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Some Reactions of Adamantane and Adamantane Derivatives

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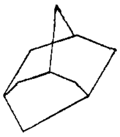
Reactions of adamantane, including bromination, chlorination, sulfonation, hydroxymethylation, nitration, and air oxidation were investigated. A rather high selectivity for attack in the tertiary position was observed for bromination and nitration. Some selectivity for tertiary substitution was demonstrated in the chlorination reaction when the proper solvent was employed. Monochloroadamantane, 1-bromoadamantane, 1-nitroadamantane, 1,3-dinitroadamantane, trinitroadamantane, 1,3-diaminoadamantane, adamantanone, 1-hydroxyadamantane, 2-aminoadamantane, hydroxymethyladamantane, and adamantanesulfonic acid monohydrate were among the compounds prepared in this study.

Until recently, very few reactions of adamantane were reported in the literature, probably because of the unavailability of the hydrocarbon itself. In the past, adamantane was obtained in small amounts from either petroleum naphtha[1] or by synthetic methods, the best of which afforded over-all yields of only a few per cent. An excellent review of the literature on the chemistry of adamantane ring systems appeared in 1954.[2] Recently, a two-step preparation of adamantane from dicyclopentadiene was reported.[3] In view of this new source of adamantane and an interesting report on the bromination and iodination of adamantane,[4] we were prompted to investigate some reactions of this unique hydrocarbon. After the work described herein was completed, the preparation of certain 2-substituted derivatives of adamantane by a hydroxylation process was reported.[5]

RESULTS AND DISCUSSION

The highly symmetrical molecule of adamantane (I) possesses six secondary carbons and four tertiary (bridgehead) carbons. It was of interest to determine the relative ease of attack at the secondary and tertiary positions in various reactions. The results reported for the bromination of adamantane indicated that the product isolated was the tertiary monobromo derivative.[4] Recently, more evidence including NMR data was offered to show that the monobromo derivative was the bridgehead compound.[6] Our work on the bromination of adamantane indicated the same conclusion. When the bromination of adamantane was carried out in a manner similar to that described by Landa and co-workers,[4] almost the entire product was monobromoadamantane. Vapor chromatography showed that only one major product and a trace amount (<1%) of a minor product (probably a dibromo derivative) of higher retention time were present. Resolution of the monobromo peak was not realized even at lower column temperatures and reduced helium rates. This fact and the sharp melting point of the product indicated that a single isomer was present. Furthermore, NMR studies indicated that the single isomers obtained was the tertiary derivative. Such a high selectivity of attack by bromine was previously observed in other bromination reactions.[7] Bromination of monobromoadamantane afforded low conversions to a dibromo derivative. When the reaction temperature was increased from 100° to 125° the attack of bromine was less selective as evidenced by the presence of additional peaks in the dibromo region of the vapor chromatograms.



I

In contrast to the reaction of bromine, chlorine attacked the hydrocarbon in a random manner to yield a complex mixture of chloro derivatives. The separation of individual isomers was not easily accomplished. According to a report of some recent work on the photochlorination of 2,3-dimethylbutane, certain aromatic solvents caused an increased selectivity for attack at the tertiary positions.[8] Even more recently, additional information concerning solvent effects in chlorination reactions was reported.[9,10] Because of the random attack observed in the photochlorination of adamantane in carbon tetrachloride, other solvents were substituted which were reported to increase the selec-

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[1] S. Landa and V. Macháček, *Coll. Czech. Chem. Comm.*, **5**, 1 (1933).

[2] H. Stetter, *Angew. Chem.*, **66**, 217 (1954).

[3] P. von R. Schleyer, *J. Am. Chem. Soc.*, **79**, 3292 (1957).

[4] S. Landa, S. Kriebel, and E. Knobloch, *Chem. Listy*, **48**, 61 (1954); *Chem. Abstr.*, **49**, 1598 (1955).

[5] P. von R. Schleyer, Abstracts of Papers, Third Delaware Valley Regional Meeting, American Chemical Society, Philadelphia, Pa., Feb. 25, 1960.

[6] H. Stetter, M. Schwary, and A. Hirschhorn, *Ber.*, **92**, 1629 (1959).

[7] A. V. Grosse and V. N. Ipatieff, *J. Org. Chem.*, **8**, 438 (1943).

[8] G. A. Russell, *J. Am. Chem. Soc.*, **79**, 2977 (1957).

[9] (a) *J. Am. Chem. Soc.*, **80**, 4987 (1959); (b) *J. Am. Chem. Soc.*, **80**, 4997 (1958); *J. Am. Chem. Soc.*, **80**, 5002 (1958).

[10] C. Walling and M. F. Mayahi, *J. Am. Chem. Soc.*, **81**, 1485 (1959).

tivity of attack. Indeed, in photochlorination experiments identical in every detail except for the solvent employed, a change in the product composition occurred. Carbon tetrachloride, benzene, and carbon disulfide were employed as the solvents in these experiments. Both monochloroadamantane isomers were formed in these reactions, but the ratio of these two isomers varied with the solvent used. Table I illustrates the ratio change as estimated from vapor chromatographic results. Monochloro isomer A, which had the shortest retention time, is believed to be 1-chloroadamantane. After isolation and purification, this isomer gave a melting point which corresponded to that reported for the 1-chloro derivative prepared by an independent route.[6] Also of interest is the fact that vapor chromatography showed that no polychlorination of adamantane occurred in carbon disulfide under the conditions employed and only a very minor amount occurred in benzene. However, when carbon tetrachloride was employed as solvent, a fair amount of polychlorination did occur.

TABLE I

EFFECT OF SOLVENT ON RATIO OF MONOCHLOROADAMANTANE ISOMERS

Solvent	Monochloro Isomer A/ Monochloro Isomer B
Carbon disulfide	2.10
Benzene	1.17
Carbon tetrachloride	0.63

Thus, the effect of certain solvents in the photochlorination of adamantane apparently is to decrease the activity of the chlorinating species as evidenced by the selectivity of attack and the decrease in polychlorination. These results are in agreement with those reported earlier.[8-10]

A derivative which contained a sulfonic acid group was isolated from the reaction of adamantane with sulfur dioxide and oxygen according to the "Hostapon" process.[11] Elemental analysis indicated that this compound was the monohydrate of adamantane sulfonic acid. Infrared analysis clearly showed the presence of a hydrated sulfonic acid group. It was not determined whether the sulfonic acid was the secondary or tertiary derivative.

The free radical addition of adamantane to formaldehyde yielded a product from which hydroxymethyladamantane was isolated.[12] Although the position of the hydroxymethyl group on the adamantane nucleus was not determined, the melting point of our derivative coincides with that reported recently for 1-hydroxymethyladamantane.[6]

It was reported that adamantane is not attacked by concentrated nitric acid even under the most severe conditions.[2] Also in our studies, no nitration occurred when adamantane reacted with 20% nitric acid at 130° and 500 psi nitrogen pressure. The absence of a mutual solvent for the reagents probably is the main reason for the failure to react.

In an attempt to carry the reaction out under more ideal conditions, a mutual solvent was employed. Nitration did occur in carbon tetrachloride when adamantane and nitrogen dioxide were subjected to 140–160° and 300 p.s.i.ga. nitrogen pressure.[13] The use of carbon tetrachloride in the reaction, however, was not satisfactory, because attack on the solvent by reaction intermediates led to the formation of chloroadamantane derivatives in addition to the nitration products.[14] The formation of chloro compounds by such an attack on carbon tetrachloride has been reported in other reactions.[15,16]

Glacial acetic acid was a more amenable solvent for the nitration reaction. The reaction of adamantane and concentrated nitric acid in this medium led to nitro compounds as the major products plus minor amounts of oxidation products (carbonyl and hydroxy derivatives). As in the bromination reaction, nitration of adamantane gave a highly selective attack in the tertiary positions. If the reaction was carried out at 140° and 500 psi nitrogen pressure, the major product was 1-nitroadamantane. Further nitration of this product at 170° and 600 p.s.i.ga. nitrogen pressure yielded 1,3-dinitroadamantane (20% yield from adamantane) as the principal product. Reaction temperatures above 170° afforded a greater proportion of oxidation products, whereas at 100° little or no reaction occurred. A trinitroadamantane derivative also was isolated from the reaction mixture.[17]

Catalytic hydrogenation of 1,3-dinitroadamantane to 1,3-diaminoadamantane was essentially quantitative. A few derivatives of this diamine (a known compound prepared by an independent route[18]) which included the picrate, the dihydro-

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(11) T. B. Brooks, *The Chemistry of the Nonbenzenoid Hydrocarbons*, Reinhold, New York, 1950, p. 190.

(12) A procedure similar to that employed by Fuller and Rust with other hydrocarbons was used (G. Fuller and F. R. Rust, *J. Am. Chem. Soc.*, **80**, 6148 (1958)).

(13) Reaction also occurred with nitrogen dioxide in the absence of a solvent, but under the conditions employed (batch reaction), the reaction was difficult to control.

(14) The presence of chloro and chloronitro derivatives of adamantane was indicated by qualitative and quantitative analyses as well as infrared analysis (a band at 9.70 μ is characteristic of chloroadamantane).

(15) P. Wilder, Jr., and A. Winston, *J. Am. Chem. Soc.*, **75**, 5370 (1953).

(16) W. G. Dauben and H. Tilles, *J. Am. Chem. Soc.*, **72**, 3183 (1950).

(17) The alkali-insolubility of this trinitro derivative and the high selectivity for attack at the tertiary positions observed in the nitration reaction suggest that this compound is the 1,3,5- isomer.

(18) V. Prelog and R. Seiwerth, *Ber.*, **74**, 1771 (1941).

chloride, a carbonate, and the dibenzamide were prepared. An agreement of the melting points of our derivatives with those of known compounds showed that our compound was the 1,3- isomer. A rather stable dinitrous acid salt of the diamine also was prepared.

Air oxidation of adamantane afforded both adamantanone and 1-hydroxyadamantane, as well as at least one unidentified polysubstituted derivative. The reaction was carried out in a mixture of benzene and glacial acetic acid (50/50 vol.%) in the presence of cobalt acetate and an organic peroxide at 140–145° and 800 p.s.i.ga. air pressure. At 100° very little oxidation occurred, while at 170° the oxidation apparently proceeded too far as evidenced by a smaller yield of total oxidate.

A comparison of the air oxidates from two runs, identical except for the peroxide used, is given in Table II. These results show that larger amounts of oxidation products were isolated when di-*t*-butyl peroxide was used as the catalyst. Also, this peroxide apparently caused a greater selectivity for attack at the tertiary positions as evidenced by the increase in the concentration of 1-hydroxyadamantane relative to the concentration of adamantanone.

TABLE II

ADAMANTANE AIR OXIDATE

	% Yield[a]	
	Run A[b]	Run B[c]
1-Hydroxyadamantane	8	21.5
Adamantanone	10	12.0
Unknown[d]	6	4.8
Total Oxidate	24	38.3

[a] Calculated from vapor chromatography results. [b] Benzoyl peroxide used as catalyst. [c] Di-*t*-butyl peroxide used as catalyst. [d] For calculation, the unknown was assumed to be a hydroxyadamantanone.

The ketone derivative was catalytically hydrogenated in the presence of ammonia to yield 2-aminoadamantane. A mixed melting point of the monohydroxyadamantane derivative isolated from the air oxidate with 1-hydroxyadamantane prepared by the hydrolysis of 1-bromoadamantane gave no depression.

In general, the reactions of adamantane indicated that attack occurs preferentially at the tertiary positions. In the case of a more reactive agent, such as a chlorine radical, the attack becomes more random. However, when the reactivity of the attacking group is moderated in some manner, a greater selectivity is realized.

EXPERIMENTAL[19]

Preparation of adamantane. The general procedure as outlined by Schleyer was employed in the preparation of adamantane.[3] Final purification of adamantane was accomplished by recrystallization from petroleum ether (b.p. 60–90°). The pure hydrocarbon melted at 268.5–269.5°.

Analysis of compounds. The infrared analyses were made on a Perkin-Elmer Model 21 spectrophotometer using sodium chloride optics. The vapor-phase chromatography was performed on an F & M Scientific Corporation high temperature vapor fractometer (Model 17A). The column consisted of 5 feet of silicone-on-Celite and temperatures are mentioned in the description of the individual experiments.

1-Bromoadamantane. Bromination of adamantane was carried out in a manner similar to the procedure employed by Landa and co-workers.[4] A mixture of 6.8 g. (0.05 mole) of adamantane and 32.0 g. (0.20 mole) of bromine was placed in a glass-lined shaker bomb and heated at 100° for 4.0 hr. at 400 p.s.i.ga. nitrogen pressure. The reaction mixture was dissolved in carbon tetrachloride, washed successively by 10% sodium sulfite solution and 5% sodium bicarbonate solution, and dried over anhydrous calcium chloride. Concentration of the dried solution and sublimation of the residue at 15–20 mm. pressure and 80–100° afforded 8.3 g. (76% yield) of white solid, m.p. 115–117°. Vapor chromatography (temperature 244°) showed that only one component was present, discounting trace quantities ($<1\%$) of another compound (higher retention time). Recrystallization of the product from methanol and subsequent sublimation yielded the pure compound, m.p. 117.0–117.5° (lit.,[6] m.p., 118°).

Anal. Calcd. for $C_{10}H_{15}Br$: C, 55.82; H, 7.03; Br, 37.1. Found: C, 55.32; H, 7.08; Br, 36.8.

Chlorination of adamantane. The photochlorination of adamantane was carried out at 25–30° by metering 0.037 mole of chlorine into a solution of 10.0 g. (0.074 mole) of adamantane in 100 ml. of solvent in the presence of illumination by a 150-watt G.E. flood lamp. The solvents employed were carbon tetrachloride, benzene, and carbon disulfide. After a short induction period (approximately 2 min.) the reaction was initiated as evidenced by the fading of the chlorine color and the evolution of hydrogen chloride. The reaction mixture was washed by 5% sodium carbonate solution, water, and dried over anhydrous sodium sulfate. The product obtained by concentration of the dried solution was shown by vapor chromatography (temperature—200°) to consist mainly of adamantane and the two monochloroadamantane isomers.

Recrystallization from methanol and sublimation of one chlorination product led to the isolation of the monochloroadamantane isomer with the shortest retention time as indicated by vapor chromatography. This waxy compound melted at 168.5–169.5° (lit.,[6] m.p. for 1-chloroadamantane, 165°).

Anal. Calcd. for $C_{10}H_{15}Cl$: C, 70.36; H, 8.86. Found: C, 70.45; H, 8.93.

Vapor chromatography of this product, however, showed that small amounts of the other monochloro isomer and adamantane were still present as minor contaminants.

Adamantane sulfonic acid hydrate. Sulfur dioxide (0.0736 mole) and oxygen (0.0736 mole) were metered simultaneously into a mixture of 5.0 g. (0.0368 mole) of adamantane, 75 ml. of acetic anhydride, and 2.0 ml. of 30% hydrogen peroxide at 70° for 1.0 hr. During the reaction period the mixture was illuminated by a 150-watt G.E. flood lamp. At the end of the reaction time, the reaction mixture was cooled and poured over 200 g. of ice. Sulfur dioxide was then passed into the ice mixture for a few minutes to decompose the intermediate peranhydride. The acid solution was filtered to remove 2.9 g. of unchanged adamantane. Concentration of the filtrate at reduced pressure yielded a pale yellow viscous residue (mixture of liquid and solid) which, after drying for several days in a vacuum desiccator, weighed 8.1 g. Ethyl acetate (10 ml.) was mixed with this residue, and the resulting insoluble white solid was filtered to give 1.25 g. of

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(19) All melting point determinations were made in sealed capillaries and are uncorrected.

material which melted with decomposition at approximately 170–175°. Recrystallization from ethyl acetate yielded colorless crystals, m.p. 174.4–175.9° (some decomposition) which, when dissolved in water, produced a strongly acidic solution.

Anal. Calcd. for $C_{10}H_{18}O_4S$: C, 51.26; H, 7.74. Found: C, 50.99; H, 7.78.

The elemental analysis indicated that the compound was the monohydrate of adamantane sulfonic acid. Infrared analysis supported the elemental analysis of showing evidence for the presence of a hydrated sulfonic acid group in the pure compound.

The ethyl acetate from which the sulfonic acid derivative was filtered was concentrated, and on standing the residue slowly crystallized (presumably additional sulfonic acid compound).

Hydroxymethyladamantane. A mixture of 20.4 g. (0.15 mole) of adamantane, 9.3 g. (0.114 mole of formaldehyde) of formalin, 2.20 g. of di-*t*-butyl peroxide and 120 ml. of benzene (thiophene-free) was heated in a stainless steel autoclave at 145° and approximately 500 p.s.i.ga. nitrogen pressure for 12 hr. The reaction mixture then was dissolved in additional benzene and ethyl ether and dried over anhydrous magnesium sulfate. Concentration of the dried solution yielded 19.5 g. of a pale yellow solid, which infrared analysis indicated was mainly unchanged adamantane with a minor amount of a hydroxy compound and a trace of a carbonyl derivative. Vapor chromatography (temperature 245°) showed that adamantane comprised 87% of the crude product while a second compound of higher retention time comprised the balance (approximately 12%) of the product. Recrystallization of the crude material from absolute ethanol effected a separation of a large amount of the less soluble adamantane. Concentration of the filtrate from this recrystallization, sublimation (100° and 15–20 mm. pressure) of the residue, and recrystallization of a portion of the sublimate from petroleum ether (b.p., 60–90°) afforded colorless crystals, m.p. 113.2–114.5° (lit.,[6] m.p. of 1-hydroxymethyladamantane, 115°).

Anal. Calcd. for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.50; H, 11.04.

Nitration of adamantane. 1-Nitroadamantane. A mixture of 68.0 g. (0.50 mole) of adamantane and 500 ml. of glacial acetic acid was charged to a stirred stainless steel 1-l. autoclave which was pressurized with nitrogen to a total pressure of 500 p.s.i.ga. After the mixture was heated to 140°, 90.0 g. (1.0 mole) of concd. nitric acid was introduced into the reaction zone by means of a feed pump at a rate of 5–6 ml. per min. When the acid feed was completed, the reaction temperature was maintained at 140° for 15 min., after which time the reaction mixture was cooled to room temperature and diluted with an excess of water to precipitate the products. The filtered solids were slurried with a mixture of 100 ml. of methanol, 150 ml. of water, and 17 g. of potassium hydroxide for 18.0 hr. at room temperature. After dilution with 150 ml. water, the alkali-insoluble material was extracted by petroleum ether (b.p., 60–90°). The petroleum ether extracts were washed by water and dried over anhydrous magnesium sulfate. Concentration of this solution afforded a white solid, m.p. 125–144°, which weighed 38.0 g. The aqueous alkali solution from which the alkali-insoluble material had been extracted was cooled to 0–3° and neutralized by the dropwise addition of an aqueous acetic acid-urea mixture according to the procedure of Kornblum and Graham.[20] The alkali-soluble nitro derivative regenerated by this procedure weighed 1.5 g. and melted over the range 136–160°. Vapor chromatography (temperature 261°) showed that the alkali-insoluble sample was largely mononitroadamantane (72%) with a smaller amount of dinitroadamantane as well as a few unidentified components in minor quantities. The separation of analytically pure mononitroadamantane from the other components of the alkali-insoluble product was difficult. However, by recrystallization from methanol and repeated sublimation (80–90° at 15–20 mm.) a pure sample of 1-nitroadamantane, a white, waxy compound, m.p. 158.5–159.0°, was obtained.[21]

Anal. Calcd. for $C_{10}H_{15}NO_2$: C, 66.27; H, 8.34; N, 7.73. Found: C, 66.22; H, 8.34; N, 7.50.

The infrared spectrum of this compound showed that the symmetrical and asymmetrical stretching bands of the NO_2 group are located at 7.32 μ and 6.52 μ, respectively.

1,3-Dinitroadamantane. This dinitro derivative, which was formed in small amounts under the above conditions, was obtained as the major product either by further nitrating the above alkali-insoluble product at 170° and 600 psi nitrogen pressure or by a more facile procedure of nitrating adamantane in two steps without isolation of the intermediate mononitro derivative. The latter procedure is described in the following. A mixture of 90 g. (0.66 mole) of adamantane and 500 g. of glacial acetic acid was charged to a stirred stainless steel 1-l. autoclave and pressurized to 500 p.s.i.ga. with nitrogen. After heating the contents of the autoclave to 140°, 85 ml. of conc. nitric acid (1.32 moles nitric acid) was introduced into the reaction zone by means of a feed pump at a rate of 8 ml. per min. At the completion of the acid feed and an additional 10-min. period, the pressure was increased to 600 p.s.i.ga. with nitrogen and the temperature was increased to 170°. At this point, 43 ml. of concd. nitric acid (0.66 mole nitric acid) was fed into the reaction zone as before. After completion of this second acid feed, the reaction mixture was maintained at 170° for 10 min. and then cooled to room temperature. The alkali-insoluble and alkali-soluble products were separated as described earlier. The white alkali-insoluble product, m.p. 160–166°, weighed 46 g., and the alkali-soluble product regenerated from its *aci*-salt weighed 7.8 g. Vapor chromatography (at 283°) of the alkali-insoluble product indicated the following composition.

Identity of Component[a]	% of Product
Adamantane	2–3
Mononitroadamantane	16
Unknown	7
Unknown	8
Dinitroadamantane	61[b]
Unknown	2
Trinitroadamantane	4

[a] In order of increasing retention times. [b] Corresponds to a 20% yield from adamantane.

Recrystallization of this alkali-insoluble product from methanol afforded a separation of the less soluble dinitro derivative. Sublimation (100° and 15–20 mm.) of pure 1,3-dinitroadamantane, m.p. 213.5–214.0°, yielded long, silky, colorless needles.

Anal. Calcd. for $C_{10}H_{14}N_2O_4$: C, 53.09; H, 6.24; N, 12.38. Found: C, 53.25; H, 6.28; N, 12.38.

The infrared spectrum of this compound placed the nitro group absorption bands at 6.48 μ and 7.32 μ.

Trinitroadamantane. One alkali-insoluble nitration product was recrystallized from an excess of methanol in order to obtain only the least soluble product. This product was extracted by boiling ethyl ether, and the insoluble white solid was recrystallized from a mixture of ethanol, petroleum ether (b.p., 90–120°), and chloroform to yield white crystals, m.p. 291.0–291.8°.

Anal. Calcd. for $C_{10}H_{13}N_3O_6$: C, 44.28; H, 4.83; N, 15.49. Found: C, 44.50; H, 5.11; N, 15.55.

The positions of the symmetrical and asymmetrical stretching nitro bands in the infrared spectrum are 7.31 μ and 6.47 μ, respectively.

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(20) N. Kornblum and G. E. Graham, *J. Am. Chem. Soc.*, **73**, 4041 (1951).

(21) Melting point reported for this compound is 173° [H. Stetter, J. Mayer *et al.*, *Ber.*, **93**, 226 (1960)].

1,3-Diaminoadamantane. A mixture of 16.2 g. of 1,3-dinitroadamantane (m.p. 213.5–214.0°), 175 ml. of absolute ethanol, and approximately 20 g. of Raney nickel was hydrogenated in a Parr apparatus at 50–60° and an initial hydrogen pressure of 50 p.s.i.ga. After 100 min. the theoretical amount of hydrogen had been absorbed. Concentration of the colorless solution (after filtration to remove catalyst) at reduced pressure (15–20 mm.) gave a semisolid residue. After drying in a vacuum desiccator for several days, the white solid weighed 11.0 g. (92.4% yield). Due to the hygroscopic nature of the diamine, a melting point was not obtained. Vapor chromatography (at 208°) of the product showed that only a single component was present.

When exposed to the atmosphere a sample of the diamine, at first, appeared wet as it rapidly absorbed water and carbon dioxide, but on standing became a dry solid. Elemental analysis indicated that one mole of carbon dioxide and two moles of water were absorbed by the diamine.

Anal. Calcd. for $C_{10}H_{18}N_2.CO_2.2\ H_2O$: C, 53.64; H, 9.00. Found: C, 53.61; H, 8.95.

1,3-Diaminoadamantane dihydrochloride. The dihydrochloride was obtained by bubbling dry hydrogen chloride into an ether solution of the diamine. The dihydrochloride was purified by dissolving in a small amount of water and reprecipitating by adding an excess of acetone. On heating this compound did not melt, but gradually decomposed above 300°, apparently decomposing completely at approximately 430°.[22]

Anal. Calcd. for $C_{10}H_{20}N_2Cl_2$: C, 50.25; H, 8.43; N, 11.71. Found: C, 49.58; H, 8.59; N, 11.84.

The picrate of this diamine was prepared according to the procedure of Shriner and Fuson.[23] The picrate melted and decomposed at approximately 300°. This result agrees fairly well with the value (290–295°) reported in the literature.[18]

Dibenzamide of 1,3-diaminoadamantane. This derivative was prepared by adding benzoyl chloride to a 10% aqueous solution of the diamine. After addition of dilute sodium hydroxide solution, the mixture was stirred for 1.0 hr. The insoluble spongy mass was separated from the aqueous solution and stirred in petroleum ether (b.p. 60–90°) to yield a white crystalline material. Recrystallization of this product from absolute ethanol gave colorless crystals, m.p. 246.5–248.0 (lit.[18] m.p., 248°).

Anal. Calcd. for $C_{24}H_{26}N_2O_2$: C, 76.97: H, 7.00; N, 7.48. Found: C, 76.94; H, 6.98; N, 7.27.

1,3-Adamantyl diammonium nitrite. A mixture of 4.4 g. (0.0265 mole) of 1,3-diaminoadamantane, 0.06 g. of cupric chloride, 20 ml. of methanol, and 5 ml. of water was placed in a small stainless steel shaker bomb, pressurized by nitric oxide to 200–300 p.s.i.ga. and heated at 70° for 3.0 hr. The reaction mixture was concentrated to a solid dark residue at reduced pressure (15–20 mm.) and last traces of water were removed azeotropically with ethanol. Treatment of this residue with a mixture of ethanol and ethyl ether yielded a white solid which was filtered and washed with a small amount of ethanol. After drying, the white solid melted at 158.5–159.5° with some decomposition and weighed 1.2 g. (17.4%). Purification was carried out by dissolving the compound in a minimum of boiling methanol and then diluting with an equal volume of boiling acetone to precipitate the product. The pure compound melted sharply with decomposition at 165.5°.

Anal. Calcd. for $C_{10}H_{20}N_4O_4$: C, 46.14; H, 7.75; N, 21.53. Found: C, 46.36; H, 7.82; N, 21.28.

The infrared spectrum of this compound confirmed the presence of the $-NH^+_3$ group as well as the $-ONO^-$ group. The presence of ionic nitrite also was indicated by a positive Griess test.

The above ammonium nitrite derivative also was obtained in 74% yield by the reaction of the diamine dihydrochloride and freshly precipitated silver nitrite according to the procedure of Monserrat and Prosper.[24]

Air oxidation of adamantane. To a 1-l. stirred stainless steel autoclave was added 60.0 g. (0.441 mole) of adamantane, 0.7 g. of cobalt acetate tetrahydrate, 0.5 g. of di-*t*-butyl peroxide, 150 ml. of glacial acetic acid, and 150 ml. of benzene. The system was pressurized with 800 p.s.i.ga. air pressure and heated to 140–145° for 4.0 hr. After cooling to room temperature the reaction mixture was diluted with 1250 ml. of water, and the insoluble material was extracted by benzene. The benzene extract was washed with water and 5% sodium bicarbonate solution, and dried over anhydrous magnesium sulfate. Concentration of the dried benzene solution yielded 46.5 g. of a yellow solid. Infrared analysis of this product indicated that carbonyl and hydroxy compounds as well as unreacted adamantane were present. Vapor chromatography (at 201°) of the oxidate identified three of the four components from their retention times. The following concentrations were estimated from the vapor chromatogram.

Component[a]	% of Oxidate
Adamantane	44
Hydroxyadamantane	31
Adamantanone	17
Unknown	7.5

[a] Listed in order of increasing retention time.

Sublimation (80–100° and 15–20 mm.) of the air oxidate afforded only a partial separation of the products.

2,4-Dinitrophenylhydrazone of adamantanone. This derivative was prepared from a mixture of hydroxyadamantane and adamantanone according to a standard procedure.[23] The compound was purified by recrystallization from a mixture of 95% ethyl alcohol and ethyl acetate to yield golden yellow silky needles, m.p. 213.5–214.5°.

Anal. Calcd. for $C_{16}H_{18}N_4O_4$: C, 58.17; H, 5.49; N, 16.96. Found: C, 58.95; H, 5.47; N, 16.19.

Oxime of adamantanone. The oxime derivative was prepared from a mixture of hydroxyadamantane and adamantanone according to Procedure B outlined by Shriner and Fuson.[25] Recrystallization of the crude oxime from aqueous ethyl alcohol gave colorless needles, m.p. 162.8–163.6.

Anal. Calcd. for $C_{10}H_{15}NO$: C, 72.69; H, 9.15; N, 8.48. Found: C, 72.74; H, 9.11; N, 9.13.

Adamantanone. A sample of the purified oxime (see above) was hydrolyzed by heating with 10% hydrochloric acid at 100° for 2.0 hr. The ketone which separated from solution was extracted by ethyl ether and the ether extract was washed by water and 5% sodium bicarbonate solution, and finally was dried over anhydrous magnesium sulfate. Sublimation (75–80° at 15–20 mm.) of the residue obtained by concentration of the ether solution yielded a white solid, m.p. 224.0–225.0°.

Anal. Calcd. for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 80.00; H, 8.99.

1-Hydroxyadamantane. A solution of 6.1 g. of a portion of the sublimed air oxidate in 100 ml. of 95% ethyl alcohol saturated with ammonia was hydrogenated in the presence of 2.0 g. of 5% palladium-on-alumina in a Parr apparatus at 50–55° and an initial hydrogen pressure of 45 p.s.i.ga.

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(22) Prelog reported that this compound did not melt below 360°.[18]

(23) R. L. Shriner and R. C. Fuson, *The Systematic Identification of Organic Compounds,* John Wiley & Sons, Inc., New York, 1948, p. 171.

(24) M. P. Monserrat and F. E. Prosper, *Rev. cienc. apl. (Madrid),* 12, 293 (1958).

(25) R. L. Shriner and R. C. Fuson, *The Systematic Identification of Organic Compounds,* John Wiley & Sons, Inc., New York, 1948, p. 202.

After the hydrogen absorption ceased, the reaction mixture was cooled to room temperature and filtered to remove the catalyst. The solid residue obtained by concentration of the alcohol solution at reduced pressure was treated with dilute hydrochloric acid to separate the amine as its water-soluble hydrochloride, and the water-insoluble hydroxy derivative was extracted by ethyl ether. After washing the ether extract with equal volumes of water and 5% sodium bicarbonate solution and drying over anhydrous magnesium sulfate, the solution was concentrated to yield 3.6 g. of white solid. Recrystallization of this product from methanol afforded a white solid, m.p. 277.0–278.0° (lit.,[6] m.p. 282°). Sublimation of this material gave colorless needles with no change in melting point.

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.82; H, 10.54.

The hydrolysis of 1-bromoadamantane by refluxing with dilute aqueous silver nitrate solution afforded a hydroxyadamantane with the same melting point as that obtained from the air oxidate derivative. A mixed melting point of these two compounds gave no depression.

2-Aminoadamantane hydrochloride. The aqueous hydrochloride acid solution from which hydroxyadamantane was separated (see above) was neutralized in 10% sodium hydroxide solution. The free amine which separated was extracted by ethyl ether and the solution was dried over anhydrous magnesium sulfate. Concentration of the solution yielded 0.6 g. of the amine, which on sublimation (75° and 15–20 mm.) afforded pure 2-aminoadamantane, m.p. 230.5–236°. (Due to the rapid absorption of water and carbon dioxide from the atmosphere, an analytically pure sample of the free amine was not obtained.)

The sublimed 2-aminoadamantane was dissolved in ethyl ether plus a small amount of ethyl alcohol, and the hydrochloride derivative was precipitated by passing dry hydrogen chloride into the solution. Recrystallization of the amine hydrochloride from isopropyl alcohol yielded colorless needles of 2-aminoadamantane hydrochloride which, on heating in a capillary, gradually decomposed over the range 300–325°.

Anal. Calcd. for $C_{10}H_{18}NCl$: C, 63.99: H, 9.67; N, 7.46. Found: C, 64.35; H, 9.59; N, 7.43.

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Condensed Cyclobutane Aromatic Compounds. XIV. Naphtho[*b*]cyclobutene: Reactions of the Aromatic Nucleus

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Peracetic acid oxidation of naphtho[*b*]cyclobutene (I) gave the quinone 1,2-dihydrocyclobuta[*b*]naphthalene-3,8-dione (II). The butadiene adduct (III) of this quinone was reduced to diol IV, which was dehydrated with rearrangement to 9,10-ethanoanthracene. The 3-nitro and 3-amino derivatives of naphtho[*b*]cyclobutene are described, and the effect of the cyclobutene ring upon the chromophores of these compounds is discussed.

The synthesis of the hydrocarbon naphtho[*b*]cyclobutene (I) was described in a previous paper of this series.[1] Some transformations of I are now described which involve attack upon the naphthalene nucleus of this molecule.

The direct oxidation of naphtho[b]cyclobutene with peracetic acid occurred readily to give, in 22% yield, a single bright yellow neutral compound $C_{12}H_8O_2$. This substance was assigned the structure 1,2-dihydrocyclobuta[b]naphthalene-3,8-dione (II) on the basis of the analogous oxidation of 2,3-dimethylnaphthalene to 2,3-dimethyl-1,4-naphthoquinone.[2] This assignment was verified by an interesting series of transformations leading to 9,10-ethanoanthracene.

I II

The new quinone II reacted with butadiene at 90–100° to give, after ninety minutes, a colorless adduct (III), m.p. 92–93°, in 93% yield. In contrast to this behavior, 2,3-dimethyl-1,4-naphthoquinone was recovered unchanged after five days under the same conditions. The greatly enhanced reactivity of quinone II as a dienophile must be attributed to the decrease in strain which results by conversion of the cyclobutene ring of II to the cyclobutane system of the adduct.

The diketone III was reduced smoothly by sodium borohydride to a single diol IV, m.p. 205.5–206°, in 79% yield. The configuration assigned to the diol, on mechanistic grounds, is that in which the hydroxyl groups are *cis* to each other as well as to the cyclohexene ring. This stereochemistry would result from attack of borohydride ion on the carbonyls of III from the less hindered cyclobutane side of the molecule.

Diol IV reacted with two equivalents of *p*-toluenesulfonyl chloride in pyridine to give directly, in 60% yield, 9,10-ethanoanthracene (V).[3] This

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(1) M. P. Cava and R. L. Shirley, *J. Am. Chem. Soc.*, 82, 654 (1960).

(2) R. T. Arnold and R. Larson, *J. Org. Chem.*, 5, 250 (1940).