ketone, mp 20.5–22.0° (*Anal.* Found: C, 81.2; H, 10.6), which was then treated with methyllithium followed by iodine-catalyzed dehydration. The major and minor products were identified as IV and V, respectively, by examination of the width at half-height of the nmr signal for the vinyl proton.[2]

We have not yet found evidence for the presence of any other tricyclic materials. Spectral data on the ketone mixture suggested the presence of up to 16% of bicyclic material as determined by signals in the nmr for the terminal methylene group and no significant absorption in the infrared for *trans*-disubstituted olefinic bonds. Moreover, we have unequivocally demonstrated the absence of the *trans,anti,cis* isomers of IV and V in the hydrocarbon mixture by establishing the nonidentity of any of the vpc peaks with those of authentic samples.[14] It is therefore evident that the major product of the cyclization of the acetal I is tricyclic material which appears to be formed stereospecifically with respect to the ring fusions. We are now examining the possibility of producing higher polycyclic systems by this approach.

Acknowledgment. We wish to thank the National Institutes of Health, the National Science Foundation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(14) A mixture of authentic hydrocarbons was prepared by catalytic hydrogenation of the unsaturated ketone VI to give the *trans,anti,cis*-perhydro ketone, mp 45–47.5° (*Anal.* Found: C, 81.5; H, 10.8), which was then treated with methyllithium followed by iodine-catalyzed dehydration.

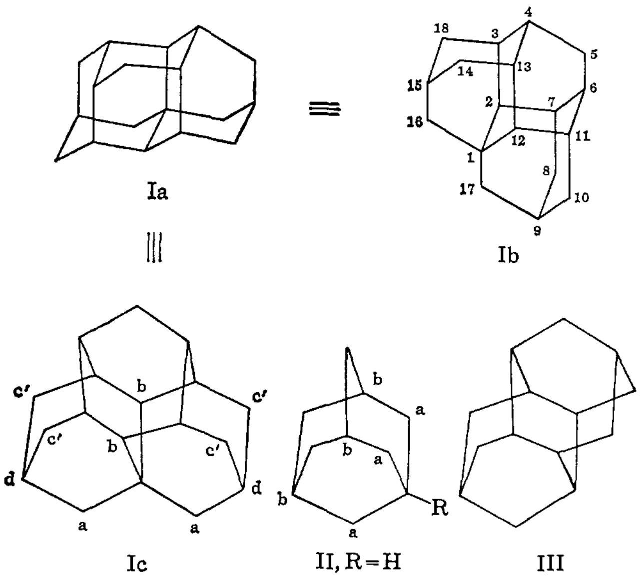
William S. Johnson, Robin B. Kinnel
Department of Chemistry, Stanford University
Stanford, California 94305

Received June 16, 1966

Triamantane

Sir:

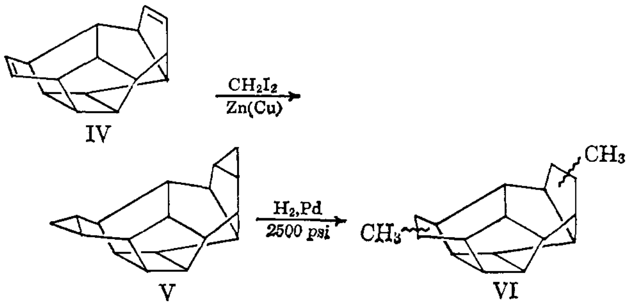
The name "triamantane" has been proposed for I, "the third member of an adamantalogous series whose three-dimensional ultimate is diamond."[1] Adamantane[2] (II) and diamantane[3] (formerly called "congressane")[1] (III) have been prepared from isomeric precursors by rearrangements catalyzed by strong Lewis acids. By means of this approach we believe we have succeeded in synthesizing triamantane (heptacyclo$[7.7.1.1^{3,15}.0^{1,12}.0^{2,7}.0^{4,13}.0^{6,11}]$octadecane, Ib).[4]



Ia Ib Ic II, R=H VII, R=C_2H_5 III

(a, +0.28 ppm, b, − 0.12 ppm)

A seven-ring hydrocarbon, $C_{18}H_{24}$, was needed as starting material for I. One of the cyclooctatetraene dimers, mp 38.5° (IV),[5] is heptacyclic and can be elaborated to the desired C and H level. This was accomplished by Simmons–Smith cyclopropanation[6] to V, followed by reductive cleavage of both cyclopropane rings.[7] These reactions were followed by gas chromatography and by observing features of the infrared, nmr, and mass spectra. The exact composition of the penultimate material, VI, is not known with certainty, but this is not at all important for the present purposes since any $C_{18}H_{24}$ heptacyclic hydrocarbon might well serve as a rearrangement precursor for triamantane. Assignment of general structure VI has been made on the basis of the expected mode of cleavage of cyclopropane rings,[7] the intense *m/e* 240 peak in the mass spectrum, and the evidence for the presence of methyl groups (band near 1375 cm^{-1} in the infrared; resonances at 1.0 ± 0.2 ppm in the nmr (measured in δ units) of area one-fourth of the total).



IV V VI

The rearrangement of VI to I was carried out in CS_2 solution under an HBr atmosphere using a 1.3- to 3-fold weight excess of an $AlBr_3$ "sludge" catalyst, prepared from $AlBr_3$ and *t*-BuBr.[8] After an initial treatment at 25°, heating at 100° for 4–6 days completed the reaction. Crystals of I could be obtained consistently in 2–5.2% yields from VI (mp 221–221.5° from acetone; *cf.* diamantane, mp 236–237°,[3] adamantane, mp 268–269°[10]). *Anal.* Calcd for $C_{18}H_{24}$: C, 89.98; H, 10.02. Found: C, 89.93; H, 10.24.

---

(1) O. Vogl, B. C. Anderson, and D. M. Simons, *Tetrahedron Letters*, No. 4, 415 (1966).

(2) P. von R. Schleyer and M. M. Donaldson, *J. Am. Chem. Soc.*, **82**, 4645 (1960).

(3) C. Cupas, P. von R. Schleyer, and D. J. Trecker, *ibid.*, **87**, 917 (1965); I. L. Karle and J. Karle, *ibid.*, **87**, 918 (1965).

(4) IUPAC name supplied by Mr. Wallace F. Sliwinski, private communication.

(5) Review: G. Schröder, "Cyclooctatetraen," Verlag Chemie GmbH, Weinheim, Germany p 60.

(6) H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **80**, 5323 (1958); **81**, 4256 (1959); R. S. Shank and H. Shechter, *J. Org. Chem.*, **24**, 1825 (1959).

(7) Review: R. L. Augustine, "Catalytic Hydrogenation," Marcel Dekker, Inc., New York, N. Y., 1965, pp 133–134.

(8) This catalyst, invented by Williams,[9] has properties similar to that described by A. Schneider, R. W. Warren and E. J. Janoski, *J. Org. Chem.*, **31**, 1617 (1966). With it, 10% yields of diamantane (III) can now be obtained from norbornene dimer.[3,9]

(9) V. Z. Williams, Jr., A.B. Thesis, Princeton University, 1965.

(10) Review: R. C. Fort, Jr., and P. von R. Schleyer, *Chem. Rev.*, **64**, 277 (1964).

The mass spectrum of I was remarkable in the relative intensity of the parent/base peak at m/e 240. Besides the $C_{18}H_{23}^+$ peak (39%), the next most intense fragmentation peak at m/e 91 ($C_7H_7^+$) was only 9% of the base! This pronounced resistance toward fragmentation is a characteristic of adamantanoid molecules.[3,10,11] Besides the usual 2900- and 1450-cm^{-1} hydrocarbon bands, there are only six other peaks of moderately weak intensity in the infrared spectrum of I. This is consistent with a structure of high symmetry, such as I (point group C_{2v}).

Four separate resonances are observed in the 100-MHz nmr spectrum of I (Figure 1) at 1.82 (area 2), 1.65 (16), 1.40 (2), and 1.24 ppm (4). When it is recalled that adamantane (II) (CH protons at 1.88 and CH_2 protons at 1.78 ppm.)[12] and diamantane (III) (all three kinds of protons at δ = 1.68 ppm)[3] give essentially a single line in the nmr, the multiplicity of bands displayed by I seems surprising, despite the eight different kinds of protons in the molecule. However, II and III are poor models for I, since the structure of the latter alone is "folded back" upon itself and C–C bond anisotropies can produce chemical shift differences. As shown in VII, a 1-ethyl group in adamantane shields the adjacent methylene groups and deshields the brigeheads protons.[12]

The methylene groups marked a in Ic should mutually shield one another. They have no counterpart in II or III, but are analogous to the indicated ring methylenes in VII. The observed shielding effect of signal a in Figure 1 is 0.41 ppm, measured from the resonance of the main body of protons, c. The methylene groups a (Ic) are unique in that there is but one adjacent proton. A doublet with area four and coupling constant 2.6 ± 0.2 Hz[12] would be predicted for their resonance, and this is exactly what is found.

The bridgehead protons marked d should be deshielded by the presence of the third adamantanoid ring (compare VII). The observed magnitude of this deshielding is 0.17 ppm (d, Figure 1). Bridgehead proton resonances in adamantane appear as featureless, broad (w_h = *ca.* 10 Hz) bands.[12] Because of the six adjacent hydrogens, the same appearance would be expected for the protons d, as found. The area measurement (two protons) also corresponds. More direct confirmation of the assignments of a and d was achieved by spin-decoupling experiments. Irradiation of resonance d collapses resonance a to a singlet. In addition, the two downfield peaks of the large c absorption are also collapsed, suggesting that the eight protons (labeled c′ in Ic) are responsible for this feature. Irradiation of a does not affect b.

The two bridgeheads b (Ic) have no counterpart in II or III, and they can be considered to be centrally a part of the two diamantane systems which comprise I (compare Ic and III). Since a bridgehead proton in adamantane (1.88 ppm) shifts upward in going to diamantane (1.68 ppm) by 0.20 ppm, there should be a comparable shift of protons b in Ic. The shift to higher fields of resonance b (Figure 1) (area two protons) is 0.18 ppm, consistent with the assignment proposed. Further, the breadth of this band (w_h = *ca.* 5 Hz) is smaller than that generally found for bridgehead resonances, but this is because protons b have only two adjacent neighbors each, and a narrower line than that from protons d is observed.

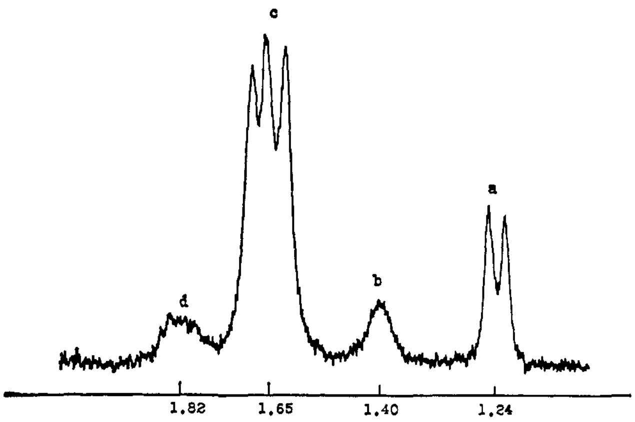


Figure 1. The 100-MHz nmr spectrum of triamantane (I); solvent $CDCl_3$, δ in parts per million from tetramethylsilane.

The mode of preparation employed would be expected[2,3,8-10,13] to lead to the thermodynamically most stable $C_{18}H_{24}$ isomer. Triamantane (I) is that molecule. All of the spectral properties of the substance obtained are in complete agreement with those expected of triamantane, although the information supplied is not really sufficiently detailed to establish the structure with absolute certainty. Accordingly, we have submitted the material for X-ray analysis. Nevertheless, we regard the degree of uncertainty in the structural assignment at present to be so low as to warrant our claim of synthesis of triamantane.

Acknowledgments. We wish to thank the Petroleum Society, the National Science Foundation, and the A. P. Sloan Foundation for support of this research. A departmental grant by the National Science Foundation was used to purchase the AEI MS-9 mass spectrometer, upon which measurements reported here were made. Dr. Kermit C. Ramey, Atlantic Refining Company, Glenolden, Pa., very kindly determined the 100-MHz nmr spectrum of triamantane. The Badische Anilin und Soda Fabrik AG, Ludwigshafen am Rhein, generously supplied a kilogram of cyclooctatetraene. A sample of cyclooctatetraene dimer was prepared at the European Research Associates Laboratories, Brussels. We wish to thank Dr. E. de Ruiter for furnishing us with this material.

---

(11) Z. Dolejšek, S. Hála, V. Hanuš, and S. Landa, *Collection Czech. Chem. Commun.*, **31**, 435 (1966).

(12) R. C. Fort, Jr., and P. von R. Schleyer, *J. Org. Chem.*, **30**, 789 (1965).

(13) P. von R. Schleyer, G. J. Gleicher, and C. A. Cupas, *ibid.*, **31**, 2014 (1966).

(14) National Science Foundation Undergraduate Research Participant, summer 1965.

(15) Alfred P. Sloan Foundation Fellow, 1962–1966.

(16) National Institutes of Health Postdoctoral Fellow, 1964–1965.

Van Zandt Williams, Jr.,[9,14] **Paul von Ragué Schleyer**[15]
Gerald Jay Gleicher, Lynn B. Rodewald[16]
Department of Chemistry, Princeton University
Princeton, New Jersey 08540
Received July 15, 1966

Vinyl Proton Abstraction during Base-Catalyzed Exchange of 2,3-Dihydrothiophene 1,1-Dioxide

Sir:

The role of carbanionic intermediates in base-catalyzed tautomerism of allylic systems is an area of high