

was refluxed for 10–15 minutes until a clear solution was obtained. The solution was cooled to room temperature to yield, after filtering and washing with 50% ethanol, 290 mg. of colorless mica-like crystals, m.p. 255–258° dec. The filtrate was diluted with water and cooled to give an additional 66 mg. of white flakes, m.p. 262–268° dec., the total yield of VI being 356 mg. (89%).

Five repetitions of this preparation gave essentially the same results. Larger amounts of ethanol produced a product of even better quality. Larger amounts of mercuric chloride accelerated the dissolution of the mercuri-bis-sydnone (VII).

C,C'-Mercuri-bis-[N-(3-pyridyl)-sydnone] (VII). (a) **From N-(3-Pyridyl)-sydnone (II).**—A solution of 489 mg. (3 mmoles) of sydnone II and 1.2 g. (14 mmoles) of anhydrous sodium acetate in 40 ml. of hot 50% ethanol was mixed with a solution of 407 mg. (1.5 mmoles) of mercuric chloride in 10 ml. of 50% ethanol and the whole refluxed for 4–5 hr. After about 15 minutes the clear solution became turbid, and tiny colorless flakes began to separate. The hot mixture was filtered and the product washed with hot ethanol to give 530 mg. (67%) of VII as colorless flakes, which were analyzed without further purification. This compound remained unchanged on heating to about 280°; above this temperature the crystals became light brown but did not melt up to 380°.

Anal. Calcd. for $C_{14}H_8N_6O_4Hg$: C, 32.03; H, 1.54; N, 16.01; Hg, 38.22. Found: C, 32.39; H, 1.63; N, 16.42; Hg, 38.5.³³

On cooling to room temperature the filtrate deposited 73 mg. of the C-chloromercurisydnone (VI) as colorless flakes,

(33) Determined gravimetrically in this Laboratory as mercuric sulfide.

m.p. 240–250° dec. The filtrate contained 95 mg. of chloride ion (theoretical 106 mg., based on 100% conversion of II to VII). If desired, the above filtrate can be reheated with additional sodium acetate to complete the conversion of VI to VII.

The mercuri-bis-sydnone VII was insoluble in all solvents except hot dimethylformamide and hot dimethyl sulfoxide. Impure samples of VII could be purified by washing thoroughly with a large variety of organic solvents used in succession. This compound did not change from colorless to yellow unless exposed to light.

(b) **From the N-(3-Pyridyl)-sydnone-Mercuric Chloride "Adduct" (V).**—A mixture of 200 mg. (0.46 mmole) of V and 80 mg. (0.98 mmole) of anhydrous sodium acetate was heated in 10 ml. of refluxing absolute ethanol for 3 hr. Hot filtration and washing with hot ethanol yielded 77 mg. (63%) of VII as tiny colorless flakes, m.p. >380°.

(c) **From C-Chloromercuri-N-(3-pyridyl)-sydnone (VI).**—A suspension of 1.99 g. (5 mmoles) of VI in 8–10 ml. of reagent-grade pyridine was swirled at room temperature for 1–2 minutes until all of the solid dissolved and then set aside. The solid granules which deposited in about 5 minutes were crushed to a powder while the mixture was stirred. The mixture was set aside for another 5 minutes and the granules were crushed again to a powder, this process being repeated several times. The product was filtered, washed with 3–4 ml. of pyridine, and dried at 110° to give 1.10 g. of a nearly white powder. An additional 0.112 g. was obtained by diluting the filtrate with ether, filtering, and washing the solid with 50% ethanol. Both fractions did not melt up to 380° and gave a negative Beilstein test for halogen. The total yield of VII was 1.21 g. (92%).

Anal. Calcd. for $C_{14}H_8N_6O_4Hg$: Hg, 38.2. Found: Hg, 37.8.³³

[CONTRIBUTION FROM FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY, PRINCETON, N. J.]

The Preparation and Reactivity of 2-Substituted Derivatives of Adamantane^{1,2}

BY PAUL VON R. SCHLEYER AND ROBERT D. NICHOLAS³

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A method of preparation of secondary monosubstituted derivatives of adamantane is described. Free radical hydroxylation of the readily available parent hydrocarbon gave both the secondary and the tertiary alcohols. These compounds were converted to other derivatives by standard methods. The consequences of molecular rigidity and constrained geometry upon solvolytic reactivity were noteworthy. Acetolysis of the secondary tosylate proceeded at a rate 15 times slower than cyclohexyl tosylate, but almost six powers of ten faster than the analogously constituted 7-norbornyl tosylate. The determining factor for the reactivity of these compounds would appear to be the restraint to rehybridization afforded by angles more acute than the normal tetrahedral value. The implications of this conclusion for the interpretation of the reactivities of other monocyclic and bicyclic systems are discussed.

The discovery of a convenient method of preparation of adamantane (I)⁴ prompted interest in the reactions of this rigid but strain-free ring system. Although many polysubstituted adamantane derivatives had been prepared during the course of synthesis of the hydrocarbon,⁵ monofunctional compounds were unknown until recently. The key reaction was the finding by Landa,

Kriebel and Knobloch⁶ that simple heating of bromine with adamantane, obtained by these workers from petroleum sources, gave quite satisfactory yields of a homogeneous monobromide. Preparative solvolysis in aqueous solvents easily gave an alcohol, believed to be tertiary. Very recently, these reactions have been improved and extended by Stetter and co-workers,^{7,8} who have confirmed the bridgehead nature of the bromide and alcohol. A large number of 1-substituted compounds have been prepared from these materials,^{6,7} but simple 2-substituted adamantane derivatives have not been described in the literature.

(1) Paper IV of a series on Bridged Ring Systems. Paper III, also concerning adamantane, P. von R. Schleyer and M. M. Donaldson, *THIS JOURNAL*, **82**, 4645 (1960). This paper is taken, in part, from the Ph.D. Thesis of R.D.N., Princeton University, 1960.

(2) A preliminary account of this work was presented at the Third Delaware Valley Regional Meeting, Am. Chem. Soc., Feb., 1960, Abstracts, p. 49.

(3) Gulf Research and Development Fellow, 1959–1960; National Science Foundation Summer Fellow, 1960.

(4) P. von R. Schleyer, *THIS JOURNAL*, **79**, 3292 (1957), and ref. 1.

(5) For work prior to 1954, an excellent review is available, H. Stetter, *Angew. Chem.*, **66**, 217 (1954). Subsequent refs. are: S. Landa and Z. Kamýček, *Coll. Czech. Chem. Comm.*, **21**, 772 (1956); **24**, 1320, 4004 (1959); H. Stetter, *et al.*, *Ber.*, **88**, 1535 (1955); **89**, 1922 (1956); **92**, 2664 (1959).

(6) S. Landa, S. Kriebel and E. Knobloch, *Chem. Listy*, **48**, 61 (1954); also see S. Landa and S. Hála, *Coll. Czech. Chem. Comm.*, **24**, 93 (1959).

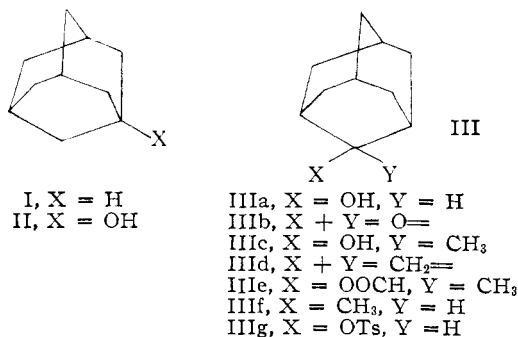
(7) H. Stetter, M. Schwarz and A. Hirschhorn, *Ber.*, **92**, 1629 (1959).

(8) H. Stetter, J. Mayer, M. Schwarz and K. Wulff, *ibid.*, **93**, 226 (1960); H. Stetter and C. Wulff, *ibid.*, **93**, 1366 (1960).

Results

Preparation of Derivatives from Adamantane.—Since methods for the synthesis of bridgehead compounds from adamantane had been developed,⁶⁻⁸ routes to the secondary derivatives were considered. In order to take advantage of the 12-to-4 ratio of secondary to tertiary hydrogens in adamantane, a non-selective free radical substitution reaction was indicated. Instead, for considerations of convenience, a reaction which was more highly discriminatory was chosen.

The new, elegant method of free radical hydroxylation of hydrocarbons using peracetic acid of Heywood, Phillips and Stansbury⁹ was applied to adamantane. The crude product was chromatographed on alumina, but only a partial separation of the 1- and 2-alcohols II and IIIa was achieved. For preparative purposes, oxidation of the crude hydroxylation mixture with the mild oxidizing agent CrO_3 in acetone¹⁰ preceded alumina chromatography. Adamantanone (IIIb), from the secondary alcohol, was easily separated from the tertiary alcohol and unchanged hydrocarbon as well as from a small amount of an unidentified reaction by-product. The ratio of ketone IIIb to tertiary alcohol II was about 1 to 3.



Reduction of adamantanonone (IIIb) with lithium aluminum hydride gave 2-adamantanol (IIIa), while addition of methyl Grignard reagent produced 2-methyl-2-adamantanol (IIIc). Dehydration of this latter compound with phosphoric acid gave the exocyclic olefin, 2-methyleneadamantane (IIId). Attempted dehydration of IIIc with formic acid¹¹ gave only ester IIIe. Hydrogenation of the olefin IIId produced 2-methyladamantane (IIIf). The structures of all these substituted adamantanes were confirmed by infrared and n.m.r. analysis.¹²

(9) D. L. Heywood, B. Phillips and H. A. Stansbury, Jr., to be published. We are extremely indebted to Dr. Heywood for carrying out the hydroxylation of adamantane.

(10) K. Bowden, I. M. Heilbron, E. R. H. Jones and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946); P. Bladon, J. M. Fabian, H. B. Henbest, H. P. Koch and G. W. Wood, *ibid.*, 2402 (1951).

(11) For examples of the dehydration of tertiary cycloalkyl alcohols, see G. Chiurdoglu, *Bull. soc. chim. Belg.*, **44**, 527 (1935); **47**, 241 (1938); F. W. Semmler and K. E. Spornitz, *Ber.*, **45**, 1553 (1912); and G. Baddeley, J. Chadwick and H. T. Taylor, *J. Chem. Soc.*, 451 (1956). C. Barkenbus, M. B. Naff and K. E. Rapp (*J. Org. Chem.*, **19**, 1316 (1954)) have presented data which indicate that the equilibrium, formic acid + acyclic olefin $\rightleftharpoons$ tertiary formate, is very much in favor of the reactants for all olefins studied except isobutene.

(12) Dr. George Van Dyke Tiers, Minnesota Mining and Manufacturing Co., very kindly determined the n.m.r. spectra. These will be reported separately with other physical observations on these compounds and other adamantane derivatives.

Acetolysis of 2-Adamantyl Tosylate.—The solvolysis of 2-adamantyl tosylate (IIIg) in anhydrous acetic acid was carried out by standard methods.¹³ The reaction was first order and was followed to about 90% completion. The product, after saponification, was starting alcohol IIIa. The rate data are summarized in Table I, where literature values for related compounds have been included for comparison.

TABLE I
RATES OF ACETOLYSIS

Tosylate	Temp., °C.	k_1 , sec. ⁻¹	$\Delta H^\ddagger$, kcal.	$\Delta S^\ddagger$, e.u.	Ref.
2-Adamantyl	100.0	$1.05 \pm 0.06 \times 10^{-4}$			
	75.15	$5.54 \pm 0.21 \times 10^{-6}$			
	25.0	3.25×10^{-9} calcd.	30.0	+3.2	
7-Norbornyl	25.0	6.36×10^{-16} calcd. ^a	37.5	+2.3	14
Cyclohexyl	25.0	4.88×10^{-8} calcd.	27.0	-1.1	15

^a Acetolysis in the presence of 0.1 M KOAc. The effect upon the rate by added salt is small. See ref. 14b.

Discussion

The unique geometrical features of the adamantane system make it an excellent model for the testing of a number of current ideas of organic theory. The architectural rigidity of the molecule, emphasized by molecular models, constrains the angles to the tetrahedral value, yet the staggered arrangement of adjacent carbon atoms is maintained throughout. Adamantane must be free from both angle and conformational strain; as a corollary, any experimental operation which disrupts the perfect geometry of the molecule should be resisted. Further, the extreme rigidity of adamantane should have demonstrable consequences, when comparisons are made with more flexible analogs. Since adamantane may be regarded as being a collection of chair cyclohexane rings, comparison with cyclohexane itself appears to be particularly apt.

The position of the 6μ carbonyl stretching band of unconjugated ketones provides a sensitive and easily determined estimate of the C-CO-C angle.^{16,17} Theoretically, the variation in position of these bands has been attributed to alterations in sp -hybridization ratios.^{18,19} The absorption frequencies of a number of ketones are listed in Table II. Using the procedure of Halford,^{16,17} values for the C-CO-C angle were calculated, employing the principal carbonyl band.²⁰ The value calculated

(13) S. Winstein, E. Grunwald and L. I. Ingraham, *THIS JOURNAL*, **70**, 821 (1948).

(14) (a) S. Winstein, M. Shatavsky, C. Norton and R. B. Woodward, *ibid.*, **77**, 4183 (1955); (b) C. Norton, Ph.D. Thesis, Harvard University, 1955.

(15) S. Winstein, *et al.*, *ibid.*, **74**, 1127 (1952); cf. H. C. Brown and G. Ham, *ibid.*, **78**, 2735 (1956).

(16) J. O. Halford, *J. Chem. Phys.*, **24**, 830 (1956); also see G. J. Karabatsos, *J. Org. Chem.*, **25**, 315 (1960).

(17) R. Zbinden and H. K. Hall, Jr., *THIS JOURNAL*, **82**, 1215 (1960).

(18) C. A. Coulson and W. A. Moffitt, *Phil. Mag.*, **40**, 1 (1949); P. D. Bartlett and M. Stiles, *THIS JOURNAL*, **77**, 2806 (1955).

(19) The 6μ C=C stretching band of 1,1-disubstituted olefins behaves similarly. The data for IIId will be discussed in a subsequent publication (ref. 12).

(20) Under high resolution many carbonyl bands are unexpectedly complex, probably due to Fermi resonance. Cf. J. Depireux, *Bull. soc. chim. Belg.*, **66**, 218 (1957); C. L. Angell, *et al.*, *Spect. Acta*, 926 (1959); P. Yates and L. L. Williams, *THIS JOURNAL*, **80**, 5896 (1958); G. Allen, P. S. Ellington and G. D. Meakins, *J. Chem. Soc.*, 1909 (1960); Professor D. S. Trifan, personal communication.

for adamantanone, 112.5° , is intermediate between that of cyclohexanone, 116.6° , and cyclopentanone, 102.2° . Some degree of restraint appears to be demonstrated. The C-CO-C angle of adamantanone cannot assume the optimum size of about 116° ,²¹ but is restricted to a smaller value by molecular rigidity.²³

TABLE II
COMPARISON OF THE POSITION OF THE C=O STRETCHING BAND^a

Ketone	ν , cm. ⁻¹	C-CO-C Angle, deg. ^b
<i>t</i> -Butyl <i>t</i> -amyl ketone ^c	1684.2	132.0
Cycloheptanone	1704.9	122.5
Pinacolone	1710.1	120.2
Cyclohexanone	1717.8	116.6
Acetone	1718.7s	116.3
	1743.8w	
Adamantanone ^d	1732.3s	112.5 av.
	1722.9ms	
Cyclopentanone	1749.8s	102.2
	1729.7w	
2-Norbornanone (norcamphor)	1751.2	101.5
8-Bicyclo[3.2.1]octanone ^e	(1757.5)	98.3
endo-Trimethylene-7-norbornanone ^f	1790.4w	
	1770.7s	92.6
	1748.1w	
Cyclobutanone ^g	(1792)	83.0

^a The spectra were determined in dilute CCl₄ solutions with a Perkin-Elmer model 21 spectrophotometer equipped with LiF optics and carefully calibrated. For representative comparisons of these data with the literature, see refs. 17, 18, 20. ^b Calculated by means of the equation, ν , cm.⁻¹ = $1278 + 68k - 2.2\phi$ (ref. 16): ϕ is the C-CO-C angle, in degrees, and the value used for $k = 10.244$ instead of $k = 10.216$,¹⁷ was chosen to make ϕ for acetone equal the literature value of 116.3° (ref. 22). ^c Kindly furnished by Professor W. A. Mosher. ^d The two bands of adamantanone were of almost equal intensity; a weighted average was used to calculate the angle. ^e Reported by R. Mayer, G. Wenschueh and W. Topelmann, *Ber.*, **91**, 1616 (1958). A. C. Cope, J. M. Grisar and P. E. Peterson, *THIS JOURNAL*, **82**, 4299 (1960), report a split peak at 1740 and 1770 cm.⁻¹. ^f Other 7-norbornanones have been reported to absorb in the region 1776-1783 cm.⁻¹; cf. P. D. Bartlett and B. E. Tate, *THIS JOURNAL*, **78**, 2473 (1956). ^g Reported by P. von R. Schleyer, Thesis, Harvard University, 1957.

The failure of the attempted dehydration of 2-methyl-2-adamantanol (IIIc) with formic acid can also be interpreted on this basis. The formation of tertiary alkyl formate with formic acid is usually precluded by an unfavorable equilibrium.¹¹ In the adamantane system it would appear that C₂ would prefer to be tetrahedrally substituted (as in IIIe) rather than trigonally hybridized (as in IIId) because of angle strain considerations.

(21) The C-CO-C angle of acetone has recently been determined to be 116.3° (ref. 22). E. J. Corey and R. A. Snee (*THIS JOURNAL*, **77**, 2505 (1955)) have pointed out that the similar angle in cyclohexanone can have a value up to 120° without introducing angle strain into the molecule. The similar positions of the carbonyl bands suggest a similarity in the size of the angles.

(22) J. D. Swalen and C. C. Costain, *J. Chem. Phys.*, **31**, 1562 (1959).

(23) The entire widening of the C₁-C₂-C₃ angle from 109.5° in adamantane to a 112.5° in adamantanone can be produced by a decrease in the C₁-C₂ and C₂-C₃ bond lengths from the sp³-sp³ value of 1.54 Å. to an sp³-sp² value of 1.51 Å. (The C-CO distance in acetone is 1.515 Å. (ref. 22); the C-CO average of four other acetyl compounds is 1.498 Å. L. C. Krisher and E. B. Wilson, Jr., *J. Chem. Phys.*, **31**, 882 (1959); cf. G. R. Somayajulin, *ibid.*, **31**, 919 (1959)).

Solvolysis of Tosylates on a Methylene Bridge.—Saturated norbornane derivatives, with substituents on the methylene bridge or 7-position (IV), show a remarkable lack of solvolytic reactivity when compared with other secondary compounds^{14,24-26} (Table I). Hydrocarbon substitution reactions carried out with norbornane give little or no 7-substituted product.^{27,28}

Several possible explanations have been advanced to account for the diminished reactivity of 7-norbornyl compounds. (1) The *exo*-hydrogen atoms hinder solvation of the transition state sterically to an unusually great extent. (2) Ionization increases steric strain ("I-Strain")²⁹ by two processes: (a) The C₁-C₇-C₄ angle (IV) is known to be restricted to a value considerably smaller than normal.³⁰ Therefore, formation of the quasi-trigonal transition state with preferred 120° angles would be resisted. (b) The favorable skew relationship of the substituents upon carbon atoms 1, 7 and 4 (IV) in the ground state would be converted to energetically unfavorable eclipsed conformations in the transition state. (3) Because the hydrogens of C₁ and C₄ are attached to bridgeheads, there would be steric inhibition of C-H hyperconjugation (Bredt's rule).³¹ The last effect was postulated to be the most important factor.²⁴

Choice between these alternatives is made possible by comparison of the 7-norbornyl with the 2-adamantyl systems, since both have many features in common. The same relationship with the bridgehead hydrogens is present, and therefore arguments 2b and 3 above should be equally applicable to the adamantane series.³² The hydrogen atoms in the vicinity of the tosyl group in IIIg should hinder solvation of the transition state to a slightly greater extent than in the norbornane series, because of their greater proximity to the functional group. This solvation factor, at best, is probably minor.^{14,33} The only appreciable environmental difference is the value of the C-C-C angle of the methylene bridge of the two compounds: 98.3° for norbornane³⁰ and 109.5° for adamantane.³⁴

(24) J. D. Roberts, F. O. Johnson and R. A. Carboni, *THIS JOURNAL*, **76**, 5692 (1954); W. G. Woods, R. A. Carboni and J. D. Roberts, *ibid.*, **78**, 5653 (1956).

(25) S. Winstein, F. Gadiant, E. T. Stafford and P. E. Kleindinst, Jr., *ibid.*, **80**, 5895 (1958).

(26) E. E. van Tamelen and C. I. Judd, **80**, *ibid.*, 6305 (1958); R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

(27) E. C. Kooyman and G. C. Vegter *ibid.*, **4**, 382 (1958).

(28) G. W. Smith, *THIS JOURNAL*, **81**, 6319 (1959); also see ref. 9 and contrast the behavior of norbornadiene, P. R. Story, *ibid.*, **82**, 2085 (1960).

(29) H. C. Brown, *J. Chem. Soc.*, 1248 (1956).

(30) A value of 98.3° has recently been calculated for this angle; H. Krieger, *Suomen Kemi*, **B31**, 348 (1958). Cf. also C. F. Wilcox, Jr., *THIS JOURNAL*, **82**, 414 (1960); J. C. Martin and P. D. Bartlett, *ibid.*, **79**, 2533 (1957); refs. 17, 24, 27 and Table II.

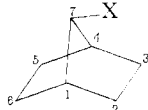
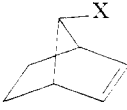
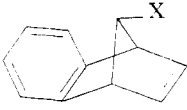
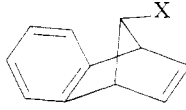
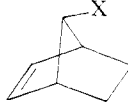
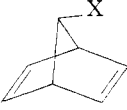
(31) V. J. Shiner, *THIS JOURNAL*, **82**, 2655 (1960).

(32) Professor J. D. Roberts (personal communication) has not been able to prepare adamantane, either as an isolable compound or as a reaction intermediate, by attempted dehydrohalogenation of 1-bromoadamantane. L. K. Montgomery and J. D. Roberts, *ibid.*, **82**, 4750 (1960).

(33) The similarity of solvation effects in the two methylene bridge compounds is further suggested by the close correspondence of their entropies of activation. (Table I). These latter values have rather large combined limits of error, however.

(34) Anchimeric assistance during solvolysis cannot be regarded as

TABLE III
RELATIVE SOLVOLYSIS RATES OF 7-NORBORNYL DERIVATIVES

					
IV	V	VI	VII	VIII	IX
Rel. rate 1	10 ⁴	10 ⁸	10 ⁸	10 ¹¹	10 ¹⁴
Refs. 14	24, 41	42	42	14, 24, 43	44

The acetolysis data of Table I reveal that the unusual lack of reactivity of 7-norbornyl tosylate is not shared by 2-adamantyl tosylate (IIIg). The latter compound solvolyzes only 15 times slower than the cyclohexyl derivative, but 7-norbornyl tosylate is seven powers of ten less reactive. We conclude, therefore, that increase in angle strain in passing from a tetrahedral ground state to a quasi-trigonal transition state is of primary importance in determining rate differences in these systems. Furthermore, this factor can in itself be responsible for rate effects of many orders of magnitude when the angle involved is constrained to abnormally small values.³⁵ It is quite possible that a significant portion of the small rate difference between cyclohexyl and 2-adamantyl tosylates may also be due to angle strain. The cyclohexane ring can accommodate any transition state angle including 120° without increase of angle strain,²¹ but the more rigid adamantane system tends to resist a process involving a change from tetrahedral to trigonal substitution at the 2-position (*vide supra*).

The relative unimportance of the factor of C-H hyperconjugation at a bridgehead in influencing the solvolysis rate of a substituent upon an adjacent carbon is particularly interesting in the light of Shiner's recent finding that the normal β -deuterium secondary isotope effect is sterically inhibited when the deuterium is situated upon a bridgehead.³¹

The demonstration of the influence of angle strain has an important bearing for the interpretation of solvolytic reactivities.³⁶ For example cyclobutyl tosylate, with approximately 90° angles between internal bonds, is abnormally reactive in solvolysis.^{29, 27, 38} Anchimeric assistance, for which abundant evidence exists,³⁷⁻³⁹ is strongly implicated. The acetolysis rate of cyclopropyl tosylate is 2×10^{-5} that of cyclohexyl tosylate.³⁷ While this rate appears to be quite slow, it can be argued that this apparent lack of reactivity is deceiving. Cyclopropyl tosylate, with 60° internal

angles, reacts two orders of magnitude *faster* than 7-norbornyl tosylate, with a 98.3° angle at the reaction site. Considerable anchimeric assistance may be present in the solvolysis of cyclopropyl derivatives.⁴⁰ It is interesting that the acetolysis product of cyclopropyl tosylate is exclusively the rearranged product, allyl acetate.³⁷

The effects produced upon the solvolysis rate of 7-substituted derivatives of norbornane by the introduction of elements of unsaturation into the bicycloheptane nucleus are nothing less than astounding. Table III summarizes the results, which have generally been interpreted in terms of anchimeric assistance due to homoallylic or other non-classical electron delocalization.^{14, 24, 41, 43, 44}

Bartlett and Giddings⁴² and Zbinden and Hall,¹⁷ on the other hand, have called attention to the change in geometry of the norbornane molecule caused by introduction of one or two elements of unsaturation, as in V or VIII and IX. While the length of the C₂-C₃ bond (and, where applicable, the C₅-C₆ bond) is decreased when double (in V or VIII) or aromatic (in VI), there is an attendant flattening of the molecule as a whole which results in an increase in the C₁-C₄ distance and, as a consequence, an increase in the C₁-C₇-C₄ angle. The postulate of Bartlett and Giddings⁴²—that at least part of the increased rate of the unsaturated compounds V-IX is due to the partial relief of the strain of the C₁-C₇-C₄ angle—is confirmed by the results of the present paper. A quantitative assessment of this factor is prevented by the unavailability of the necessary molecular structure data.

Experimental⁴⁵

Hydroxylation of Adamantane.⁹—A solution of 150 g. (1.1 moles) of adamantane^{1,4} in 1870 g. of methylene chloride was mixed with 422 g. of a solution of 103 g. (1.35 moles) of peracetic acid in ethyl acetate.⁴⁶ While being stirred vigorously, the solution was irradiated with a 100-watt Hanovia ultraviolet light placed in an immersion well in the

(40) Cf. S. Winstein, *et al.*, *ibid.*, **81**, 6523, 6524 (1959), for an analogy. In cyclopropane itself, the intermediate might be represented as i.



(41) S. Winstein and E. T. Stafford, *ibid.*, **79**, 505 (1957).

(42) P. D. Bartlett and W. P. Giddings, *ibid.*, **82**, 1240 (1960).

(43) S. Winstein and G. Ordonneau, *ibid.*, **82**, 2084 (1960).

(44) S. Winstein and M. Shatavsky, *ibid.*, **78**, 592 (1956).

(45) Melting points were determined in sealed, soft-glass capillaries by means of a Hershberg apparatus using calibrated Anschütz thermometers. Microanalyses were by Mr. George Robertson, Florham Park, N. J.

(46) B. Phillips, F. C. Frostick, Jr., and P. S. Starcher, *ibid.*, **79**, 5982 (1957); B. Phillips, P. S. Starcher and B. D. Ash, *J. Org. Chem.*, **23**, 1823 (1958).

being probable on theoretical grounds since driving force is lacking nor can it be supported experimentally, since only unrearranged secondary acetate was formed during acetolysis of IIIg. 7-Norbornyl brosylate, interestingly, gave 9% rearranged products (ref. 25).

(35) An alternative explanation stresses the greater *p*-character of the carbon-to-carbon bonds in such a strained relationship, and the attendant greater difficulty of the partial localization of the necessary transition state *p*-orbital (ref. 36).

(36) A. Streitwieser, Jr., *Chem. Revs.*, **56**, 571 (1956).

(37) J. D. Roberts and V. C. Chambers, *THIS JOURNAL*, **73**, 5034 (1951).

(38) H. C. Brown and G. Ham, *ibid.*, **78**, 2735 (1956); Brown H. C. and K. Ichikawa, *Tetrahedron*, **1**, 221 (1957).

(39) R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver and J. D. Roberts, *THIS JOURNAL*, **81**, 4390 (1959), and refs. cited therein.

center of the solution. Gas evolution was evident from the start. The temperature was maintained at 40–45° for the 21-hr. irradiation period; at the end of this time 94.8% of the peracid had been consumed. The solution was concentrated to near dryness with a water aspirator, treated twice in succession with 100-ml. portions of toluene and re-evaporated to dryness. Final drying in a desiccator gave 155 g. of white solid.

Chromatography of Crude Hydroxylated Adamantane.—A portion (9.16 g.) of the above material was dissolved in the minimum amount of benzene-petroleum ether (30–60°). This solution was added to the top of a column of 500 g. of chromatography grade alumina, and the chromatogram was conducted in the usual manner. Each fraction eluted consisted of 150–200 ml. of solution.

Eluting solvent	Frac-tions	Wt., g.	Comment
50% benzene in petr. ether	3–5	5.21	Adamantane
2–20% ether in petr. ether	6–25	0.31	Indefinite material
20% ether in petr. ether	26–30	0.21	^a
20–0% petr. ether in ether	31–48	None	
2% methanol in ether	49–51	0.25	^b
	52–57	1.98	^c
5% methanol in ether	58–64	0.35	More highly oxygenated material
100% methanol	65–72	0.52	
		8.83	Total recovered

^a Unidentified material with a carbonyl peak at 5.78 μ in the infrared (see below). ^b M.p., crude, 271–271.5°; infrared analysis showed this material to be an alcohol (2-adamantanol) contaminated with some 1-adamantanol. Besides the 2.77 μ OH peak, 2-adamantanol (IIa) has characteristic bands at 9.50, 9.71 and 10.08 μ . ^c M.p. of crude material, 257–258°; recrystallization from 30–60° petroleum ether at –70° raised the m.p. to 287.2–288.5°, which was unchanged by further recrystallization; reported for 1-adamantanol II: m.p. 288.5–290°, 282°. This material, which was identical with 1-adamantanol (II) prepared by the literature method,^{6,7} had characteristic infrared bands at 8.98, 9.21, 10.18 and 10.75 μ .

1-Adamantanol (II).—*Anal.* Calcd. for C₁₀H₁₆O: C, 78.89; H, 10.59. Found: C, 79.08; H, 10.47.

***p*-Nitrobenzoate of 1-Adamantanol (II).**—Recrystallization from ethanol gave a derivative of m.p. 185.8–186.1°.

Anal. Calcd. for C₁₇H₁₉NO₄: C, 67.76; H, 6.36. Found: C, 67.75; H, 6.53.

Attempted Oxidation of 1-Adamantanol (II).—Attempted CrO₃-acetone¹⁰ oxidation of 1-adamantanol (II) gave only starting material. The recovery was 90%.

Chromic Acid Oxidation of Hydroxylated Adamantane.—Crude, hydroxylated adamantane (100 g.) was partially dissolved in 1 l. of C.P. acetone. The oxygenated components went into solution but not all of the adamantane. Chromic acid-sulfuric acid solution¹¹ was added dropwise until an excess was present, and the reaction mixture was stirred overnight. The acetone solution was decanted from the precipitated chromic sulfate and adamantane, and was dried with sodium sulfate. Adamantane, 30 g., was recovered by dissolving the chromium salts in water and filtering. Evaporation of the acetone solution yielded 70 g. of white solid.

Chromatography of Chromic Acid Treated Hydroxylated Adamantane.—The entire 70 g. from the above reaction was chromatographed, using 2.5 kg. of alumina. Standard procedures were used.

Eluting solvent	Frac-tions	Wt., g.	Comments
50% benzene in petr. ether	1–15	32.12	Adamantane
100% ethyl ether	16–23	7.18	^a
5% methanol in ether	24–30	4.51	^b
	31–35	8.52	1-Adamantanol
40% methanol in ether	36–40	15.44	1-Adamantanol
100% methanol	41–44	1.79	Polyoxygenated material
		69.56	Total recovered

^a The ketone band at 5.79 μ identified the material as adamantanone (IIIb). Recrystallization from petroleum ether at –70° gave white crystals of m.p. 281.2–282.8°.

^b The infrared spectrum showed a prominent C=O peak at 5.78 μ . Recrystallization from cyclohexane gave material of m.p. 285.4–286.6° unchanged by further purification.

Adamantanone (IIIb).—*Anal.* Calcd. for C₁₀H₁₄O: C, 79.95; H, 9.39. Found: C, 80.20; H, 9.57.

2,4-Dinitrophenylhydrazone of Adamantanone (IIIb).—The derivative had m.p. 221–222.5° after recrystallization from ethanol.

Anal. Calcd. for C₁₆H₁₈N₄O₄: C, 58.17; H, 5.49. Found: C, 58.12; H, 5.68.

Carbonyl Compound M. P. 286°.—*Anal.* Calcd. for C₁₂H₁₈O₂: C, 74.19; H, 9.34. Found: C, 74.46; H, 9.40. Found duplicate analysis:¹² C, 74.10; H, 9.16.

The obvious structural assignment—acetate ester—is ruled out by both the infrared spectrum (no 8.1 μ acetate band)⁴⁸ and by n.m.r. analysis (no methyl group present).¹² The structure of this material, which was also found in the chromatogram of hydroxylated adamantane (see above), is being investigated.

Composition of Hydroxylated Adamantane Mixture.—From the results of the preceding chromatogram the composition of the hydroxylated adamantane mixture can be estimated to be: adamantane, 62.1%; 1-adamantanol (II), 24.0%; 2-adamantanol (IIa), 7.2%; unknown carbonyl compound, m.p. 286°, 4.5%; and polyoxygenated material, 1.8%. The total yield of hydroxyadamantanes based on unrecovered adamantane was 74%.

Reduction of Adamantanone. 2-Adamantanol (IIIa).—Adamantanone (IIIb) (3.0 g.) was reduced with lithium aluminum hydride in ether. The reduction was worked up by adding saturated Na₂SO₄ solution to decompose excess hydride. Decantation from the precipitated salts gave a dry ether solution, which, when evaporated, gave 2.75 g. (91%) of crude 2-adamantanol (IIIa). Four recrystallizations from cyclohexane produced the analytical sample, m.p. 296.2–297.7°. The mixed m.p. with 1-adamantanol was 286.0–289.2°.

Anal. Calcd. for C₁₀H₁₆O: C, 78.89; H, 10.59. Found: C, 78.66; H, 10.74.

2-Adamantyl *p*-Toluenesulfonate (IIIg).—2-Adamantanol (1.5 g.) was treated with 3 g. of freshly purified⁴⁹ *p*-toluenesulfonyl chloride in 40 ml. of pyridine, which had been dried by distillation of the A. R. grade over barium oxide. The reaction temperature was 0° and the reaction time was one week. The solution, which had deposited crystals of pyridine hydrochloride, was poured into ice-water and the precipitate filtered off after stirring. Recrystallization from petroleum ether at –70° gave 2-adamantyl tosylate, 1.8 g. of a white solid, m.p. 82.7–83.7°. A further recrystallization did not alter the m.p.

Anal. Calcd. for C₁₇H₂₂SO₄: C, 66.50; H, 7.24; S, 10.46. Found: C, 66.63; H, 7.41; S, 10.59.

Preparation of 2-Methyl-2-adamantanol (IIIc).—The Grignard reagent prepared from 14.2 g. of methyl iodide and 2.3 g. of magnesium was treated with 3.0 g. of adamantanone (IIIb). Following the conventional work-up, there remained a pale yellow solid which gave 2.47 g. of a white solid, m.p. 207.8–209.0° after recrystallization from petroleum ether.

Anal. Calcd. for C₁₁H₁₈O: C, 79.46; H, 10.92. Found: C, 79.25; H, 10.92.

***p*-Nitrobenzoate of 2-Methyl-2-adamantanol.**—The derivative after recrystallization from ethanol had m.p. 133.1–133.7°.

Anal. Calcd. for C₁₈H₂₁NO₄: C, 67.31; H, 6.98; N, 4.62. Found: C, 67.50; H, 6.91; N, 4.44.

Preparation of Methyleneadamantane (IIId).—2-Methyl-2-adamantanol (IIIc) (1.0 g.) was heated with 10 ml. of 85% phosphoric acid. The white solid which had collected by sublimation was taken up in ether, washed twice with 5% K₂CO₃ solution and then with water. The ether solution was dried with solid Na₂SO₄ and evaporated to give 0.76 g. of white solid. The infrared spectrum of this material had characteristic olefin bands at 3.24, 6.04 and 11.34 μ , but no alcohol peaks. Two sublimations of this substance gave 0.46 g. of a waxy, white solid, m.p. 135.8–136.5°.

(47) By the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

(48) L. J. Bellamy, "Infra-red Spectra of Complex Molecules," J. Wiley and Sons, Inc., New York, N. Y., 2nd ed., 1958, p. 179.

(49) S. W. Pelletier, *Chemistry & Industry*, 1034 (1953).

Preparation of 2-Methyladamantane (III_f).—Methyleneadamantane (III_d) (1.42 g.) was hydrogenated in ether solution using PtO₂ catalyst, using a Parr apparatus. Evaporation of the solvent left a solid which was purified by sublimation to yield 1.1 g. of a white solid. Recrystallization from ethanol gave white crystals, m.p. 143.8–146.0°. The compound is quite different from 1-methyladamantane, m.p. 103°. ⁷

Anal. Calcd. for C₁₁H₁₈: C, 87.92; H, 12.08. Found: C, 87.67; H, 12.01.

Reaction of 2-Methyl-2-adamantanol with Formic Acid.—A solution of 1.0 g. of 2-methyl-2-adamantanol (III_c) in 40 ml. of 98–100% formic acid was heated for 3 hours on the steam-bath. The reaction mixture was poured into water and extracted with ether. The ether extracts were dried over K₂CO₃ and Na₂SO₄. Evaporation gave 0.98 g. of an oil, which showed none of the bands characteristic of methyleneadamantane (III_d) in the infrared, but rather possessed a strong carbonyl peak at 5.78μ and a formate ester band⁴⁸ at 8.42μ.

The material, presumed to be the formate ester III_e, was not characterized or purified further, but was saponified directly with 2.0 g. of KOH in alcohol solution. Work-up gave 0.85 g. of a yellow-white solid. One recrystalliza-

tion from petroleum ether gave a white solid identical with the starting material, 2-methyl-2-adamantanol (III_c).

Kinetic Procedures.—Standard titrimetric procedures were employed.^{15–15,24–26,37,38,42,43} Aliquots of 0.03–0.04 molar solutions of the tosylate ester were sealed into ampoules. Carefully dried and fractionally distilled acetic acid was used as the solvent. At the appropriate times the aliquots were titrated with 0.05 molar sodium acetate in acetic acid to the brom thymol blue end-point. Experimentally determined infinity titers were used to calculate the rate constants. Two separate runs were made at each temperature; their agreement was good. The constant temperature baths were checked against an NBS calibrated thermometer.

Solvolysis Product of 2-Adamantyl Tosylate.—The combined acetic acid solutions from the kinetic runs were made "basic" by adding excess Na₂CO₃ and were refluxed overnight. The solution was poured into water, and extracted with ether. After washing and drying, the ether solution was evaporated to give an oil which had infrared peaks at 5.75 (ester carbonyl) and at 8.05μ (acetate).⁴⁸ The acetate was saponified in ethanol with 1 g. of KOH. The solid residue present after the work-up was sublimed to give a material whose infrared spectrum was identical with that of pure 2-adamantanol (III_a).

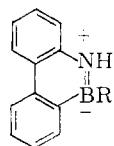
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, QUEEN MARY COLLEGE, UNIVERSITY OF LONDON, LONDON, ENG.]

New Heteroaromatic Compounds. Part VIII. The Reactions of Some Borazarophenanthrenes¹ with Methyl- and Phenyllithium

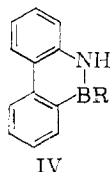
BY M. J. S. DEWAR² AND P. M. MAITLIS

RECEIVED JUNE 27, 1960

Previous papers³ in this series have described a number of derivatives of 10,9-borazarophenanthrene (I), all of which have an imino group in the 9-position. The original purpose of this investigation was to prepare 9-substituted-10,9-borazarophenanthrenes.



I, R = H
II, R = Me
III, R = Ph



IV

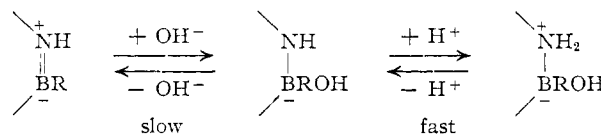
Since previous work³ has indicated that these compounds are aromatic, the dipolar resonance structures I must make significant contributions to their ground states. (For this reason they are formulated^{1,3} in terms of dipolar structures rather than uncharged structures (IV).) This suggests that the imino group should show acidity similar to that of the imino groups in five-membered heterocyclics such as pyrrole or indole where again dipolar resonance structures are important. We were therefore surprised to find that the 10-methyl derivative II failed to react with dimethyl sulfate in presence of alkali and that the potassio derivative could not be prepared by the usual methods.

(1) For nomenclature see M. J. S. Dewar and R. Dietz, *J. Chem. Soc.*, 2728 (1959).

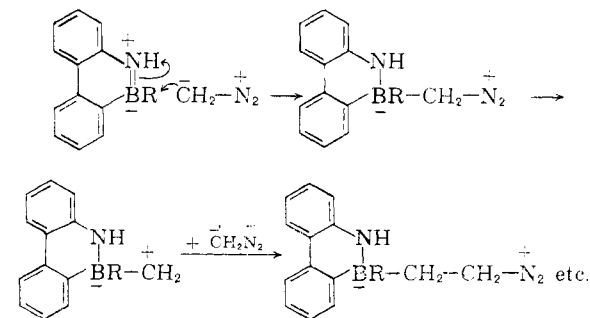
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(3) Cf. M. J. S. Dewar, V. P. Kubba and R. Pettit, *J. Chem. Soc.*, 3073 (1958). M. J. S. Dewar and V. P. Kubba, *Tetrahedron*, **7**, 213 (1959).

It is true that the imino hydrogen exchanged rapidly in alkaline deuterium oxide, but this exchange could have involved an addition-elimination mechanism, *i.e.*



Attempts to methylate II with diazomethane also failed; a vigorous reaction took place leading to a polymer (presumably polymethylene), but II could be recovered quantitatively. Evidently II, like boron trifluoride, catalyzes the decomposition of diazomethane very efficiently; a likely mechanism seems to be



Here again the borazarophenanthrene acts as a Lewis acid rather than a proton donor.

We finally obtained the 9-lithio derivative (V) of II by reaction with one mole of methylolithium in ether, methane being evolved; and with freshly