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The Relative Stability of Bridged Hydrocarbons. II. *endo*- and *exo*-Trimethylenenorbornane. The Formation of Adamantane[1,2]

BY PAUL VON R. SCHLEYER AND MALCOLM M. DONALDSON[3]

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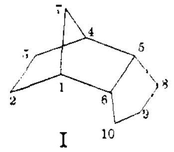
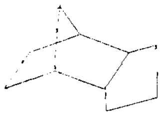
Strong sulfuric acid rearranged *endo*-trimethylenenorbornane (*endo*-tetrahydrodicyclopentadiene) (I) to the *exo* isomer III. The equilibrium mixture contained 99% *exo* and 1% *endo* material. It is shown that the rearrangement–addition of protonic acids to dicyclopentadiene also does not occur with complete *endo* to *exo* conversion. With aluminum halides, more powerful Lewis acid catalysts, further isomerization of I and III to adamantane (IX) occurred. This profound rearrangement, which makes adamantane readily accessible for the first time, is pictured as proceeding by a multi-stage ionic process. Conditions are described which make it possible to obtain a 10–20% yield of adamantane.

In 1903, Eijkman[4a] observed that prolonged heating of *endo*-trimethylenenorbornane (*endo*-tetrahydrodicyclopentadiene, I),[4b] m.p. 77°, in the presence of concentrated sulfuric acid to which a small amount of fuming sulfuric acid had been added, gave an isomeric material, melting at about 9°. At that time the structure of the starting material had not been established, but Eijkman proposed that the transformation might be some kind of *cis–trans* isomerization. The reaction does not appear to have been repeated, but the subsequent elucidation of the correct structure (I)[5] of the starting material has allowed speculation into the nature of the isomerization product. For example, the *trans* structure II has been proposed in the review literature.[6] This suggestion, however, is unlikely, since models show that three methylene groups cannot bridge the 2-*exo* and the 3-*endo* positions of the bicyclo[2.2.1] heptane nucleus without the introduction of a prohibitive amount of strain.[7]



I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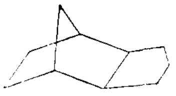
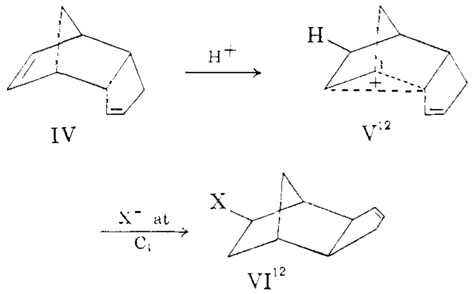
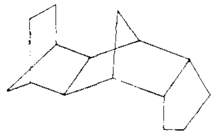
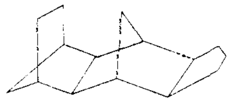

III

There are many rearrangements in the dicyclopentadiene series in which the five-membered ring is transformed from the *cis-endo* to the *cis-exo* configuration.[8–11] An example is the addition of protonic acids to dicyclopentadiene, (IV); this Wagner–Meerwein rearrangement is considered to proceed through a bridged-ion intermediate V.[3] Consequently, it was felt that *exo*-trimethylenenorbornane, III, was a more likely structure than II.



This expectation was further strengthened by analogy with compounds VII and VIII, for which heat of combustion data are available.[13] The *endo* isomer VII was found to be 3.6 kcal. less stable than VIII. A similar difference would be predicted for compounds I and III; equilibration between the two, if possible, should favor the *exo* isomer. On the other hand, III is a known compound,[8] and its physical properties do not agree with those of the isomerization product re-


VII


VIII

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[1] Paper III of a series on Bridged Ring Systems; paper II, L. Kaplan, H. Kwart and P. von R. Schleyer, THIS JOURNAL, **82**, 2341 (1960).

[2] For preliminary accounts of this work, see P. von R. Schleyer, *ibid.*, **79**, 3292 (1957); P. von R. Schleyer and M. M. Donaldson, Abstracts, 133rd Natl. Mtg., Am. Chem. Soc., San Francisco, Cal., Apr., 1958, p. 95-N.

[3] Armstrong Cork Fellow, 1956–1957. The material here presented was taken, in part, from the Ph.D. Thesis of M.M.D., Princeton University, 1958.

[4] (a) J. F. Eijkman, *Chem. Weekblad*, **1**, 7 (1903); **3**, 685 (1906). (b) The nomenclature used here, which emphasizes the relationship between the dicyclopentadiene and the norbornane ring systems, will be that suggested previously (P. von R. Schleyer and M. M. Donaldson, THIS JOURNAL, **78**, 5702 (1956)).

[5] E. Josephy and E. Radt, Eds., "Elsevier's Encyclopaedia of Organic Chemistry," Vol. 13, Elsevier Publishing Co., Inc., New York, N. Y., 1946, p. 1018.

[6] G. Egloff, G. Hulla and V. I. Kormarewsky, "Isomerization of Pure Hydrocarbons," Reinhold Publishing Corp., New York, N. Y., 1942, p. 122.

[7] The situation is analogous to the bicyclo[3.3.0]octanes; heat of combustion studies have shown the *cis* isomer to be 6.1 kcal. per mole more stable than the *trans*. (R. P. Linstead, *Ann. Repts. (Chem. Soc. London)*, **32**, 313 (1935)).

[8] H. A. Bruson and T. W. Riener, THIS JOURNAL, **67**, 723, 1178 (1945); **68**, 8 (1946).

[9] P. D. Bartlett and A. Schneider, *ibid.*, **68**, 6 (1946); R. Barnes. Ph.D. Thesis, Harvard University, 1950; P. D. Bartlett, Abstracts, 12th National Organic Symposium, Denver, Colo., June, 1951, pp. 4–7.

[10] F. Bergmann and H. Japhe, THIS JOURNAL, **69**, 1826 (1947); *Anal. Chem.*, **20**, 146 (1948).

[11] P. Wilder, Jr., C. F. Culberson and G. T. Youngblood, THIS JOURNAL, **81**, 655 (1959).

[12] The products of these addition reactions have been shown to be mixtures of the two double bond isomers, *i.e.*, with the double bond and functional group on the same side of the molecule, as in VI, and on opposite sides (P. von R. Schleyer, Ph.D. Thesis, Harvard University, 1957).

[13] K. Alder and G. Stein, *Ber.*, **67**, 613 (1934); G. Becker and W. A. Roth, *ibid.*, **67**, 627 (1934).

ported by Eijkman. For example, an authentic sample of VII would not freeze even at −80°.[8] However, the data listed by Eijkman are not inconsistent for a mixture of III and starting material I, for compounds in this series tend to be isomorphic.[14]

It was the purpose of the present work to determine the structure of the isomerization product, to ascertain the position of equilibrium between I and III, and to search for isomerization products other than III which would possess different ring systems.

Results

Isomerization with Sulfuric Acid.—The literature dealing with the isomerization of alkanes by sulfuric acid reveals that 99.8% acid is uniquely effective.[15,16] Acid of that concentration (actually 99.9%) was prepared and used in these investigations. Equal weights of I and sulfuric acid were stirred for 24 hours either on the steam-bath or at room temperature; after work-up with no attempt at fractionation, the product was analyzed by gas chromatography. The product from several similar runs, low melting solids, contained from 33 to 58% of starting material. The remainder had the same retention time as authentic III. When these mixtures were subjected to further treatment with sulfuric acid, the product analyzed for 99.0 ± 0.6% III and 1.0 ± 0.6% I. No traces of any other compounds were detectable by gas chromatography. The infrared spectrum and physical properties of the 99% *exo* product were identical with that of authentic III. Further treatment of this final mixture failed to alter significantly the percentages of I and III and, therefore it was concluded that equilibrium had been reached.

The free energy difference between isomers I and III was slightly in excess of 3 kcal./mole, a figure in excellent agreement with the (enthalpy) difference between VII and VIII. However, it was deemed advisable to approach equilibrium from the other direction; consequently, several attempts were made to obtain pure III. The most reasonable method seemed to be an efficient fractional distillation, since the boiling points of I (191.7°) and III (185.2°) were relatively far apart. In spite of this difference, it was not possible to remove the small amount of I in III by this method.

Attempted Preparation of Pure III.—Attempts to prepare pure III by chemical methods were next undertaken. The first route, suggested by work of Bartlett and Schneider,[9] started with the bromide VI (X = Br), prepared by the reaction of aqueous HBr with dicyclopentadiene IV. The Grignard reagent from the bromide was treated with water and the resulting olefin was hydrogenated catalytically. Gas chromatographic analysis showed the product to contain 6.7% I and 93.3% III. It is believed that this composition reflects that of the bromide mixture obtained from IV by HBr addition. All of the subsequent steps proceeded in high yield, and none would be expected to lead to rearrangement.

The second method for the preparation of III was essentially the same as that in the literature.[8] Formic acid addition to dicyclopentadiene,[12] followed by saponification, gave the alcohol VI (X = OH). Conversion of the latter to the parent alkane followed the experimentally simple sequence of catalytic hydrogenation of the double bond, oxidation to the ketone and Wolff–Kishner reduction. Analysis of the product revealed a composition of 1% I and 99% III. One can conclude that complete thermodynamic control was exhibited in the addition of formic acid to dicyclopentadiene, but not in the similar addition of aqueous HBr. The high dielectric constant and poor nucleophilic reactivity of formic acid solvent afford reactions a maximum opportunity for rearrangement.[17]

These results represent the first demonstration that addition reactions to dicyclopentadiene of the type under consideration do not proceed with complete *endo* to *exo* rearrangement. It was not possible to approach the I–III equilibrium from the direction of the *exo* isomer III, but the results of the reactions studied served to confirm the belief that the 1–99% mixture was near the equilibrium one.[17a]

Isomerization with Aluminum Halides.—In view of the sluggish action of sulfuric acid upon *endo*-trimethylenenorbornane (I), the effect of the more potent Lewis acid catalysts,[15] aluminum chloride and bromide, was investigated.

In a preliminary experiment with I and $AlCl_3$ at steam-bath temperature, the product was fractionally distilled. Fragmentation products constituted a small fore-cut. Most of the material was III, b.p. 185°. At the very end of the distillation, a small amount of very high melting solid appeared, m.p. after sublimation, 269.6–270.8°. The infrared spectrum, unlike that of I and III and other bicyclo[2.2.1]heptane derivatives, was very simple, indicating a highly symmetrical species. The monomeric nature of the compound was confirmed by the appearance of the parent peak in the mass spectra at 136 *m/e*, which peak also was unusual for such a relatively high molecular weight alkane in being the most intense in the entire spectrum. Elemental analysis was also consonant with an isomer of the starting material.

Two highly symmetrical structures were considered; adamantane (tricyclo[$3.3.1.1^{3,7}$]decane) (IX)[18] and the unknown *trans*-tricyclo[$4.2.1.1^{2,5}$]-decane (X). The properties of the product suggested adamantane (m.p. 268.5–270°[18]), but X seemed the more likely since it could form from III by a simple carbonium ion shift.[19] The formation

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[14] J. Pirsch, *Angew. Chem.*, **51**, 73 (1938); **57**, 40 (1944).

[15] H. Pines and J. M. Mavity in B. T. Brooks, *et al.*, eds., "The Chemistry of Petroleum Hydrocarbons," Vol. 3, Reinhold Publishing Corp., New York, N. Y., 1955, Chapt. 39, pp. 9–58.

[16] A. K. Roebuck and B. L. Evering, THIS JOURNAL, **75**, 1631 (1953).

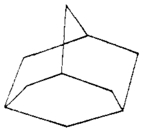
[17] (a) S. Winstein, *et al.*, *ibid.*, **74**, 1140 (1952); (b) J. D. Roberts, C. C. Lee and W. H. Saunders, Jr., *ibid.*, **76**, 4501 (1954); (c) A. C. Cope, J. M. Grisar and D. E. Peterson, *ibid.*, **81**, 1640 (1959).

[17a] ADDED IN PROOF.—*Cf.*, S. J. Cristol, W. K. Seifert and S. B. Soloway, *ibid.*, **82**, 2351 (1960), with regard to the completeness of the *endo* to *exo* rearrangement.

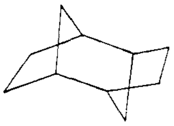
[18] For a review, see H. Stetter, *Angew. Chem.*, **66**, 217 (1954).

[19] Several deliberate attempts to produce compounds with the carbon skeleton of X by rearrangement from suitable precursors related to III have been without success.

of IX must necessarily involve a far more complicated mechanism.



IX



X

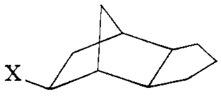
Nevertheless, further comparison established the identity of the rearrangement product and adamantane beyond doubt. A synthetic sample and the rearrangement product were compared directly by the following methods[20]: infrared[21] and mass spectral[24] analysis, X-ray powder diffraction pattern,[25] gas chromatographic and mixed melting point behavior.

The course of the isomerization could be followed by periodic extraction of samples directly from the reaction mixture and analysis by gas chromatography. The conversion of I into III was very rapid, but further isomerization into adamantane was slow. An attempt to isomerize adamantane with aluminum bromide and with aluminum chloride in methylcyclohexane solvent was also made. No reverse rearrangement could be detected. In methylcyclohexane at the boiling point, compound I was isomerized by $AlCl_3$ to a mixture of 99.1% III and 0.9% I. Adamantane was not formed.

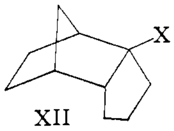
Ways to maximize the yield of adamantane were investigated. At the reflux temperature of the hydrocarbon, the aluminum halides caused a rapid conversion to IX, but at these temperatures there was also considerable fragmentation. Yields of 10–15% were obtained by chilling the product to Dry-Ice temperature and filtering off the crude adamantane. At steam-bath temperature there was less fragmentation, but no improvement in yield, even for prolonged reaction times. The best yield of pure sublimed adamantane, 18.8%, was obtained using a large amount of $AlBr_3$ catalyst, with *sec*-butyl bromide promoter, and HBr co-catalyst,[26] and stirring at room temperature for two days. The mother liquors from the work-up were shown by gas chromatography to contain about 8% additional adamantane, much of which could have been isolated by fractional distillation, but this was not done.[26a]

Other Reactions with I.—It was hoped that other alkane–carbonium ion reactions which resulted in the deposition of a functional group upon the molecular framework might reveal the preferred position of hydride abstraction of the starting material. Two such reactions were investigated.

Hydrogen–halogen exchange,[27] applied to norbornane itself,[28] gave a 22–24% yield of *exo*-norbornyl chloride. The reaction of *t*-butyl chloride and aluminum chloride with *endo*-trimethylenenorbornane (I) was more difficult to effect. At higher temperatures than generally used for the reaction, a low yield of chloride, not identical with the known *exo*-trimethylene-2-*exo*-norbornylchloride (XI, X = Cl),[8] formed. This was tentatively identified as *endo*-trimethylene-5-*exo*-norbornyl chloride (XII, X = Cl) by drastic sodium hydroxide–boiling ethylene glycol dehydrohalogenation to *exo*-trimethylene-8-norbornene (VI, X = H).[29] Neither rearrangement[30] nor reaction was observed with aluminum chloride and XI (X = Cl), with or without isobutane being present.



XI



XII

The second experiment involved the treatment of I with chromic anhydride in acetic acid–acetic anhydride solution.[31] From the small amount of acetate which was formed, saponification gave a crude alcohol, characterized as the *p*-nitrobenzoate, m.p. 143.6–144.5°. This was not identical with the same derivative of XI(X = OH) nor with other trimethylenenorbornanols[32] but showed no depression of melting point when mixed with a sample of the *p*-nitrobenzoate of *endo*-trimethylene-5-*exo*-norbornanol (XII, X = OH).[33] Other evidence confirmed this identity.

Discussion

The *endo–exo* Equilibrium.—Direct equilibration experiments with a diversity of monosubstituted norbornane derivatives have demonstrated the 2- to 4-fold greater stability of the 2-*exo* over the

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[20] Very kindly carried out by Dr. R. A. Dean, The British Petroleum Products, Ltd. We are very much indebted to Dr. Dean for his efforts.

[21] The infrared spectrum of rearrangement adamantane (Catalog of Infrared Spectral Data, A.P.I. Research Project 44, Carnegie Institute of Technology, Pittsburgh, Pennsylvania, No. 2040 and ref. 22) may be compared with published spectra (R. Mecke and H. Spiesecke, *Ber.*, **88**, 1997 (1954); refs. 22 and 23).

[22] B. J. Mair, M. Shamaiengar, N. C. Krauskop and F. D. Rossini, *Anal. Chem.*, **31**, 2082 (1959).

[23] S. Landa, *et al.*, *Chem. Listy*, **48**, 61 (1954); *Coll. Czech. Chem. Comm.*, **21**, 772 (1956); **24**, 93, 1320 (1959).

[24] The mass spectral cracking patterns of rearrangement (No. 1558) and synthetic (No. 939) adamantane have been published in the A.P.I. Catalog of Mass Spectral Data, ref. 21.

[25] W. Nowacki, *Helv. Chim. Acta*, **28**, 1233 (1945).

[26] H. Pines, E. Aristoff and V. N. Ipatieff, THIS JOURNAL, **75**, 4775 (1953).

[26a] ADDED IN PROOF.—A recent Belgian patent (583,579, Oct. 12, 1959, to the Du Pont Co.) reports yields of up to 30% of adamantane by the use of BF_3-HF catalyst.

[27] P. D. Bartlett, F. E. Condon and A. Schneider, *ibid.*, **66**, 1531 (1944).

[28] L. Schmerling, *ibid.*, **68**, 195 (1946).

[29] This process can be formulated as an E-1 elimination rearrangement similar to other transformations in this series; *cf.* refs. 5 and 11. The phosphoric acid dehydration of the corresponding alcohol XII (X = OH) gave the same product (VI, X = H).

[30] *Cf.* the action of aluminum chloride upon perchloro-dicyclopentadiene. (E. T. McBee, *et al.*, *ibid.*, **78**, 1511 (1956)).

[31] N. J. Toivonen, *Acta Chem. Scand.*, **3**, 991 (1949); J. Roček, *Coll. Czech. Chem. Comm.*, **23**, 833 (1958), and earlier papers in the same series; W. F. Sager and A. Bradley, THIS JOURNAL, **78**, 1187 (1956); W. F. Sager, *ibid.*, **78**, 4970 (1956); G. Foster and W. J. Hickinbottom, *J. Chem. Soc.*, 215 (1960); K. B. Wiberg and R. J. Evans, *Tetrahedron*, **8**, 313 (1960).

[32] Almost all the possible alcohols in both the *endo* and *exo* series are now known; see refs. 3, 6, 8, 9 and R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

[33] The preparation, by Dr. D. L. Heywood of the Union Carbide Chemicals Co., and structure proof of this compound will be presented subsequently. We wish to express our appreciation to Dr. Heywood for furnishing a sample of this material.

2-*endo* configuration.[34] Recently, in a definitive study, Cope, Ciganek and LeBel[35] have determined a free energy difference of 0.62 kcal. per mole at 90° in favor of the *exo* isomer of 2-carbomethoxynorbornane. The factors which influence the stability of the two isomers are: first, the strongly unfavorable interaction with the eclipsed methylene at C-3, presumably equal for both epimers. Second, an *endo* group suffers from a boat *meta*-axial interaction with the *endo* hydrogen on C-6. An *exo*-group encounters a similar but less serious 1,3-type interaction with the *syn*-hydrogen upon C-7. It is this greater distance of the C-7 *syn* hydrogen[36] which is responsible for the greater stability of the *exo* isomers. Third, the bridgehead hydrogen at C-1, in the bicyclo[2.2.1]heptane series, is not perfectly skewed with regard to the C-2 methylene group as it would be in the corresponding boat conformation of cyclohexane. Instead the geometrical consequences of forming the C-1,4 methylene bridge are that the bridgehead hydrogen is bent upward, more into opposition with a 2-*exo* group.[36] This influence, favoring a 2-*endo* substituent, has generally been overlooked.

The net effect of all of these interactions is to favor the *exo* configuration to a small extent. In the case of trimethylenenorbornane, with two substituent groups upon the 5- and 6-positions, the ΔF of isomerization of about 3 kcal. per mole is considerably more than twice that of a monosubstituted norbornane. Examination of a model of the *endo* isomer I reveals that whatever conformation adopted by the substituent five-membered ring, the geometry is such that the non-bonded interactions between the *endo*-hydrogens at C-2 and C-3 and the *endo*-hydrogens of C-8 and C-10 are particularly unfavorable, more so than would be the case if the substituents on C-5 and C-6 were free to rotate.[37]

Mechanism of the Isomerization of I to III.—The Lewis acid-catalyzed isomerization of alkanes proceeds by an ionic chain mechanism.[15,38] The propagating step involves the carbonium ion abstraction of a hydride ion from the alkane. The new carbonium ion so generated may rearrange before continuing the chain. The novel feature of this reaction is that virtually any position of a molecule is a potential carbonium ion site, but tertiary hydrogens generally react more readily than secondary. Further, there is the possibility, as exemplified in this research, of further reaction of an initially formed product by a repetition of the same process.

Theoretical considerations, tentatively supported by evidence discussed above, suggest that the tertiary hydrogen at C-5 of I should be the most reactive. However, it is entirely possible that the tertiary carbonium ion may be only a dead-end, and may not function as an intermediate in the *endo*–*exo* rearrangement of I into III. Each of the possible transformation pathways from this tertiary ion to III has an energetically unfavorable intermediate, *e.g.*, II, for a two-step inversion process at C-5 and C-6, or an otherwise unattractive step.[3] Although the tertiary carbonium ion may form rapidly and easily, it would be expected to react with a hydride ion from the *exo*-side[39] preferentially, resulting in the regeneration of starting material.

The 2-*exo*-hydrogen of I, although secondary, should have enhanced reactivity because of anchimeric assistance.[9] Formation of a (bridged) carbonium ion at this position would easily lead to III by Wagner–Meerwein rearrangement.[8–11] It is not unlikely that this is the isomerization mechanism, even though the secondary hydrogen is less reactive than the tertiary.

Mechanism of the Formation of Adamantane.—The mechanism of the much more complicated rearrangement of I or III to adamantane is even more nebulous. The driving force for this profound transformation is the relief of the large amount of strain inherent in the bicyclo[2.2.1]heptane ring system. Adamantane is free from both angular strain and conformational strain since the angles are tetrahedral and adjacent groups are perfectly skewed. There is a small entropy loss in proceeding to the highly symmetrical adamantane, however. Adamantane should be 20–25 kcal. more stable than either trimethylenenorbornane.[40] If this is true, then it is clear that the formation of adamantane is not completely equilibrium controlled. The energy considerations dictate that none of the starting material should be present at the end of the reaction. We do not know why complete conversion cannot be accomplished experimentally.[42] The failure to detect any intermediates in the reaction mixture suggests the possibility that the first step in the transformation is the least favorable, and that all subsequent steps proceed rapidly to completion.

We have adopted the entirely speculative but attractive mechanism shown below as a working hypothesis for further study of this process. The key step, and the least probable one, is the 2,6-alkyl shift, XIII to XIV. (After XIII, the ions are not written as bridged for representational simplicity.) There are no precedents for 2,6-alkyl migrations in this system, but 2,6-hydride shifts are common.[17b]

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(34) 2-Carbomethoxy: K. Alder and G. Stein, *Ann.*, **514**, 211 (1934) and ref. 35; 2-carboxaldehyde: K. Alder, *et al.*, *Ann.*, **525**, 183, 247 (1936); *Ber.*, **71**, 1939 (1938); 2-nitro and 2-hydroxy: ref. 17b. *Cf.*, also C. W. Shoppee, *Chem. and Ind.*, 86 (1952) and D. H. R. Barton, *J. Chem. Soc.*, 1027 (1953).

(35) A. C. Cope, E. Ciganek and N. A. LeBel, THIS JOURNAL, **81**, 2799 (1959).

(36) H. Krieger, *Suomen Kemi.*, **B32**, 109 (1959).

(37) These hydrogen repulsions are reduced by the introduction of a double bond at C-2 or at C-8, and the energy difference between *endo* and *exo* isomers becomes less. See refs. 13, 34 and 35. In the present study no significant compositional difference was detected between the alkane isomerization product and the formic acid addition product of dicyclopentadiene (*vide supra*), but these results are not conclusive.

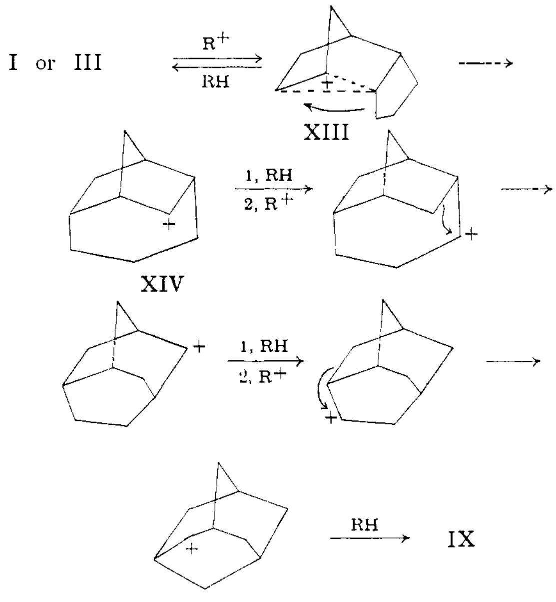
(38) D. A. McCaulay, THIS JOURNAL, **81**, 6437 (1959).

(39) A close analogy is found in the reaction of 1-methylnorbornane with aluminum chloride. Partial conversion to 2-*endo*-methylnorbornane but not to the more stable 2-*exo* isomer occurs very readily, because of the stereochemical consequences of the bridged ion intermediate (C. D. Woody, unpublished result).

(40) The reported heat of combustion values for adamantane[41] and for III[13] are nearly identical. Repetition of these determinations is highly desirable.

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

(42) Certain methyl substituted trimethylenenorbornanes do rearrange completely to methyladamantanes under similar conditions (R. D. Nicholas, unpublished work).



Hydride transfer to XIV and regeneration of a carbonium ion at a carbon atom permitting a favorable ring expansion is followed by a similar process on the other side of the molecule to give adamantane. Even if this pathway is followed, the actual process is very much more complex, since carbonium ions can be generated at other sites and additional rearrangement possibilities exist.

Adamantane was discovered[41] as a constituent of petroleum where it is present in minute amounts.[22,23] Although efficient methods of recovery from this source have been developed, enormous quantities of material must be manipulated. The original synthesis of adamantane[43] has been improved considerably,[44] but the difficulty of preparing adamantane in quantity by this multi-step process is still prohibitive. The simple preparation described in this paper makes adamantane readily available for study. In subsequent publications further examples of these rearrangements and information concerning their mechanism will be presented. Methods of converting adamantane to functionally substituted derivatives will be described,[23,45] and the reactivity and the reactions of these compounds will be considered.

Acknowledgments.—The authors wish to thank several friends for suggesting mechanisms for the adamantane rearrangement and for discussions. The gas chromatography apparatus was purchased with a grant-in-aid from the Food Machinery and Chemical Corp.

Experimental[46]

***endo*-Trimethylenenorbornane (I).**—Catalytic hydrogenation[6,8] of dicyclopentadiene gave a nearly quantitative yield of *endo*-trimethylenenorbornane, b.p. 191.7° (760 mm.) when distilled through the 100-cm. column, m.p. 77.2–77.6° after recrystallization from methanol (lit.[8] b.p. 193°, m.p. 77°). It is important to use distilled dicyclopentadiene which is solid at room temperature (lit.[6] m.p. 32.9°), but then the crude hydrogenation product is sufficiently pure for isomerization after simple distillation.

Isomerization of I with Sulfuric Acid.—In a typical run, 100 g. (1.02 moles) of 99.9% sulfuric acid and 100 g. (0.735 mole) of *endo*-trimethylenenorbornane were stirred for one day in a 500-ml. 3-necked flask. Upon addition of the hydrocarbon, the reaction was slightly exothermic and sulfur dioxide was liberated. The reaction mixture was poured onto ice and then steam distilled. The product was separated, the water layer was extracted with petroleum ether, and the combined organic layers were washed with Na_2CO_3 solution and dried over K_2CO_3. The product distilled at atmospheric pressure from 183–186°. It was analyzed by means of a Perkin–Elmer model 154-B gas chromatograph, employing either a silicone oil or a dinonyl phthalate column. The following table summarizes the results.

Starting material	Time, hr.	Temp.	Product recovery, %	% III (*exo*)	% I (*endo*)
Pure I	20	Room	..	63	37
Pure I	(100 g. HSO_3Cl in place of H_2SO_4 exploded)				
Pure I	24	Steam bath	66.7	42	58
Pure I	24	Room	57.1	67	33
Pure I	24	Room	61.3	56	44
58% III + 42% I	24	Steam bath	92.0	98.9	1.1[a]
98.9% III + 1.1% I	24	Room	..	99.6	0.4[a]

[a] Analysis of small amounts of *endo* isomer was difficult. The quoted values are uncertain to the extent of at least 0.5%. The accuracy of the analytical method was checked with artifically prepared mixtures containing several % of I.

Trimethylenenorborane from VI (X = Br).—The bromide VI (X = Br), from the addition of 48% aqueous HBr to dicyclopentadiene,[8] was converted to the Grignard reagent and the latter decomposed with water.[9] The resultant product, *exo*-trimethylene-8-norbornene (VI, X = H), was hydrogenated with PtO_2 catalyst in a Parr apparatus, to give trimethylenenorbornane which analyzed 93.3% *exo* (III) and 6.7% *endo* (I).

***exo*-Trimethylenenorbornane (III) from VI (X = OOCH).**—Dicyclopentadiene was refluxed with twice its weight of 98% formic acid for 4 hours,[10] and the excess formic acid was distilled off. The remaining crude formate (VI, X = OOCH) was saponified directly to the alcohol VI (X = OH)[8] in 87% yield. The saturated alcohol XI (X = OH) was obtained nearly quantitatively as a white solid after catalytic hydrogenation.[8] Oxidation to *exo*-trimethylene-2-norbornanone[8] was accomplished in about 85% yield by the chromic acid–acetone procedure.[47] Huang-Minlon[48] modified Wolff-Kishner reduction of the ketone, employing ethylene glycol as the solvent and distilling the product directly from the reaction flask after 4 hours refluxing, gave a hydrocarbon analyzing for 99% *exo*-trimethylenenorbornane (III) and 1% *endo* isomer I.

Aluminum Halides and Trimethylenenorbornanes. A. Initial Experiment.—To a flask containing 15 g. of aluminum chloride, 91 g. of melted *endo*-trimethylene-norbornane (I) was added. An exothermic reaction, the isomerization of I to the *exo* isomer III, took place. The mixture was stirred on the steam-bath overnight. The cooled reaction product was decanted from the aluminum chloride "sludge"; yield of crude material, 83 g. This was purified by an initial distillation at water-pump pressure; b.p. 62–66°

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(43) V. Prelog and R. Seiwerth, *Ber.*, **74**, 1644, 1769 (1941).

(44) H. Stetter, O. E. Bänder and W. Neumann, *ibid.*, **89**, 1922 (1956); S. Landa and Z. Kamýček, *Coll. Czech. Chem. Comm.*, **24**, 1320 (1959).

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

(46) Melting points were determined in a Hershberg apparatus and are corrected. Fractional distillations were carried out through a 1.3 × 100 cm. column, packed with Podbielniak Heli-Pak. Gas chromatographic analyses were carried out with a Perkin–Elmer model 154-B apparatus, employing "C" (silicone oil) columns, for the most part. Mr. George Robertson, Florham Park, N. J., performed the microanalyses.

(47) P. Bladon, *et al.*, *J. Chem. Soc.*, 2407 (1951); K. Bowden, *et al.*, *ibid.*, 39 (1946).

(48) Huang-Minlon, THIS JOURNAL, **68**, 2487 (1946); **71**, 3301 (1949).

(11 mm.), 78.4 g. Distillation through the 100-cm. column gave the fractions

Cut	B.p. (cor. to 760 mm.), °C.	$n^{20}D$	Wt., g.	Comments
1	175–183.5	1.47462	1.0	Fragmentation products
2	183.5–184.9	1.48529	15.3	Mainly III
3, 4, 5	184.9–185.0	All 1.48615	35.3	"Pure" III
6	185.0–187.5	1.48672	4.1	
7	187.5–190	Solid	2.8	Overheat jacket

By refluxing ether in the apparatus, and washing, a total of about 5 g. of solid (adamantane) was obtained. The remainder of the material was pot residue and distillation loss.

B. **Purification and Identification of *exo*-Trimethylenenorbornane(III).**—A total of 192 g. of the best cuts of the 185° material from two preparations similar to the above was redistilled fractionally over 3 g. of sodium using the 100-cm. column. Fractions totaling 181 g. were obtained; 146 g. of this boiled within a few tenths of a degree of 185.2° (760 mm.) and fractions totaling 103 g. had a constant refractive index, $n^{20}D$ 1.48709. The infrared spectrum of the heart cuts were indistinguishable from that of authentic material (*vide supra*) and from the sulfuric acid rearrangement product. The spectra, taken on a thin film of the liquid, were very rich in detail. Gas chromatography further confirmed the identity of the samples; however, *endo*-trimethylenenorbornane was still present to the extent of about 1%; lit.[8] b.p. 83.5–84.5° (28 ml.), $n^{25}D$ 1.4868.

C. **Purification and Identification of Adamantane (IX).**—The solid from the distillation was washed with a little petroleum ether to free it from impurities and sublimed. Resublimation gave material of m.p. 269.6–270.8° (sealed tube), part of which was submitted for analysis and part was sent to Dr. R. A. Dean for comparison with synthetic material.[20] A similar sample was transmitted to Professor F. D. Rossini, Director, American Petroleum Institute Research Projects[21,22,24]; lit.[18] m.p. 268.5–270°. The infrared spectrum[21] and mass spectral cracking pattern[24] were identical with those published. The sample was identical in all respects with synthetic[20] and petroleum[22] adamantane.

Anal. Calcd. for $C_{10}H_{16}$. C, 88.16; H, 11.84. Found: C, 88.31; H, 11.99.

D. **The Reaction Course *vs.* Time.**—A three-necked flask fitted with reflux condenser, stirrer and a thermometer extending into the liquid was used to contain 12 g. of $AlCl_3$ and 200 g. of I. The stirred mixture was heated and at various times the stirrer was stopped, the catalyst allowed to settle, and a small sample taken by hypodermic syringe for gas chromatographic analysis. A summary of the progress of the reaction is

Net time, min.	Liquid temp., °C.	% *endo* (I)	% *exo* (III)	Net time, min.	Liquid temp., °C.	% *endo* (I)	% *exo* (III)
10	Heating	83	17	80	125	26	74
20	120	55	45	240[a]	125	1	99
30	125	48	52	480[b]	185		
50	125	36	64	1200[c]	185		

[a] Trace fragmentation products, raised temp. [b] Adamantane peak appeared, added 5 g. of $AlCl_3$. [c] Distilled product directly from flask.

A total of 178 g. of product, b.p. 181–193°, was obtained. Since the pot remainder weighed 25 g., a loss of 14 g. of volatile material was experienced. The crude distillate, was cooled to Dry Ice–alcohol temperature to complete the precipitation of adamantane. Rapid filtration through a coarse filter gave 17.5 g. of crude product. Gas chromatographic analysis of the filtrate showed the presence of an appreciable (about 8%) additional amount of adamantane which remained in solution at the low temperatures and a small total amount of a large number of fragmentation products. Sublimation gave 14.8 g. of material, m.p. 268.2–270.2°, and 2 g. of less pure substance.

Similar experiments carried out with a larger proportion of $AlCl_3$ gave a much more rapid conversion of I to III.

E. **Preparative Experiments. General Procedures.**—The rearrangement reactions of alkanes with aluminum halide catalysts are markedly influenced by trace impurities.[15] The reactions were somewhat erratic, especially the ones carried out at the lower temperatures. Nevertheless, adamantane was obtained in every case, but not always in large enough amounts to isolate by cooling and precipitation. Reactions were carried out from room to reflux temperature; the former was possible because of the rapid conversion of I into III. At the end of the reaction, the product was either distilled directly from the flask, at atmospheric or at water-pump pressure, or decanted from the aluminum halide sludge, or water was added and the layers separated or the mixture was steam distilled. Cooling the mixed hydrocarbon product to Dry Ice temperature, filtration and sublimation was used in every case. Alternatively, adamantane can be recrystallized from petroleum ether by cooling the solution to −80°. The substance remaining in the isomerization filtrate can be isolated by fractional distillation, but this was inconvenient. The filtrate, largely III, can be used to prepare more adamantane by treatment with catalyst as before. It is best to use material that does not contain very much fragmentation product. It is possible that the thiourea complex procedure[23] might permit the recovery of much of the adamantane from the filtrate, but this was not tried.

The most convenient and reliable method involved heating I with 10–15% of its weight of $AlCl_3$ overnight at 150–160° with stirring. Cooling, decantation, precipitation and sublimation yielded at least 10% of adamantane of good purity.

F. **Procedure for Optimum Yields.**—A 250-ml. three-necked flask was charged with 39.2 g. (0.147 mole) of aluminum bromide, 100 g. (0.735 mole) of *endo*-trimethylenenorbornane and 2.5 g. (0.0184 mole) of *sec*-butyl bromide. The reaction mixture was stirred at room temperature for 48 hours; during the first 6 hours hydrogen bromide was bubbled in below the liquid level. Water was added slowly with stirring, while the flask was cooled in an ice-bath, to hydrolyze the aluminum bromide. Excess water was added, the layers separated, and the water extracted with petroleum ether. After drying the combined organic layers over sodium sulfate, the solvent was stripped at atmospheric pressure. Adamantane was precipitated by cooling in a Dry Ice-bath. Filtration gave a 26.4 g. crude yield. After sublimation the yield was 18.8% (18.8 g.). The filtrate was distilled, b.p. 73–75° (18 mm.), and subjected to gas chromatography. It analyzed for 90.7% *exo*-trimethylenenorbornane (III) and 9.3% adamantane mixed with a little starting material I. Total recovery was 69.2 g. Duplicate runs gave altogether comparable results, but runs using only 10 g. of $AlBr_3$ to 100 g. of I yielded insufficient adamantane to be isolated by precipitation.

G. **Rearrangement of *exo*-Trimethylenenorbornane (III).**—Pure (99%) III was subjected to the action of $AlCl_3$, 10% by weight, at the reflux temperature for 8 hours. The apparatus was connected to a Dry Ice trap which collected most of the volatile fragmentation products, 8 g. from 132 g. of starting material. As with the *endo* isomer as starting material, extensive fragmentation occurred with these drastic conditions, as evidenced by more than 17 peaks in the gas chromatograph. The crude product, 111 g., had b.p. 75–190°. From this run 11.1 g. of sublimed adamantane was obtained. The pot residue was 22 g.; therefore, losses were 4 g.

H. **Rearrangement with a Solvent.**[49]—Methylcyclohexane, although it exhibits carbon scrambling, gives little gross change with aluminum halide catalysts.[50] It was chosen as a solvent.

A mixture of 21 g. I in 150 ml. of methylcyclohexane was heated under reflux with 10 g. of aluminum chloride. The product was worked up with water, followed at the end by distillation. The product, 18.0 g., b.p. 70–73° (12 mm.), analyzed for 99.1% *exo* isomer III and 0.9% *endo* I. There was no evidence for the formation of adamantane.

Attempted Rearrangement of Adamantane (IX). A. No Solvent.—Adamantane (IX) was heated with aluminum bromide, well above the melting point of the latter. Sublimation caused serious difficulties which might have been avoided by using a sealed tube. Nevertheless, no rearrangement could be detected in the product by gas chromatography.

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(49) Experiment performed by Mr. R. D. Nicholas.

(50) H. Pines and R. W. Meyerholtz, Jr., THIS JOURNAL, **77**, 5392 (1955).

B. Methylcyclohexane Solvent.[49]—No rearrangement was observed when adamantane was heated with aluminum chloride, using methylcyclohexane solvent. The details of the experiment were as with *endo*-trimethylenenorbornane (I).

Hydrogen-halogen Exchange with endo-Trimethylenenorbornane (I).—A 500-ml. 3-necked flask equipped with stirrer was charged with 100 g. (0.735 mole) of *endo*-trimethylenenorbornane (I) and 74 g. of *t*-butyl chloride and the reaction mixture cooled in an ice-bath. To this, 10 g. of aluminum chloride was added slowly and the reaction mixture was allowed to come to room temperature while stirring. A gas was given off, but the reaction did not appear to be exothermic. When heated on a steam-bath a vigorous evolution of gas took place, a sample of which was collected in a Dry Ice–acetone-bath. It did not decolorize bromine and boiled somewhat below 0°, properties compatable with isobutane, an expected reaction product. The reaction mixture refluxed at 52° initially, the boiling point of *t*-butyl chloride; the temperature then rose slowly to 65°, when the reaction was stopped. Water was added to decompose the aluminum chloride and the product was extracted with ether, washed with sodium carbonate and water and dried over sodium sulfate. Fractional distillation through a Vigreux column yielded solid starting material, b.p. 71–90° (14 mm.), and oily product, b.p. 90–125° (14 mm.), 21.2 g. Redistillation of the latter gave 11.4 g., b.p. 110–111° (17 mm.), characterized by infrared spectrum. Experiments conducted at lower temperatures failed to give any chloride product, only starting material.[27,28]

The chloride was dehydrohalogenated by 10 g. of sodium hydroxide in 114 g. of ethylene glycol at the boiling point. The olefin was distilled as it formed. After the appropriate preliminary isolation and purification steps, the olefin was distilled, b.p. 68–70° (17 mm.). The infrared spectrum was essentially identical with that of authentic *exo*-trimethylene-8-norbornene (VI,X = H) (*vide supra*).

Treatment of *exo*-Trimethylene-2-*exo*-norbornyl Chloride (XI, X = Cl) with $AlCl_3$.—A cold solution of 50 g. of *exo*-trimethylene-2-*exo*-norbornyl chloride[8] and 25 g. of isobutane was treated with 5 g. of $AlCl_3$. Stirring was continued overnight during which time the reaction mixture warmed to room temperature. Work-up revealed the presence of neither the expected hydrogen–halogen interchange product (III) nor of any rearranged product. The infrared spectrum of recovered chloride, b.p. 102–103° (13 mm.), was identical with that of the starting material.

A second experiment, omitting the isobutane and continuing the stirring at room temperature for 24 hours, also yielded only unchanged starting material, b.p. 106–107° (17 mm.), lit.[8] b.p. 102–104° (11–12 mm.).

Chromic Acid Oxidation of *endo*-Trimethylenenorbornane (I).—A reaction mixture consisting of 29.5 g. (0.226 mole) of *endo*-trimethylenenorbornane (I), 175 ml. of acetic acid and 175 ml. of acetic anhydride, and 47 g. (0.47 mole) of chromic anhydride was stirred at 80° for 90 minutes.[31] The solvent was stripped at reduced pressure, and the reaction mixture poured into water, extracted with ether, washed with sodium carbonate, and dried over sodium sulfate. Distillation gave the cuts: (1) b.p. up to 100° (15 mm.), 4.4 g. of solid, starting material; (2) b.p. 124–128° (15.5 mm), 3.8 g. of acetate, by infrared examination; (3) b.p. 128–176° (15 mm.), 2.5 g.; b.p. 176–177° (16 mm.), 2.3 g. The latter two cuts were highly oxygenated, because of the appearance of several bands in the carbonyl region of the infrared spectrum.

The acetate (3.8 g.) cut was saponified by 1.65 g. of potassium hydroxide dissolved in 15 ml. of ethanol and 1 ml. of water at reflux. After work-up, the product, b.p. 120–122° (16 mm.), was isolated by distillation; yield 1.15 g. (39%) of white solid, m.p. crude 94–109°. Besides the presence of a carbonyl band at 5.75 μ, the spectrum was identical with that of pure *endo*-trimethylene-5-*exo*-norbornyl alcohol (XII, X = OH), m.p. 135.6–136.0°.[33] Positive identification was made by derivatization.

***p*-Nitrobenzoate of XII, X = OH.**—The derivative was recrystallized six times from ethanol, m.p. 143.6–144.5°. *Anal.* Calcd. for $C_{17}H_{19}NO_4$: C, 67.76; H, 6.36. Found: C, 67.76; H, 6.25. The *p*-nitrobenzoate when made from authentic material[33] required 3 recrystallizations to give m.p. 144.6–145.2°, mixed m.p. 144.4–145.0°.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Tertiary Amines from Methiodides and Lithium Aluminum Hydride[1]

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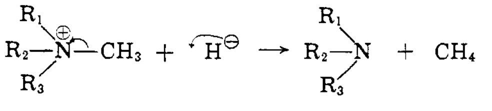
Suitable conditions for a little-used general synthesis of N,N-dimethyl tertiary amines from primary amines are described. The primary amine is treated with methyl iodide and a base, and the methiodide so obtained is reduced with lithium aluminum hydride in boiling tetrahydrofuran, forming a tertiary amine and methane. This method is compared with a standard procedure for methylating primary amines, the Clarke–Eschweiler reaction (treatment with formaldehyde and formic acid) in the preparation of N,N-dimethyl-(+)-neomenthylamine, N,N-dimethyl-(−)-menthylamine and (−)-N,N,α-trimethylbenzylamine. In each case the tertiary amines obtained by the two methods had identical optical rotations, indicating that the Clarke–Eschweiler method proceeds without epimerization of the carbon atom to which the amino group is attached.

The reduction of a quaternary ammonium salt to a tertiary amine with lithium aluminum hydride was first reported by Kenner and Murray[2] who suggested that this reaction proceeds by an SN2 displacement by hydride ion on the N-methyl group.


(1)

Other methods of removing a methyl group from a quaternary salt involve treatment with potassium thiophenolate in triethylene glycol at 150–220°[3] or with ethanolamine at elevated temperatures.[4] It has been known for a long time that primary amines may be converted easily into quaternary iodides by the action of methyl iodide in the presence of a base. Combination of this method with lithium aluminum hydride reduction of the quaternary iodides to tertiary amines seemed to offer an attractive way of converting primary amines into N,N-dimethyl tertiary amines (path A in eq. 2), especially in cases where the standard method for dimethylating primary amines, treatment with formaldehyde and formic acid (the Clarke–Esch-

$$\begin{tikzcd} RNH_2 \arrow[r, "CH_3I/base"] \arrow[rr, bend right, "HCHO/HCOOH"'] & RN(CH_3)_3I \arrow[r, "LiAlH_4"] & RN(CH_3)_2 \ (A) \\ & & (B) \end{tikzcd} \qquad (2)$$

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[1] Supported in part by the Office of Ordnance Research, U. S. Army, under Contract No. DA-19-020-ORD-4542.

[2] G. W. Kenner and M. A. Murray, *J. Chem. Soc.*, 406 (1950).

[3] E. R. Trumbull, J. Häberli and H. Ammon, Abstracts of Papers, American Chemical Society Meeting, Chicago, Ill., Sept. 7–12, 1958, p. 76-P.

[4] S. Hünig and W. Baron, *Chem. Ber.*, **90**, 395 (1957).