$CpCo(PPh_3)_2$,[10] $CpCo(PPh_3)(PMe_3)$,[11] PMe_3,[12] and PPh_3-d_{15}[13] were all prepared by previously published methods. Toluene-d_8 was vacuum transferred from a purple sodium/benzophenone/tetraglyme ketyl solution.

NMR Experiments. ^1H nuclear magnetic resonance (NMR) spectra were recorded on a high-field (180.09-MHz) instrument equipped with a Bruker magnet, Nicolet Technology Corp. Model 1180 data system and electronics assembled by Mr. Rudi Nunlist (U.C., Berkeley). Spectra were recorded at -60 °C, the probe being maintained at that temperature by a precooled nitrogen stream.

NMR experiments were carried out as follows. Various amounts of PPh_3-d_{15} (see Table I) were weighed into standard 5-mm NMR tubes fused to 14/20 ground-glass joints. The sample tubes were taken into the drybox and each prepared in the following manner. A standard solution of $CpCo(PPh_3)_2$ was prepared by dissolving 0.052 g (0.080 mmol) of that compound in 2.00 mL of toluene-d_8; 0.250 mL of that solution was transferred into each NMR tube by syringe. Toluene-d_8 was added to the tubes to bring the total volume of the solution in each tube to 0.50 mL. In turn, each tube was capped with a Teflon needle valve, taken out of the drybox and placed on a vacuum line. The samples were degassed by three freeze-pump-thaw cycles on the vacuum line and charged with PMe_3 while frozen at -196 °C. The phosphine was added by expansion into a 25.85-mL known volume bulb (above the sample tube) to a pressure of 4.79 torr (as measured by using an MKS Baratron capacitance manometer) followed by vacuum transfer of the contents of the bulb into the NMR tube. The tube was sealed with a flame and stored at -196 °C until ready for use. At that time, the tubes were thawed at -78 °C and shaken at that temperature before being dropped into the precooled NMR probe. Spectra were taken under computer control until completion of each reaction.

(10) Yamazaki, H.; Hagihara, N. *J. Organomet. Chem.* **1977**, *139*, 157.
(11) (a) McAlister, D. R. Ph.D. Thesis, California Institute of Technology, Pasadena, CA, 1978; (b) Leonhard, K.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 649.
(12) Bianco, V. D.; Doronzo, S. *Inorg. Snyth.* **1976**, *16*, 164.
(13) Wolfsberger, W.; Schmidbaur, E. *Synth. React. Inorg. Met.-Org. Chem.* **1974**, *4*, 149 modified by using *n*-Bu_2O solvent as suggested by R. R. Schrock.

Acknowledgment. We are grateful for financial support of this work from the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract No. W-7405-48. H.E.B. was supported by a Fannie and John Hertz Foundation fellowship.

Complete Substitution Stereochemistry of Solvolysis of 1-Methyl-2-adamantyl Tosylate and 4-Methyl-*exo*- and 4-Methyl-*endo*-4-protoadamantyl 3,5-Dinitrobenzoate

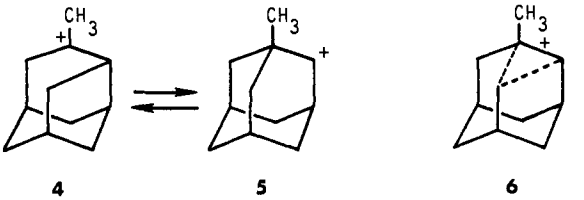
J. Eric Nordlander* and Jerome E. Haky

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received June 30, 1980*

Abstract: Formation of 1-methyl-2-adamantanol in the solvolysis of 1-methyl-2-adamantyl-*4-d* tosylate (**14**-OTs/**15**-OTs), 4-methyl-*exo*-4-protoadamantyl-*5-d* 3,5-dinitrobenzoate (**10**-ODNB/**11**-ODNB), and 4-methyl-*endo*-4-protoadamantyl-*5-d* 3,5-dinitrobenzoate (**12**-ODNB/**13**-ODNB) in 60% aqueous dioxane has been found in each case to occur with >97% stereoselectivity. The pathway without rearrangement (from **14**-OTs/**15**-OTs) produces retention of configuration, while the routes involving rearrangment (from **10**-ODNB/**11**-ODNB and **12**-ODNB/**13**-ODNB) afford inversion of configuration at the migration origin. Concurrent displacement with rearrangment from the 1-methyl-2-adamantyl reactant proceeds with migration only of the substituted bridge backside to the tosylate. These and earlier published data constitute a complete stereochemical description of representative solvolysis of the title reactants. The new results strongly complement previous evidence for a bridged cation intermediate, **6**.

Introduction

The 4-alkyl-4-protoadamantyl and 1-alkyl-2-adamantyl systems are closely connected in solvolysis.[1-8] 4-Methyl-*exo*-4-protoadamantyl 3,5-dinitrobenzoate (**1**-ODNB) and 1-methyl-2-adamantyl tosylate (**2**-OTs) are hydrolyzed in 60% acetone[4] and in 60% dioxane[8] to comparable mixtures of the two corresponding alcohols plus 4-methylprotoadamantene and 4-methyleneprotoadamantane, and the same products are formed from 4-methyl-*endo*-4-protoadamantyl 3,5-dinitrobenzoate (**3**-ODNB)[4,8] (Scheme I). The Wagner-Meerwein related carbenium ions, **4** and **5**, derived from these reactants would be expected to be similar in energy, since the more stable charge locus[9] in **4** weighs against the relatively strain-free tricyclic constitution[10] of **5**. This balance



4 **5** **6**

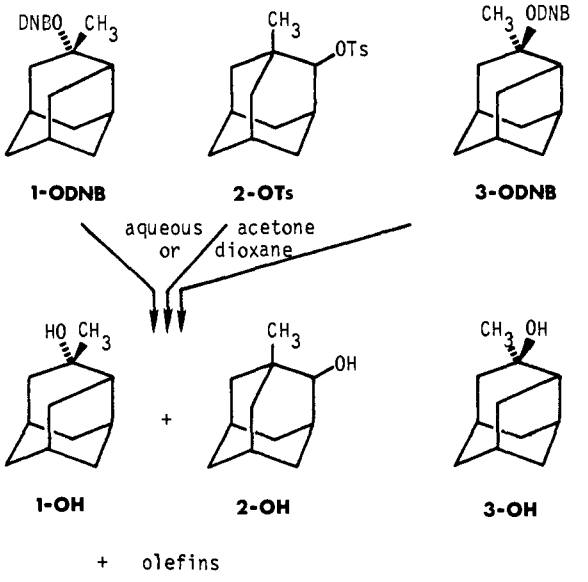
raises the possibility that a single-bridged ion, **6**, may be favored over an equilibrium between the two localized ions.

Schleyer and co-workers[4,5] in 1974 presented detailed evidence for the direct formation of **6** in the aqueous acetone solvolysis of both **1**-ODNB and **2**-OTs. *endo*-Protoadamantyl reactant **3**-ODNB was considered also to react via **6** following unassisted ionization. These conclusions were based on product, kinetic, stable-ion, and stereochemical results, including the exclusive formation of exo alcohol **1**-OH over the epimeric **3**-OH, an observation subsequently made also for aqueous dioxane by Majerski et al.[8] Complementary rate and product data for other 1-substituted adamantyl tosylates were reported by Lenoir in 1973.[2,3]

(1) Lenoir, D.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1970**, 941.
(2) Lenoir, D. *Chem. Ber.* **1973**, *106*, 78.
(3) Lenoir, D. *Chem. Ber.* **1973**, *106*, 2366.
(4) Lenoir, D.; Raber, D. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1974**, *96*, 2149.
(5) Lenoir, D.; Mison, P.; Hyson, E.; Schleyer, P. v. R.; Saunders, M.; Vogel, P.; Telkowski, L. A. *J. Am. Chem. Soc.* **1974**, *96*, 2157.
(6) Fărcaşiu, D. *J. Am. Chem. Soc.* **1976**, *98*, 5301.
(7) Fărcaşiu, D. *J. Org. Chem.* **1978**, *43*, 3878.
(8) Kovačević, D.; Goričnik, B.; Majerski, Z. *J. Org. Chem.* **1978**, *43*, 4008.
(9) Arnett, E. M.; Pienta, N. *J. Am. Chem. Soc.* **1980**, *102*, 3329. Arnett, E. M.; Pienta, N.; Petro, C. *Ibid.* **1980**, *102*, 398. Arnett, E. M.; Petro, C. *Ibid.* **1978**, *100*, 2563, 5402, 5408. Bittner, E. W.; Arnett, E. M.; Saunders, M. *Ibid.* **1976**, *98*, 3734.
(10) Clark, T.; Knox, T. M.; Mackle, H.; McKervey, M. A.; Rooney, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 3835; **1979**, *101*, 2404.

0002-7863/81/1503-1518$01.25/0

Scheme I



The case for bridged ion **6** was challenged in 1976–1978 by Fărcaşiu,[6,7] who advanced new experimental findings and reinterpreted those in the literature to support the rapid interconversion of discrete species **4** and **5**. More recently Majerski and coworkers[8] have presented methyl-d_3 solvolysis isotope effects, and Schleyer, Lenoir, Olah, et al.[11] have reported a far-reaching ^{13}C NMR stable-ion study, in both cases reinforcing the bridged-ion hypothesis.

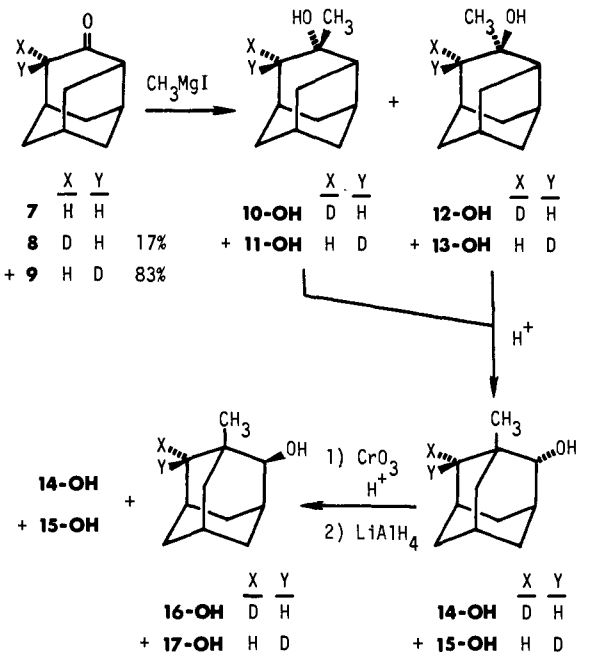
An important line of evidence previously undeveloped for this problem is the stereochemistry of formation of 1-alkyl-2-adamantyl solvolysis products from **1**-ODNB, **2**-OTs, and **3**-ODNB. Schleyer has made preliminary mention of a polarimetric study of the hydrolysis of 1-methyl-2-adamantyl tosylate.[12] We report here the results of a deuterium-label investigation of all three reactants.

Results

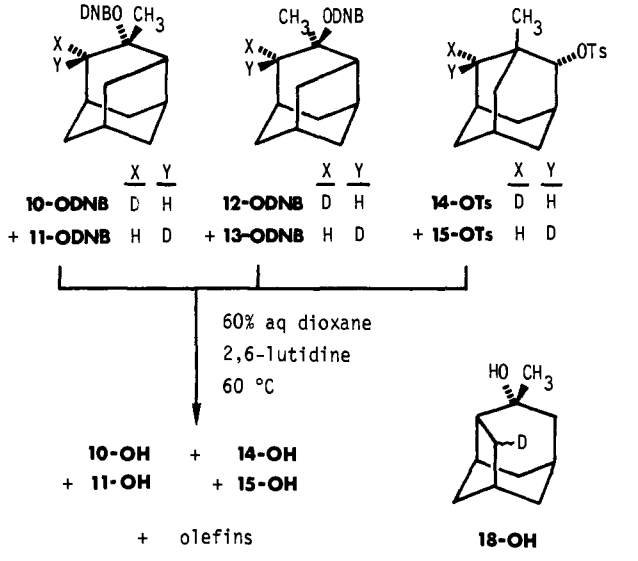
Synthesis. 5-Deuterated 4-methyl-4-protoadamantanols and 4-deuterated 1-methyl-2(a)-adamantanol were prepared as outlined in Scheme II. Addition of D_2O to the lithium enolate (from lithium diisopropylamide) of 4-protoadamantanone (**7**) in THF solution at −75 °C produced 5-labeled ketone, **8**/**9**, found by ^2H NMR analysis[13] to consist principally (83%) of the endo epimer **9**, signifying deuterium capture from the normally more hindered side.[1,14-18] Reaction of the ketone with methylmagnesium iodide[1,4,5,8,15,18] in ether yielded the desired tertiary alcohols **10**-OH/**11**-OH (40%) and **12**-OH/**13**-OH(60%), which were separated chromatographically as needed. ^2H NMR inspection of the two materials showed[13] the configurational distribution of the label to be the same as in the precursory ketone.

Treatment[1,8,15,18] of the mixed alcohols **10**-OH–**13**-OH with catalytic H_2SO_4 in boiling aqueous acetone effected isomerization wholly to the two 1-methyl-2(a)-adamantanols-*4-d*, **14**-OH/**15**-OH. The product exhibited only two ^2H NMR signals in the presence of Pr(fod)$_3$, whereas the fourfold mixture **14**-OH–**17**-OH

Scheme II



Scheme III



generated by reduction of the derived ketone showed the expected[13] four peaks. The sequence of Pr(fod)$_3$-dispersed ^2H chemical shifts assigned to **14**-OH–**17**-OH is the same as that established earlier for the parent 2-adamantanols-*4-d*.[13] Close precedent for the indicated rearrangement of **10**-OH–**13**-OH with inversion at the migration origin exists in the analogous isomerization of *exo*-4-protoadamantyl-*5-d* 3,5-dinitrobenzoate.[13]

Alcohols **10**-OH/**11**-OH and **12**-OH/**13**-OH were converted to the 3,5-dinitrobenzoates, **10**-ODNB/**11**-ODNB and **12**-ODNB/**13**-ODNB, respectively, and alcohols **14**-OH/**15**-OH to the *p*-toluenesulfonates, **14**-OTs/**15**-OTs, in the usual manner.[4,8]

Solvolysis. Substrates **10**-ODNB/**11**-ODNB, **12**-ODNB/**13**-ODNB, and **14**-OTs/**15**-OTs were each solvolyzed for >10 half-lives[8] in 60% aqueous dioxane containing 1.1 equiv of 2,6-lutidine at 60 °C. The unrearranged and rearranged alcohol products were separated by preparative thin-layer chromatography and analyzed by ^2H NMR (Scheme III). From all three reactions the adamantyl alcohol was entirely **14**-OH/**15**-OH formed from **10**-ODNB/**11**-ODNB and **12**-ODNB/**13**-ODNB by inversion at the migration origin and from **14**-OTs/**15**-OTs by retention of configuration. None of the epimeric **16**-OH/**17**-OH could be detected (<3% under the spectrometric conditions employed). The

(11) Schleyer, P. v. R.; Lenoir, D.; Mison, P.; Liang, G.; Surya Prakash, G. K.; Olah, G. A. *J. Am. Chem. Soc.* **1980**, *102*, 683.
(12) Schleyer, P. v. R., comments in Brown, H. C. "The Nonclassical Ion Problem"; Plenum Press: New York, 1977; p 281.
(13) Nordlander, J. E.; Haky, J. E. *J. Org. Chem.* **1980**, *45*, 4780.
(14) Lenoir, D.; Schleyer, P. v. R.; Cupas, C. A.; Heyd. W. E. *J. Chem. Soc., Chem. Commun.* **1971**, 26.
(15) Cuddy, B. D.; Grant, D.; McKervey, M. A. *J. Chem. Soc. C* **1971**, 3173. *J. Chem. Soc., Chem. Commun.* **1971**, 27.
(16) Boyd, J.; Overton, K. H. *J. Chem. Soc., Perkin Trans. 1* **1972**, 2533. *J. Chem. Soc., Chem. Commun.* **1971**, 211.
(17) Lenoir, D.; Hall, R. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1974**, *96*, 2138.
(18) Lenoir, D.; Glaser, R.; Mison P.; Schleyer, P. v. R. *J. Org. Chem.* **1971**, *36*, 1821. Chakrabarti, J. K.; Hotten, T. M.; Rackham, D. M.; Tupper, D. E. *J. Chem. Soc., Perkin Trans. 1* **1976**, 1893.

Table I. Stereochemistry of Solvolysis of 2-Adamantyl Tosylate

solvent	temp, °C	ret, %	inv, %	ref
HOAc	100	67	33	20
HOAc, NaOAc	100	65	35	20
	100	72	28	*a*
HCO_2H, HCO_2Na	100	80	20	20
CF_3CO_2H, CF_3CO_2Na	100	64	36	20
50% aqueous acetone, 2,6-lutidine	100	84	16	20
60% aqueous dioxane, 2,6-lutidine	78	76	24	*a*

[a] Singleton, D. A.; Haky, J. E., unpublished results with 2(e)-adamantyl-*4(e)-d* tosylate.

protoadamantyl substitution product in each case was **10**-OH/**11**-OH (>97%), demonstrating migration only of the bond backside to the tosylate in **14**-OTs/**15**-OTs. Frontside rearrangment would have produced 2-deuterated 4-methyl-*exo*-4-protoadamantanol, **18**, whose ^2H NMR detectability (≥3%) was established from the ^1H spectrum of **1**-OH with added $Pr(fod)_3$.

Discussion

The present and earlier published[1,3,8] data furnish a complete stereochemical description of representative solvolytic displacement from reactants **1**-ODNB, **2**-OTs, and **3**-ODNB. The collective results are in accord with product formation throughout from bridged ion **6** and at variance with the alternative intermediacy of carbenium ions **4** and **5**.

The previously reported[1,3,8] exclusive formation of 4-methyl-*exo*-(**1**-OH) over 4-methyl-*endo*-4-protoadamantanol (**3**-OH) in these reactions supported **6** by establishing stereoselectivity substantially surpassing that exhibited characteristically at C(4) by the protoadamantyl system in other reactions (protoadamantene[14-18] and 4-protoadamantanone[1,4,5,8,15,17,18]). Additional mechanistic tightness in the production of **1**-OH is now revealed by the backside stereospecificity of methylene migration proceeding from 1-methyl-2-adamantyl tosylate, **14**-OTs/**15**-OTs → **10**-OH/**11**-OH. This constraint is embodied in the proposed[4,5] direct formation of **6** from **2**-OTs. Alternative explanation in terms of interconverting open ions, on the other hand, would require **5**, nominally of C_s symmetry, to undergo intramolecular nucleophilic attack (**5** → **4**) wholly at the original backside but intermolecular nucleophilic capture entirely at the frontside (see below).

Cogent evidence is provided by the comprehensive high stereoselectivity of 1-methyl-2-adamantanol formation (Scheme III). While the corresponding localized cation, **5**, would be equally reactive per se at both faces, results to be expected under ion-pair conditions[19] can be approximated by those observed in parent 2-adamantyl tosylate solvolysis. Whiting[20] has interpolated this behavior from measurements with the diastereomeric 5-methyl-labeled tosylates, as summarized in Table I. We have utilized a C(4)-deuterium label[13] to obtain preliminary complementary data, included in Table I. In common solvents retention is favored over inversion by a factor of 1.8–5.3. This selectivity can be understood as the combined consequence of backside steric hindrance and the hyperpolarization of a solvent molecule within a solvent-separated ion pair;[8,17,21] weak bridging in the 2-adamantyl cation may make a further contribution.[17,22]

Introduction of a 1-methyl substituent into 2-adamantyl tosylate increases frontside selectivity in formation of the unrearranged alcohol to the point of being exclusive by our measurement, **14**-OTs/**15**-OTs → **14**-OH/**15**-OH. Bridged ion **6** offers the most attractive explanation of this effect together with the marked concomitant rate enhancement observed by Lenoir, Raber, and Schleyer.[1,3,4]

Most impressive stereochemically is maintenance of the same restrictive terminal pathway for 1-methyl-2-adamantanol formation from both stereoisomeric 4-methyl-4-protoadamantyl esters **10**-ODNB/**11**-ODNB and **12**-ODNB/**13**-ODNB. No anion association hypothesis can reasonably explain these observations in terms of open cation **5**. Delocalized ion **6** appears to offer a uniquely satisfactory interpretation.

Majerski and co-workers on observation of closely similar relative yields of substitution products **1**-OH and **2**-OH from the epimeric 4-methyl-4-protoadamantyl dinitrobenzoates **1**-ODNB and **3**-ODNB have suggested the common intermediacy of a bridged exo solvent-separated ion pair, derived from the endo substrate **3**-ODNB by ionization, dissociation, and rapid four-centered carbonium ion isomerization during which the counterion remains stationary.[8] This possibility is contradicted by the present finding that labeled endo ester **12**-ODNB/**13**-ODNB produces only alcohols **10**-OH/**11**-OH and **14**-OH/**15**-OH. The proposed rearrangement from **3**-ODNB would have led instead to alcohols **18**-OH and **16**-OH/**17**-OH, shown to be absent. Endo reactant **3**-ODNB thus yields products from bridged ion **6** after ionization, dissociation, and simple frontside σ-bond delocalization.

Experimental Section

General Data. Melting points (volatile samples in sealed capillary tubes) are uncorrected. ^1H NMR spectra were obtained with a Varian A-60-A, HA-100, or XL-100 instrument, using $CDCl_3$ as solvent and tetramethylsilane as internal standard. ^2H NMR spectra were obtained at 15.4 MHz with the Varian XL-100-15 system in the Fourier transform mode with modulated proton decoupling; chemical shifts were measured relative to $CDCl_3$ and are expressed with reference to internal $(CD_3)_4Si$.[23]

4-Protoadamantanone-*exo*-*5*-*d* and -*endo*-*5*-*d* (8/9). To 223 mg (2.2 mmol) of diisopropylamine (Aldrich, distilled from potassium hydroxide immediately before use) cooled to 0 °C in a flame-dried 50-mL three-necked flask equipped with a rubber septum, magnetic stirrer, and dry N_2 atmosphere was added by syringe 1.4 mL of 1.5 M *n*-butyllithium (2.1 mmol) in hexane (Ventron). The mixture was stirred at 0 °C for 1 h, 5 mL of dry tetrahydrofuran was added, and the solution was cooled to −78 °C. A solution of 302 mg (2.00 mmol) of 4-protoadamantanone[24] in 5 mL of tetrahydrofuran was then added via syringe over a 15-min period. After 15 min of further stirring, 220 mg (11 mmol) of deuterium oxide (99.8%, Norell) was added. The mixture was allowed to warm to room temperature, poured into 100 mL of water, and extracted with ether. After the mixture was dried ($MgSO_4$), the ether was removed by rotary evaporation, leaving a white solid, which was purified by sublimation, giving 242 mg (1.60 mmol, 80%) of labeled 4-protoadamantanone: mp 207–210 °C (lit.[24] 210–212 °C); ^2H NMR (15 mg of substrate + 70 mg of $Pr(fod)_3$ in 400 μL of $CHCl_3$) δ −3.59 (17%, **8**[13]), −2.45 (83%, **9**[13]); MS (M+), *m/e* 150 (d_0, 19%), 151 (d_1, 81%) (Hewlett-Packard Model 5985-B quadrupole spectrometer); ^1H NMR as expected.[24]

4-Methyl-*exo*-4-protoadamantanol-*exo*-*5*-*d* and -*endo*-*5*-*d* (10-OH/11-OH) and 4-Methyl-*endo*-4-protoadamantanol-*exo*-*5*-*d* and -*endo*-*5*-*d* (12-OH/13-OH). A mixture of the deuterated epimeric alchohols **10**-OH/**11**-OH + **12**-OH/**13**-OH was obtained in 90% yield by standard addition[15,18] of methylmagnesium iodide to ketones **8**/**9** in ether. The pure epimeric alcohols **10**-OH/**11**-OH and **12**-OH/**13**-OH were obtained in 25% and 60% yield, respectively, by column chromatography.[8] For **10**-OH/**11**-OH: mp 82–83 °C (lit.[8] 82–83 °C); ^2H NMR (15 mg of substrate + 70 mg of $Pr(fod)_3$ in 400 μL of $CHCl_3$) δ −10.9 (17%, 10-OH), −5.8 (83%, **11**-OH); ^1H NMR as expected.[17] For **12**-OH/**13**-OH: mp 85–87 °C(lit.[8] 86–88 °C); ^2H NMR (15 mg of substrate + 70

(19) Raber, D. J.; Harris, J. M.; Schleyer, P. v. R. In "Ions and Ion Pairs in Organic Reactions"; Szwarc, M., Ed.; Wiley-Interscience: New York, 1974; Vol. 2, Chapter 3.

(20) Bone, J. A.; Pritt, J. R.; Whiting, M. C. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1447.

(21) Sneen, R. A.; Larsen, J. W. *J. Am. Chem. Soc.* **1969**, *91*, 6031. Raber, D. J.; Harris, J. M.; Hall, R. E.; Schleyer, P. v. R. *Ibid.* **1971**, *93*, 4821. Harris, J. M.; Fagan, J. F.; Walden, F. A.; Clark, D. C. *Tetrahedron Lett.* **1972**, 3023. Sneen, R. A. *Acc. Chem. Res.* **1973**, *6*, 46. Harris, J. M.; Becker, A.; Clark, D. C.; Fagan, J. F.; Kennan, S. L. *Tetrahedron Lett.* **1973**, 3813. Harris, J. M.; Clark, D. C.; Becker, A.; Fagan, J. F. *J. Am. Chem. Soc.* **1974**, *96*, 4478. Harris, J. M.; Becker A.; Fagan, J. F.; Walden, F. A. *Ibid.* **1974**, *96*, 4484. Bentley, T. W.; Schleyer, P. v. R. *Ibid.* **1976**, *98*, 7658; Bentley, T. W.; Schleyer, P. v. R. *Adv. Phys. Org. Chem.* **1977**, *14*, 1.

(22) Bone, J. A.; Whiting, M. C. *J. Chem. Soc., Chem. Commun.* **1970**, 115. Storesund, H. J.; Whiting, M. C. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1452.

(23) Jensen H.; Schaumberg, K. *Acta Chem. Scand.* **1971**, *25*, 663. Diehl, P. In "Nuclear Magnetic Resonance Spectroscopy of Nuclei Other than Protons"; Axenrod, T., Webb, G. A., Eds.; Wiley: New York, 1974; Chapter 18.

(24) Majerski, Z.; Hameršak, Z. *Org. Synth.* **1979**, *59*, 147.

mg of $Pr(fod)_3$ in 400 μL of $CHCl_3$) δ −4.35 (17%, **12**-OH), −7.68 (83%, **13**-OH); ^1H NMR as expected.[17]

1-Methyl-2(a)-adamantanol-*4(a)-d* and -*4(e)-d* (14-OH/15-OH). A crude mixture of **10**-OH/**11**-OH + **12**-OH/**13**-OH (170 mg, 10 mmol) was isomerized to the corresponding 1-methyl-2(a)-adamantanols, **14**-OH/**15**-OH, in boiling 80% aqueous acetone containing 0.3% H_2SO_4 as employed for the unlabeled alcohols by Majerski et al.[8] mp 157–159 °C (lit.[8] 158–160 °C); ^2H NMR (15 mg of substrate + 75 mg of $Pr(fod)_3$ in 400 μL of $CHCl_3$) δ −10.0 (17%, **14**-OH^{13}), −4.7 (83%, **15**-OH^{13}); ^1H NMR as expected.[17] The binary nature of this product and the configurational assignments were confirmed by oxidation–reduction to produce the four-isomer mixture as follows.

Four Diastereomeric 1-Methyl-2-adamantanols-*4-d* (14-OH–17-OH). Labeled 1-methyl-2(a)-adamantanols **14**-OH/**15**-OH (170 mg, 10 mmol) were oxidized in 90% yield to the corresponding ketones by the method of Numan and Wynberg.[25] This product was in turn reduced in 85% yield with $LiAlH_4$ in ether[26] to the four diastereomeric 1-methyl-2-adamantanols-*4-d*, **14**-OH–**17**-OH. The shift-enhanced ^2H NMR spectrum of the mixture (15 mg of substrate + 75 mg of $Pr(fod)_3$ in 400 μL of $CHCl_3$) consisted of the expected[13] four signals at δ −2.7 (42%), −3.2 (9%), −4.7 (41%), and −10.0 (8%). The latter two peaks are those of **15**-OH and **14**-OH, respectively, by chemical shift identity with those of the precedent twofold mixture (above), while the former must be those of **17**-OH and **16**-OH, respectively, in consideration of their relative intensities as well as relative induced shifts.[13]

4-Methyl-*exo*-4-protoadamantyl-*exo-5-d* and -*endo-5-d* 3,5-Dinitrobenzoate (10-ODNB/11-ODNB) and 4-Methyl-*endo*-4-protoadamantyl-*exo-5-d* and -*endo-5-d* 3,5-Dinitrobenzoate (12-ODNB/13-ODNB). Epimeric alcohols **10**-OH/**11**-OH and **12**-OH/**13**-OH were each converted to the 3,5-dinitrobenzoate in 70% yield by using the procedure described by Majerski et al.[8] for the preparation of the undeuterated esters. For **10**-ODNB/**11**-ODNB: mp 110–112 °C (lit.[8] 113–114 °C); ^1H NMR as expected.[4] For **12**-ODNB/**13**-ODNB: mp 127–130 °C (lit.[8] 130–131 °C); ^1H NMR as expected.[4]

1-Methyl-2(a)-adamantyl-*4(a)-d* and -*4(e)-d* Tosylate (14-OTs/15-OTs). Alcohol **14**-OH/**15**-OH was converted to the tosylate in 60% yield using the procedure employed by Majerski[8] for the undeuterated ester: mp 113–114 °C (lit.[8] 113–114 °C); ^1H NMR as expected.[4]

Solvolyses of 10-ODNB/11-ODNB, 12-ODNB/13-ODNB, and 14-OTs/15-OTs in Aqueous Dioxane. The solvolysis procedure for the three substrates was as follows. Deuterated ester (250 mg, 0.69 mmol) was dissolved in 25 mL of 60% aqueous dioxane containing 82 mg (0.77 mmol) of 2,6-lutidine (Aldrich), and the resulting solution was stirred at 60 °C for >10 half-lives:[8] 12 h for **10**-ODNB/**11**-ODNB, 50 h for **12**-ODNB/**13**-ODNB, and 13 h for **14**-OTs/**15**-OTs. The mixture was then allowed to cool, poured into 200 mL of water, and extracted with five 50-mL portions of pentane. The combined pentane extracts were washed successively with water, 5% aqueous hydrochloric acid, saturated aqueous sodium bicarbonate, and saturated brine. After the mixture was dried ($MgSO_4$) the pentane was removed by rotary evaporation, leaving a yellow liquid from which 1-methyl-2-adamantanol and 4-methyl-*exo*-4-protoadamantanol were isolated by preparative TLC (silica gel with 3:7 ethyl acetate–hexane as eluant). From all three esters the ^2H NMR spectrum of the 1-methyl-2-adamantanol product (15 mg of substrate + 75 mg of $Pr(fod)_3$ in 400 μL of $CHCl_3$) showed only two peaks, corresponding to **14**-OH (δ −10.0, 17%) and **15**-OH (δ −4.7, 83%); no peaks corresponding to **16**-OH (δ −2.7) or **17**-OH (δ −3.2) could be detected (<3%). The ^2H NMR spectrum of the 4-methyl-*exo*-4-protoadamantanol product (15 mg of substrate + 70 mg of $Pr(fod)_3$ in 400 μL of $CHCl_3$) in each case showed only two peaks, corresponding to **10**-OH (δ −10.9, 17%) and **11**-OH (δ −5.8, 83%).

The similarly dispersed ^1H spectrum of undeuterated 4-methyl-*exo*-4-protoadamantanol (**1**-OH) (15 mg of substrate + 70 mg of $Pr(fod)_3$ in 400 μL of $CDCl_3$) provided positive evidence for the absence (<3%) of 2-deuterated 4-methyl-*exo*-4-protoadamantanol, **18**-OH, from the **10**-OH/**11**-OH solvolysis product. The exo- and endo-5-proton signals at δ −10.9 and −5.8, respectively, were integrated for 1 H each and were well separated (>0.75 ppm) from the other proton absorptions. Since ^1H and ^2H NMR chemical shifts are parallel,[23] the possible superimposition of 2-*d* and 5-*d* peaks in the ^2H spectrum was thus excluded.

Acknowledgment. Support of this work by National Science Foundation Grants CHE 75-04284-A02 and CHE 78-21790 is gratefully acknowledged. Thanks are expressed to Stephen T. Ingalls for the mass spectrometry and to Dr. Zdenko Majerski for helpful comments.

(25) Numan, H.; Wynberg, H. *J. Org. Chem.* **1978**, *43*, 2232.
(26) Fieser, L. F.; Fieser, M. "Reagents For Organic Synthesis"; Wiley: New York, 1967; Vol. 1, p 584.

Studies of Free Radicals at High Pressures. 2. Kinetics for a Variety of Reactions[1]

P. R. Marriott and D. Griller*

Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6. *Received July 3, 1980*

Abstract: Kinetic EPR studies of a variety of free-radical reactions have been carried out at high pressures. Volumes of activation were measured for the β-scission reactions of di-*tert*-butyliminyl (3.0 ± 1.0 cm^3 mol^{-1}) and triethoxy-*tert*-butoxyphosphoranyl (0.2 ± 1.9 cm^3 mol^{-1}), for the self-reaction of di-*tert*-butyliminyl (−18.0 ± 5.3 cm^3 mol^{-1}), and for the rearrangements of 2,4,6-tri-*tert*-butylphenyl (5.3 ± 1.7 cm^3 mol^{-1}) and 2,4,6-tris(perdeuterio-*tert*-butyl)phenyl (−1.2 ± 2.0 cm^3 mol^{-1}). These measurements improve the descriptions of the transition states for the various reactions and in the case of the phenyl rearrangements provide supporting evidence for a mechanism involving quantum mechanical tunneling.

The properties of the transition state for a chemical reaction are often inferred from measurements of the activation parameters for that reaction. The activation energy, ΔE^*, is the parameter which is most easily, and hence most often, determined. However, the description of the transition state can be substantially improved if the volume of activation, ΔV^*, is also measured.[2]

The volume of activation represents the change in volume which occurs when reactants pass to transition state. It is obtained from the pressure dependence of the rate constant,[3] and its magnitude is generally characteristic of the rate-determining pathway.[4-7]

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = \frac{-\Delta V^*}{RT} \quad (1)$$

(1) Issued as NRCC publication No. 19163. For Part 1, see ref 14b.
(2) For reviews on the effects of pressure on organic reactions see: Hamann, S. D. *Annu. Rev. Phys. Chem.* **1964**, 15, 349. Whalley, E. *Ibid.* **1967**, *18*, 205. Eckert, C. A. *Ibid.* 1972, *23*, 239. LeNoble, W. J. *High Temp.—High Pressures* **1977**, *9*, 493. "High Pressure Chemistry"; Kelm, H., Ed.; D. Reidel Publishing Co.: Dordrecht, Holland, 1978.
(3) Kohnstam, G. *Prog. React. Kinet.* **1970**, *5*, 335.
(4) LeNoble, W. J. *Prog. Phys. Org. Chem.* **1967**, *5*, 207.
(5) Asano, T.; LeNoble, W. J. *Chem. Rev.* **1978**, *78*, 407.
(6) Neuman, R. C. *Acc. Chem. Res.* **1972**, *5*, 381.

0002-7863/81/1503-1521$01.25/0