyl tosylate is the most ob-

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(61) W. D. Closson and G. T. Kwiatkowski, *Tetrahedron*, **21**, 2779 (1965).

(62) K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(63) S. Winstein, C. Hanson, and E. Grunwald, *J. Am. Chem. Soc.*, **70**, 812 (1948).

(64) S. Winstein, E. Grunwald, and L. Ingraham, *ibid.*, **70**, 821 (1948).

Table III. Comparison of the Rates of Solvolysis of Tosylates in Acetic Acid at 25° and 3,5-Dinitrobenzoates in 60% Aqueous Acetone at 100°

Compound	Rate of 3,5-DNB,[a] sec^{-1}	Ref	Rate of tosylate,[b] sec^{-1}	Ref	Rate of tosylate/rate of 3,5-DNB
Cyclopropylcarbinyl	4.3×10^{-7}	28	2.2×10^{-4}	*e*	510
1-Methylcyclopropylcarbinyl	2.1×10^{-6}	28	1.0×10^{-3}	*e*	490
exo-6-Bicyclo[3.1.0]hexylcarbinyl	1.7×10^{-5}	28	8.0×10^{-3}	*f*	470
8,9-Dehydro-2-adamantyl	3.0×10^{-3}[c]		14.7×10^{-1}[d]		490[c]
2-Adamantyl			3.3×10^{-9}[c]	50	. . .

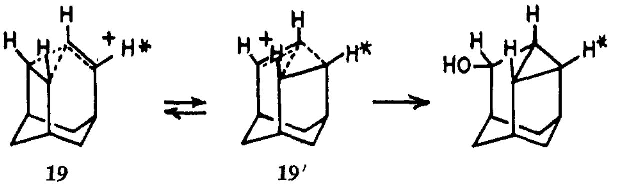
[a] In 60% aqueous acetone at 100°. [b] In acetic acid at 25°. [c] Extrapolated to this temperature. [d] Calculated. [e] D. D. Roberts, *J. Org. Chem.*, **29,** 294 (1964). [f] K. B. Wiberg and A. J. Ashe, III, *Tetrahedron Letters*, 1553 (1965); *J. Am. Chem. Soc.*, **90,** 63 (1968). Table VI of the full paper contains misprints in relative rate citations for *exo*-6-bicyclo[3.1.0]hexylcarbinyl tosylate and 3,5-dinitrobenzoate.

vious choice; its rate of acetolysis at 25° is 3.3×10^{-9}.[50]

More sophisticated estimates of the unassisted rate may be obtained by applying the Schleyer–Foote correlation[65,66] relating the solvolysis rate and the carbonyl stretching frequency of the corresponding ketone. According to the simple relationship,[65] the infrared carbonyl stretching frequency for dehydroadamantanone, 1705 cm^{-1}, may be used to calculate an unassisted rate of acetolysis of 4.7×10^{-6} sec^{-1} for dehydroadamantyl tosylate. With a modified version of this relationship,[66] which attempts to take into account torsional strain, nonbonded interaction strain, and inductive effects, the calculated acetolysis rate is 4.1×10^{-6} sec^{-1}.

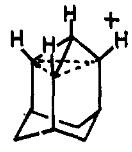
If 2-adamantyl tosylate is used as a model for the localized 8,9-dehydro-2-adamantanyl cation, the rate enhancement associated with the assisted formation of a cation from 8,9-dehydro-2-adamantyl tosylate is 4×10^8. If the values obtained from the Schleyer–Foote correlation are used, one estimates that the rate is about 3 or 4×10^5 times as fast as it would have been if the transition state had resembled a simple localized cation. Although there is some question as to magnitude, there undoubtedly is a large rate enhancement in solvolyses giving the dehydroadamantyl cation.

The current status of cyclopropylcarbinyl cation chemistry urges adoption of the bridged representation **19** for the delocalized dehydroadamantyl cation.[28,29,67,68] We attribute the scrambling to a migration of the C(8)–C(9) bond in the dehydroadamantyl cation produced through solvolysis, a rearrangement enabling the system to achieve nearly complete, but not complete, equivalence of the three positions 2, 8, and 9.



19 **19′**

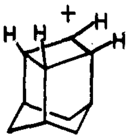
The constraints on the dehydroadamantyl system guarantee that the rearrangement **19** → **19′** does not occur by way of an ion geometrically akin to the theoretically more plausible of the two tricyclobutonium ions, **3**. Indeed, these constraints are compatible with the possible intervention of the theoretically less attractive ion analogous to **4**, **20**.



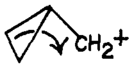
20

It will be noted that neither the rate data nor the absence of complete equivalence of positions 2, 8, and 9 in the product alcohol may be utilized in argument against the intervention of cation **20** as the activated complex separating the delocalized cyclopropylcarbinyl cations **19** and **19′**. However, cation **20** does not seem an adequate formulation; its theoretical liabilities appear insuperable.

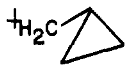
Another possibility, indirect rearrangement by way of cyclobutyl cations (**21**), seems less attractive than a direct route. Wiberg and coworkers[67,69] have argued that an experimental decision might be made between these two modes of rearrangement; under conditions where no cyclobutyl products are obtained, and yet scrambling of label occurs, the direct rearrangement **22** → **22′** would be indicated. These are precisely the observations made in the present study: scrambling without rearrangement.



21

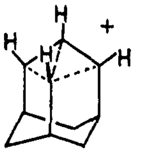


22

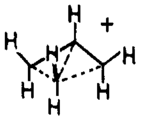


22′

We propose that the ion linking degenerate cyclopropylcarbinyl cations (**19** and **19′**, or **22** and **22′**) is of C_s symmetry and may be usefully represented by formulations such as **23** and **24**.



23



24

This formulation may be attained by considering either how a C_{3v} tricyclobutonium ion like **4** might distort to break the symmetry-imposed degeneracy of the two highest energy bonding molecular orbitals which, in the cation, are to accommodate but two electrons; or how a C_4H_7 cation would appear if a methylene group were to adopt a position halfway between its locations in two cyclopropylcarbinyl cations, given a geometry

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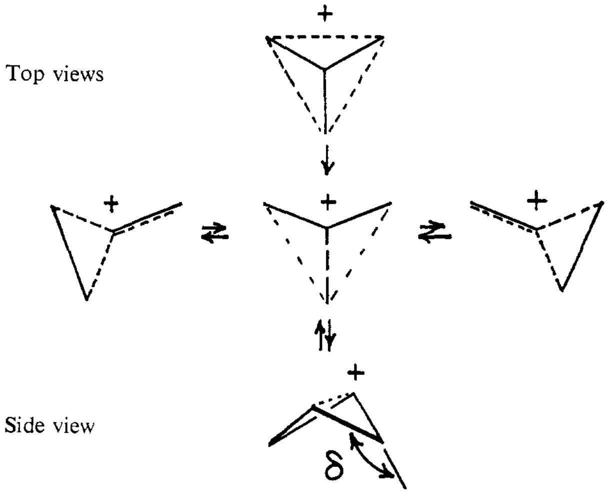
(65) C. S. Foote, *J. Am. Chem. Soc.*, **86,** 1853 (1964).
(66) P. von R. Schleyer, *ibid.*, **86,** 1854 (1964).
(67) K. B. Wiberg, G. A. Hess, Jr., and A. J. Ashe, III, in ref 12.
(68) H. G. Richey, Jr., in ref 12.
(69) See Wiberg and Ashe, Table III, footnote *f*.

similar to that which must be present in the dehydroadamantyl ion; or, finally, how a puckered cyclobutyl cation would look if the angle of pucker were to be reduced. Hoffmann[70] has inferred a substantial 1,3-bonding interaction in the puckered cyclobutyl cation. We find that further reduction of the angle δ is energetically feasible; the 1,3-bonding interaction grows while other bonds weaken.[33]



The minimum interpretation from these studies on the 8,9-dehydro-2-adamantyl cation would be: access to a tricyclobutonium ion geometry similar to **3** is not mandatory for positional equilibration in potentially C_{3v} symmetric systems. The inferential results of the investigation, leading to formulation of a symmetrical "bisected" bicyclobutonium ion, seem both new and useful. Although there is no reason to expect that any one structure should describe satisfactorily all cyclopropylcarbinyl systems, no matter what the substitution or reaction conditions, or that one type of short-lived species should be uniformly consequential in all investigations of cyclopropylcarbinyl cations, the bisected bicyclobutonium ion is of general utility as a conceptual tool. Applications using this ion to rationalize the chemistry of substituted cyclopropylcarbinyl systems will be developed elsewhere.

Experimental Section

All melting and boiling points are uncorrected. The infrared spectra were obtained with a Perkin-Elmer Model 521 grating infrared spectrophotometer or a Perkin-Elmer Model 137 Infracord. Nmr spectra were determined at 60 Mc with Varian A-60, A-60A, and A-56/60 analytical nmr spectrometers. Except as noted otherwise, all infrared spectra of new compounds were determined on solutions in chloroform and nmr spectra in deuteriochloroform. Microanalyses were done by J. Németh and his associates. The ratio of deuterated to nondeuterated alcohol and ketone in the various samples was determined by mass spectrometry with a variable-temperature vacuum lock inlet system. These ratios were calculated from the relative heights of the P and P + 1 peaks as measured from expanded-scale light spot recordings of the molecular ion regions of the various samples. Two to three scans of the molecular ion region at each of several different eV and kV setttings were obtained for all samples. The scans were made between a nominal 6 and 15 eV. The final per cent d_1 used was an average of all the scans made for the sample.

A semiautomatic Tri-Carb liquid scintillation counter was used to determine the tritium activities. The scintillator solution employed consisted of 6 g/l. of 2,5-diphenyloxazole and 100 mg/l. of 2-*p*-phenylenebis(5-phenyloxazole) in toluene. The quench correction was determined by the channels ratio method; red scaler 50–240, green scaler 240–1000. A new quenching curve was prepared each week. A gain setting of 50.0% was used. Between 2- and 6-mg quantities of the samples were weighed on a microbalance that could be read to $^1/_{1000}$th of a milligram. The samples were then taken up in 15 ml of scintillator solution and counted.

3,4-Dibromobicyclo[3.2.1]octa-2,6-diene, prepared in 40% yield from norbornadiene, potassium *t*-butoxide, and bromoform in pentane at −20°, had bp 80–81° (0.6 mm) (lit.[35] bp 77° (0.05 mm)) and an infrared absorption spectrum in agreement with expectations.[35]

3-Bromobicyclo[3.2.1]octa-2,6-diene. Reduction of 3,4-dibromobicyclo[3.2.1]octa-2,6-diene (172 g, 0.65 mol) with lithium aluminum hydride (32 g, 0.84 mol) in ether gave 85.4 g (71%) of product, bp 61–62° (4 mm) (lit.[35] bp 63° (5 mm)), having nmr and infrared spectra in close agreement with those previously reported.[35]

3-Carboxybicyclo[3.2.1]octa-2,6-diene. In a flame-dried 1-l., three-necked Morton flask, equipped with a high-speed stirrer, nitrogen inlet, addition funnel, and reflux condenser protected by a drying tube, were placed 8.0 g (0.33 g-atom) of magnesium turnings and 0.94 g (0.0045 mol) of 1,2-dibromoethane. The magnesium was covered by tetrahydrofuran distilled from lithium aluminum hydride directly into the flask. After the reaction had started, 50 g (0.270 mol) of 3-bromobicyclo[3.2.1]octa-2,6-diene was added dropwise as 400 ml of tetrahydrofuran was distilled into the flask. The reaction mixture was refluxed under nitrogen with vigorous stirring during the addition and for 3 hr after the addition was complete. The bright clear yellow solution was then cooled and poured into a rapidly stirred slurry of Dry Ice and ether contained in a 2-l. beaker. The resulting mixture was concentrated to a thick paste on a rotary evaporator and shaken with a mixture of 5% hydrochloric acid (100 ml) and ether (150 ml). The acidic layer was washed twice with 150-ml portions of ether, and the combined ether layers were washed with three 100-ml portions of 5% potassium hydroxide. The combined potassium hydroxide solutions were washed with 100 ml of ether, acidified with a 10% hydrochloric acid solution, and extracted with three 100-ml portions of ether. The combined ether extracts were washed with 100 ml of water and dried over magnesium sulfate. Removal of the ether by flash distillation gave 24.6 g (61%) of a light yellow solid, mp 128–138°. This crude material was sufficiently pure to be used in the next step of the synthesis. Recrystallization of the crude acid from pentane or absolute ethanol followed by sublimation (75° (0.3 mm)) gave the analytically pure acid, mp 143–145°; infrared absorptions at 2500–3400 and at 1680 s, 1620 s, 1420 s, 1342 m, 1313 m, 1295 s, 1265 s, 1110 m, 1080 m, 950 m, 920 m, and 705 m cm^{-1}; nmr absorptions at τ −1.95 (s, 1), 2.55 (d, 1, J = 7 Hz), a doublet of doublets centered at 3.85 (1, J = 5 and 3 Hz), 4.20 (m, 1), and 6.9–8.6 (m, 6).

Anal. Calcd for $C_9H_{11}O_2$: C, 71.98; H, 6.71. Found: C, 71.93; H, 6.70.

endo- **and** *exo*-**3-Carboxybicyclo[3.2.1]oct-6-enes.** Into a flame-dried, 2-l., three-necked, round-bottomed flask, equipped with a Trubore stirrer, Dry Ice condenser protected by a drying tube, and a gas-inlet tube, was condensed 1 l. of liquid ammonia under an argon atmosphere. Crude 3-carboxybicyclo[3.2.1]octa-2,6-diene (16.4 g, 0.109 mol) was dissolved in the ammonia and 42.4 g (1.109 g-atom) of potassium metal was added slowly in small pieces to the stirred solution. The resulting deep blue mixture was stirred for 45 min to dissolve the potassium; then 700 ml of dry isopropyl alcohol was added dropwise. Near the end of this addition the reaction mixture turned colorless. The reaction was stirred 2 hr, and the ammonia was allowed to evaporate overnight. The residue was then concentrated to a thick slurry on a rotary evaporator. This slurry was taken up in 150 ml of water, washed with 100 ml of ether, and acidified with 25% hydrochloric acid. The reaction mixture was extracted with three 200-ml portions of ether. The combined ether extracts were washed with 100 ml of water and dried over magnesium sulfate. Removal of the ether on a rotary evaporator followed by vacuum distillation of the residue gave 11.5 g (69%) of colorless oil which, on standing overnight, set to crystals, mp 41–55°. In smaller scale runs, yields reached 90%. The infrared spectrum of this mixture of *endo* and *exo* isomers showed absorptions at 2500–3400, 1690 s, 1462 m, 1410 m, 1357 m, 1295 m, 1235 s, 1080 m, 904 m, and 702 m cm^{-1}; nmr absorptions, τ −1.8 (s, 1), unsymmetrical singlet at 4.20 (2), and complex absorptions at 7.0–9.0 (9). Preparation of an anilide[60] gave a derivative of mp 192–193°.

Anal. Calcd for $C_{15}H_{17}NO$: C, 79.27; H, 7.54; N, 6.16. Found: C, 79.26; H, 7.58; N, 6.02.

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(70) R. Hoffmann, unpublished.

Hydrolactone of *endo*-3-Carboxybicyclo[3.2.1]oct-6-ene. To a cooled and stirred solution of 340 mg of the *exo–endo* mixture of 3-carboxybicyclo[3.2.1]oct-6-ene in 10 ml of acetic acid was added 4.6 ml of concentrated sulfuric acid. The mixture was allowed to stir with cooling for 2 hr, left at room temperature overnight, poured onto ice, and extracted twice with ether. The ether extracts were washed twice with 5% potassium hydroxide and twice with water and dried over sodium sulfate. Removal of the ether on a rotary evaporator gave 134 mg (39.4%) of colorless crystals. Sublimation of these crystals at 50–60° (3 mm) provided the analytical sample, mp 220°; infrared absorptions: 2940 s, 2870 m, 1740 s, 1450 m, 1380 s, 1343 m, 1125 s, 1090 s, 1055 s, 1045 s, 1015 s, 990 m, and 980 m cm^{-1}; nmr spectrum: broad triplet centered at τ 4.9 (0.83, J = 8 Hz) and complex absorptions between 7.0 and 8.5 (11).

Anal. Calcd for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 70.92; H, 7.95.

Iodolactone of *endo*-3-Carboxybicyclo[3.2.1]oct-6-ene. To a solution of 2.37 g (0.016 mol) of *endo*- and *exo*-3-carboxybicyclo-[3.2.1]oct-6-enes in 90 ml of 0.5 *N* sodium bicarbonate and 4 ml of 1.0 *N* sodium hydroxide was added a solution containing 7.6 g (0.030 mol) of iodine and 14.9 g (0.090 mol) of potassium iodide in 45 ml of water. The reaction flask was stoppered and allowed to stand in the dark for 25 hr. The mixture was then extracted with 200 ml of chloroform, and the chloroform extract was washed successively with a solution of 8 g of sodium thiosulfate in 20 ml of water, 30 ml of water, 35 ml of 0.5 *N* sodium bicarbonate, and 30 ml of water. The chloroform solution was dried over sodium sulfate; the chloroform was removed to give 2.6 g (59.6%) of crystals, mp 89–96°. Two recrystallizations from hexane gave the analytical sample, mp 98–98.5°; infrared absorptions at 2940 m, 1745 s, 1460 w, 1442 w, 1368 m, 1340 m, 1155 m, 1133 m, 1072 s, 1048 m, 1030 s, 1002 m, 962 w, 924 w, and 872 w cm^{-1}; nmr spectrum: τ 4.67 (d, 1, J = 6.5 Hz), 5.75 (d, 1, J = 4 Hz), and complex absorptions between 7.0 and 8.5 (9.6).

Anal. Calcd for $C_9H_{11}O_2I$: C, 38.87; H, 3.99. Found: C, 39.15; H, 3.92.

***exo*-3-Carboxybicyclo[3.2.1]oct-6-ene.** The aqueous solutions saved from the iodolactone preparation were acidified and extracted with 50-, 100-, and 100-ml portions of ether. The combined ethereal extracts were dried over sodium sulfate. Removal of the ether on a rotary evaporator yielded 0.82 g (34.6%) of light yellow crystals. This crude material was recrystallized from hexane and sublimed three times to yield analytically pure material, mp 121–123°; infrared absorptions at 2500–3500 s, 1700 s, 1638 w, 1447 m, 1415 m, 1130 to 1350 s, 1060 w, and 870 w cm^{-1}; nmr spectrum: τ −1.80 (s, 1), 4.07 (s, 2), 7.31 (m, 3), and 7.8–8.9 (m, 6.5).

Anal. Calcd for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 70.81; H, 8.18.

***endo*-3-Carboxybicyclo[3.2.1]oct-6-ene.** A mixture of 2.4 g (0.086 mol) of the iodolactone from *endo*-3-carboxybicyclo[3.2.1]-oct-6-ene, 15.6 g of zinc dust, and 95 ml of 95% ethanol was stirred at reflux for 5 hr, cooled, and filtered. The ethanol was removed on a rotary evaporator and the resulting oil shaken with 25 ml of 15% sodium hydroxide and 30 ml of a 1:1 ether–chloroform solution. The water layer was separated, acidified, and filtered to give 230 mg of colorless crystals; ether extraction of the acidified solution afforded an additional 540 mg of product. Sublimation of the first crop of crystals at 70° (3.5 mm) gave pure *endo* acid, mp 137.5–141.5°; infrared absorptions at 2400–3600 s, 1690 s, 1465 m, 1410 m, 1358 m, 1338 m, 1312 m, 1296 m, 1130 w, 1078 w, 990 w, 904 m, 875 w, and 833 w cm^{-1}; nmr spectrum: τ −2.1 (s, 1), 4.10 (s, 2), and 7.2–8.8 (m, 9.7).

Anal. Calcd for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 70.77; H, 7.94.

***exo*- and *endo*-3-Bicyclo[3.2.1]oct-6-enoyl Chloride.** A solution of 3.18 g (20.9 mmol) of a mixture of *exo*- and *endo*-3-carboxybicyclo-[3.2.1]oct-6-enes was titrated to a phenolphthalein end point with 1.00 *N* sodium hydroxide. The solvent was removed on a rotary evaporator, and the salt was dried overnight at 75° (0.05 mm). The dry salt was then placed in 30 ml of benzene containing 0.6 ml of pyridine, cooled to 5°, and stirred as 11.0 g (87 mmol) of oxalyl chloride was added dropwise over a 20-min period. After being stirred for 2 hr at 5°, the reaction mixture was filtered, and the solvent and excess oxalyl chloride were removed on a rotary evaporator. The infrared spectrum of the neat acid chlorides showed absorptions at 3040 w, 2920 s, 2850 m, 1800 s, 1775 s, 1750 w, 1350 m, 1160 m, 1020 m, 940 s, 915 m, 855 s, 785 s, 725 s, and 680 s cm^{-1}.

***exo*- and *endo*-3-Bicyclo[3.2.1]oct-6-enyl Diazomethyl Ketones.** The mixture of acid chlorides prepared above was dissolved in 75 ml of ether; an ethereal solution of diazomethane, derived from 15.9 g of N-methylnitrosourea, distilled, and dried over potassium hydroxide,[71] was added rapidly with stirring and cooling. The reaction mixture was stirred with cooling for 5 hr, left overnight, and concentrated under a stream of argon. The neat red oil obtained had infrared absorptions at 3100 w, 2970 s, 2880 m, 2100 s, 1640 s, 1360 s, 1160 m, 1115 m, and 1020 w cm^{-1}.

8,9-Dehydro-2-adamantanone. The unpurified diazo ketones prepared above, 140 ml of tetrahydrofuran, and 9 g of anhydrous cupric sulfate were stirred at reflux with exclusion of moisture for 5.5 hr, cooled, and filtered. Concentration of the filtrate gave an oil. On treatment with 50 ml of ether, the oil afforded 2.0 g of tan solid. Removal of the ether yielded approximately 1.8 g of yellow oil. Chromatography of this oil on 32 g of silica gel with benzene as the eluent led to 50 50-ml fractions. Fractions 5–30 contained 0.75 g of white solid. This solid was recrystallized twice from an ether–pentane mixture at −65° and then sublimed (75° (20 mm)) to give 657 mg of white solid, mp 206.5–207.5°; infrared absorptions (CCl_4) at 3040, 2940, 2864, 1705, 1343, 1053, 939, and 888 cm^{-1}. The carbonyl stretch was accurately determined in spectrograde CCl_4 with a Beckman IR 7 grating spectrophotometer. The nmr spectrum (CCl_4) showed complex absorptions at τ 7.4–8.6. The molecular weight for $C_{10}H_{12}O$, 148, was confirmed by mass spectrometry.

Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 81.05; H, 8.37.

The 2,4-dinitrophenylhydrazone of 8,9-dehydro-2-adamantanone, mp 215–217°, had $\lambda_{\max}^{CHCl_3}$ 376 mμ.

Anal. Calcd for $C_{16}H_{16}O_4N_4$: C, 58.53; H, 4.91; N, 17.07. Found: C, 58.77; H, 5.01; N, 16.77.

endo-3-Carboxybicyclo[3.2.1]oct-6-ene was converted by this route to 262 mg (26.9%) of dehydroadamantanone, mp 203–205°.

8,9-Dehydro-2-adamantanol. To a stirred, ice-cooled solution of 277 mg (7.3 mmol) of sodium borohydride in 3 ml of methanol was added dropwise 74 mg (0.51 mmol) of dehydroadamantanone in 3 ml of methanol. The reaction mixture was warmed to room temperature and stirred for 35 min, then diluted with 25 ml of water and extracted with six 10-ml portions of ether. The combined ethereal extracts were washed twice with 10-ml portions of water and dried over magnesium sulfate. Removal of the ether on a rotary evaporator gave 78 mg of white solid, mp 209–211°. This solid was sublimed (75° (10 mm)) to give 70 mg (93%) of white crystals, mp 210.5–212.5°; infrared absorptions at 3600 m, 3430 m, 3030 w, 3004 m, 2934 s, 2862 m, 1447 w, 1430 w, 1385 w, 1365 w, 1320 w, 1220 w, 1050 m, 1030 s, 1020 s, 990 s, 985 s, and 905 w cm^{-1}; nmr spectrum: unresolved triplet at τ 5.85 (1) and complex absorptions between 7.7 and 9.0 (14). The molecular weight for $C_{10}H_{14}O$, 150, was confirmed by mass spectrometry.

Anal. Calcd for $C_{10}H_{14}O$: C, 79.96, H, 9.39. Found: C, 79.99; H, 9.65.

8,9-Dehydro-2-adamantyl 3,5-Dinitrobenzoate. In a 15-ml centrifuge tube was placed 52 mg (0.35 mmol) of dehydroadamantanol in 0.20 ml of dry pyridine. To this ice-cooled solution was added 103 mg (0.45 mmol) of recrystallized 3,5-dinitrobenzoyl chloride in 1.0 ml of dry pyridine. The reaction mixture was stirred, warmed, and allowed to stand and intermittently agitated at room temperature for 3.5 hr. First a few chips of ice and then 5 ml of cold water were added to the reaction mixture with stirring. An oil separated and quickly set to crystals. The crystals were separated and washed successively with two 3-ml portions of cold water, 3 ml of cold 0.5 *N* sodium bicarbonate, and two additional 3-ml portions of cold water. The resulting solid was taken up in 6 ml of hot ethanol, filtered, and cooled slowly to −12° to give 97 mg of cream-colored crystals, mp 121.5–122.5°. An additional 8 mg of crystals, mp 118–119°, was obtained on diluting the mother liquors with water for a total yield of 88%. The nmr spectrum of the product showed absorptions at τ 0.7 (s, 3), 4.45 (t, 1, J = 4 Hz), and complex absorptions between 7.5 and 8.8 (12).

Anal. Calcd for $C_{17}H_{16}N_2O_6$: C, 59.30; H, 4.68; N, 8.14. Found: C, 59.38; H, 4.79; N, 8.48.

Solvolysis of 8,9-Dehydro-2-adamantyl 3,5-Dinitrobenzoate. Acetone was purified by refluxing analytical reagent grade acetone over calcium chloride for 3 hr and then fractionating it through a 25-cm Vigreux column. The water used was obtained by fractionating deionized water through a 12-cm Vigreux column.

Analytically pure dinitrobenzoate was solvolyzed in 60% by volume aqueous acetone at 45.02 ± 0.02, 59.97 ± 0.05, and 74.30

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(71) F. Arndt, "Organic Syntheses," Coll. Vol. II, A. H. Blatt, Ed., John Wiley and Sons, Inc., New York, N. Y., 1943, p 165.

± 0.05°. The rates of solvolysis of the ester were determined by means of the sealed-ampoule technique with solutions about 0.0029 M in 3,5-dinitrobenzoate and titrating the aliquots with about 0.0029 M sodium hydroxide to the brom thymol blue end point. To get reproducible end points with these dilute solutions, titrations were performed under an inert atmosphere. The first point was taken after temperature equilibration had occurred. The ampoules were quenched in ice water immediately upon removal from the bath. The ampoules were then warmed to room temperature and opened. Aliquots (5 ml) were measured and titrated. Two or three tubes containing only solvent were also placed in the kinetic bath and removed and titrated at various times. The sodium hydroxide solution was standardized immediately before each run against Mallinckrodt Analytical Reagent Grade Primary Standard potassium acid phthalate. If a run required more than 1 day, the base was standardized each day. All titrations were carried out with a 5-ml automatic-reloading microburet which could be read to 0.01 ml. Aliquots were taken with a 5-ml automatic delivery pipet. Infinity titers were generally taken after 8–12 half-lives. In no case did the infinity titer vary from the calculated value by more than 8%. A typical solvolysis run is described below.

8,9-Dehydro-2-adamantyl 3,5-dinitrobenzoate (53.6 mg, 0.000156 mol) was placed in a 50-ml volumetric flask. After 30 ml of acetone had been added by means of a 15-ml volumetric pipet, the flask was filled to the mark with distilled water. After the solution had been shaken vigorously, 6-ml aliquots were placed in eight dry 15 × 125 mm test tubes which had been swept with argon immediately prior to use. These tubes, along with two containing only solvent, were swept briefly with a stream of argon, sealed, and placed in a constant temperature bath maintained at 59.95 ± 0.05° (thermometer calibrated with an NBS standard thermometer). At appropriate times, tubes were removed from the bath, quenched with ice water, and warmed to room temperature. The tubes were then opened and 5-ml aliquots titrated to a brom thymol blue end point with standard sodium hydroxide. Zero time was taken as the time the first tube was quenched.

The first-order rate constants were determined with an IBM 7094 computer using a program written by Petrovich.[72]

The Arrhenius energy of activation was calculated from the slope of a computer-generated, best-fit least-squares line through the points of a plot of log k *vs.* $1/T$.

2-Deuterio-8,9-dehydro-2-adamantanol. Reduction of 225 mg (1.5 mmol) of dehydroadamantanone in 10 ml of methanol with 761 mg (18.2 mmol) of sodium borodeuteride (Alpha Inorganics, 99.5% isotopically pure) in 8 ml of methanol, prepared by the procedure detailed above for the unlabeled alcohol, gave 216 mg (95%) of white crystals, mp 212–213.5° after sublimation. Mass spectral analysis showed this material to be 90% d_1, 10% d_0.

A second preparation, with a different batch of sodium borodeuteride, converted 210 mg of ketone into 202 mg (95%) of product alcohol, mp 211–213°. Mass spectral analysis showed this material to be 94% d_1, 6% d_0.

2-Tritio-8,9-dehydro-2-adamantanol. Dehydroadamantanone, upon reduction with sodium borotritide (Nuclear Chicago Corporation), gave 95% of the labeled alcohol, mp 206–207°. After dilution with cold material, the sample had mp 208–210° and an activity of 11.9 μCi/mmol.

3,5-Dinitrobenzoate derivatives from both of the 2-deuterio-8,9-dehydro-2-adamantanol samples and 2-tritio-8,9-dehydro-2-adamantanol were prepared in the manner described previously for the unlabeled 3,5-dinitrobenzoate. The two deuterium-labeled 3,5-dinitrobenzoates melted at 121–121.5 and 120.5–121.5°. The tritium-labeled 3,5-dinitrobenzoate melted at 119–120°. The nmr spectrum of the 3,5-dinitrobenzoate from the 90% d_1 2-deuterio-8,9-dehydro-2-adamantanol showed the absence of a signal at τ 4.45.

Solvolysis Product from 8,9-Dehydro-2-adamantyl 3,5-Dinitrobenzoate. Dehydroadamantanol was isolated many times from solvolyses of the 3,5-dinitrobenzoate in 60% aqueous acetone and from control runs in which the alcohol was placed under simulated solvolysis conditions. The work-up procedures were similar in all cases; only a typical example will be described.

In a 2 × 62 cm combustion tube were placed 89 mg (0.259 mmol) of dehydroadamantyl 3,5-dinitrobenzoate and 80 ml of 60% aqueous acetone. The tube was flushed with argon, sealed, and placed in a tube furnace for 60 min at 105–110°. The contents of the tube were cooled and combined with 90 ml of ether. The resulting solution was saturated with solid sodium chloride. The aqueous layer which separated was washed with two 20-ml portions of ether. The combined organic layers were dried over magnesium sulfate and concentrated by distillation through a Vigreux column and finally under a stream of argon to give an oily solid. This material was taken up in 30 ml of ether and extracted successively with 9- and 5-ml portions of 0.5 N sodium bicarbonate and 4 ml of water; the sodium bicarbonate wash was unnecessary when the reaction had been run in the presence of excess 2,4,6-collidine. The combined aqueous washes were extracted with 10 ml of ether. After this ethereal solution had been washed with water, it was combined with the main ether solution. The combined solutions were dried over sodium sulfate and concentrated on a rotary evaporator to give 50 mg of white solid, mp 125–145°. Analysis of this material by glpc on a 0.5-m XF 1150 column (10% on Chromosorb W) at 122° showed, in addition to peaks at very short retention time, only one peak having a retention time identical with that of pure dehydroadamantanol. Between 20 and 25 mg (52–65% yield) of the material, mp 211.5–212.5°, was obtained from glpc collection of the sample. The infrared and mass spectra of this compound were identical with those of pure dehydroadamantanol.

Solvolysis Product Yield by Isotope Dilution. In a 2 × 62 cm combustion tube were placed 27.6 mg (0.0802 mmol) of 2-tritio-8,9-dehydro-2-adamantyl 3,5-dinitrobenzoate (11.9 μCi/mmol), 13.8 mg (0.114 mmol) of 2,4,6-collidine, and 25 ml of 60% aqueous acetone. The tube was flushed with argon, sealed, and heated at 105° for 75 min. After the tube had been opened, 9.0 mg of unlabeled dehydroadamantanol was added. Work-up was then carried out in the normal manner. The specific activity of the alcohol isolated by glpc was 6.54 μCi/mmol. In a parallel run, starting from the same tritium-labeled 3,5-dinitrobenzoate, the specific activity of isolated, undiluted alcohol was 11.1 μCi/mmol.

Oxidation of 8,9-Dehydro-2-adamantanol. A large number of oxidations of both labeled and unlabeled dehydroadamantanol to the corresponding ketone was carried out with chromium trioxide in pyridine. A typical oxidation is described.

In a 15-ml centrifuge tube were placed 14 mg (0.093 mmol) of dehydroadamantanol and 0.25 ml of dry pyridine (distilled from barium oxide). To the resulting solution was added a suspension of 30 mg (0.30 mmol) of chromium trioxide in 0.75 ml of pyridine. This mixture was allowed to stand at room temperature with occasional stirring for 21 hr. At the end of this time, the mixture had turned black and considerable solid had formed. This mixture was stirred with 10 ml of ether and filtered through a bed of Filter-Cel. The reaction tube was washed with two additional 10-ml portions of ether; these, too, were poured through the filter pad. The clear, colorless filtrate was washed with four 3-ml portions of water and dried over magnesium sulfate. The ether solution was concentrated to 1 ml on a rotary evaporator. Analysis of this solution by glpc on a 0.5-m XF 1150 column (10% on Chromosorb W) at 122° showed, in addition to solvent peaks, only one peak. This peak had a retention time which was the same as that of dehydroadamantanone. Collection of this material by glpc gave 9 mg of white solid, mp 204–205°. The infrared and mass spectra were identical with those of pure dehydroadamantanone.

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[72] J. Petrovich, Ph.D. Thesis, University of Illinois, Urbana, Ill., 1964.