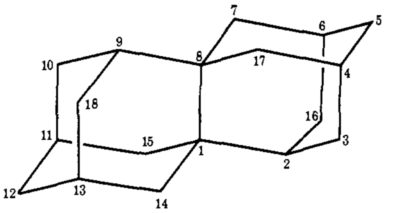
[2]Diadamantane, the First Member of a New Class of Diamondoid Hydrocarbons

Sir:

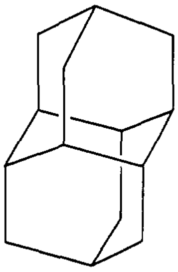
Hexacyclo[9.3.1.1^{2,6}.1^{4,8}.1^{9,13}.0^{1,8}]octadecane (I) is the first member of a homologous series of diamond-lattice hydrocarbons having condensed adamantane units with two carbon atoms in common. We have been able to synthesize I in good yield by $AlBr_3$-catalyzed isomerization, the method which has proven so effective in the preparation of adamantane,[1] diamantane (II),[2] triamantane,[3] and related cage hydrocarbons.[4]

We propose to designate I–IV as [*n*]diadamantanes, since all have two adamantane units with one or more atoms in common. This semitrivial nomenclature is easily extended to higher diamondoid molecules.[6]



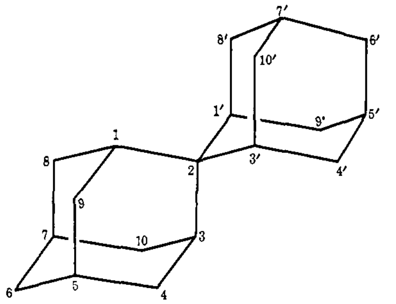
I

[2]diadamantane



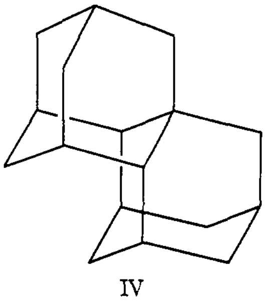
II

[6]diadamantane (diamantane)[2]



III

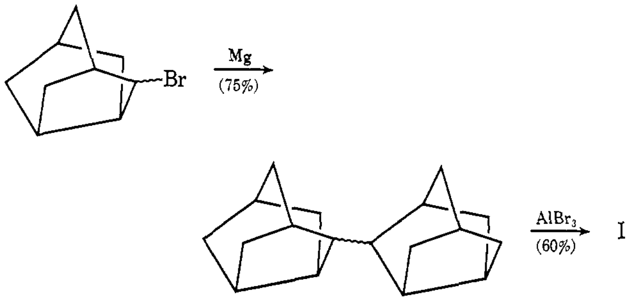
[1]diadamantane (spiro(adamantane- 2,2'-adamantane))[5]



IV

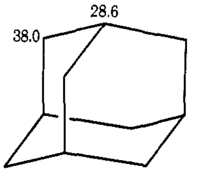
[3]diadamantane

The isomeric hexacyclic alkane chosen for rearrangement to I was 2,2'-binoradamantane (V). When 2-noradamantyl bromide (obtained in 95% yield by treatment of 2-noradamantanol[7] with PBr_5) was coupled with magnesium in ether, V (as a mixture of isomers) resulted in 75% yield. Stirring V for 1 hr at room temperature with a saturated solution of $AlBr_3$ in carbon disulfide or cyclohexane gave a 60% isolated yield of a new material, mp 194.0–195.2° (ethanol). Microanalysis (Calcd for $C_{18}H_{26}$: C, 89.19; H, 10.81. Found: C, 88.96; H, 10.89) and the mass spectrum confirmed the empirical formula of I. As in other diamondoid molecules[1–3,5] the parent mass spectral peak (at *m/e* = 242) was also the base peak. The second most intense peak (at *m/e* = 185) corresponds to M − 57; a similar peak is observed in the mass spectrum of adamantane.[4b]

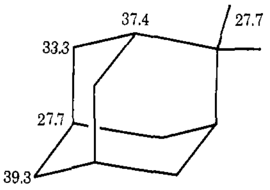


V

There are six different types of carbon atoms in I. The natural abundance, proton-decoupled and single-frequency off-resonance decoupled ^{13}C nmr spectra of a carbon tetrachloride solution of I exhibit $(CH_2)_2$, $(CH_2)_4 + (CH)_2$, $(CH_2)_4$, and $(CH)_4$ signals at 39.4, 37.5, 32.2, and 29.3 ppm downfield from tetramethylsilane, respectively. The long relaxation time of the quaternary carbons prevents their signals from being recorded. While the number of signals and their intensity ratio of 1:3:2:2, respectively, fit the symmetry requirements of [2]diadamantane (I), the structure determination rests on the ^{13}C chemical shift assignments of model compounds adamantane (VI),[8] 2,2-dimethyladamantane (VII),[9] and [1]diadamantane (III).[5]



VI



VII

The ^{13}C nmr spectrum of VII in carbon tetrachloride reveals CH_2, $(CH)_2$, $(CH_2)_4$, $(CH)_2$, and $(CH_3)_2$ signals

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(1) P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **79**, 3292 (1957); P. v. R. Schleyer and M. M. Donaldson, *ibid.*, **82**, 4645 (1960).

(2) C. Cupas, P. v. R. Schleyer, and D. J. Trecker, *J. Amer. Chem. Soc.*, **87**, 917 (1965); T. M. Gund, V. Z. Williams, Jr., E. Osawa, and P. v. R. Schleyer, *Tetrahedron Lett.*, 3877 (1970); T. Courtney, D. E. Johnson, M. A. McKervey, and J. J. Rooney, *J. Chem. Soc. Perkin Trans. 1*, 2691 (1972).

(3) V. Z. Williams, Jr., P. v. R. Schleyer, G. J. Gleicher, and L. B. Rodewald, *J. Amer. Chem. Soc.*, **88**, 3862 (1966).

(4) Reviews: (a) R. C. Fort, Jr., and P. v. R. Schleyer, *Chem. Rev.*, **64**, 277 (1964); (b) Z. Weidenhoffer and S. Hala, *Sb. Ved. Pr., Vys. Sk. Chemickotechnol. Pardubice*, **22**, 5 (1971); (c) R. C. Bingham and P. v. R. Schleyer, *Fortschr. Chem. Forsch.*, **18**, 1 (1971); (d) E. M. Engler and P. v. R. Schleyer, *MTP Rev. Sci.*, in press.

(5) (a) E. Boelema, J. Strating, and H. Wynberg, *Tetrahedron Lett.*, 1175 (1972); (b) W. D. Graham and P. v. R. Schleyer, *ibid.*, 1179 (1972).

(6) It is probably best to retain "diamantane," "triamantane," "tetramantane," etc. as alternative trivial names for II and similar homologs.

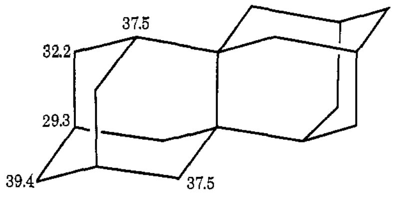
(7) A. Nickon, G. D. Pandit, and R. O. Williams, *Tetrahedron Lett.*, 2851 (1967); J. S. Wishnok, P. v. R. Schleyer, E. Funke, G. D. Pandit, R. O. Williams, and A. Nickon, *J. Org. Chem.*, **38**, 539 (1973).

(8) T. Pehk, E. Lippmaa, V. V. Sevostjanova, M. M. Krayuschkin, and A. I. Tarasova, *Org. Magn. Resonance*, **3**, 783 (1971).

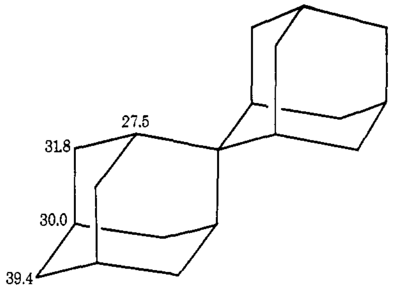
(9) V. Buss, R. Gleiter, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 3927 (1971).

at 39.3, 37.4, 33.3, 27.7, and 27.7 ppm, respectively. The symmetry of VII dictates the methylene shift assignments. Differentiation of the two methine sets is based on one being deshielded by β-methyl groups.

The spectrum of a carbon tetrachloride solution of III exhibits $(CH_2)_2$, $(CH_2)_8$, $(CH)_4$, and $(CH)_4$ signals at 39.4, 31.8, 30.0, and 27.5 ppm, respectively. The shift assignment emulates that of VII except for the expected upfield position of C_1 and C_3 owing to the influence of 1,3-diaxial interactions from the vicinal adamantane unit.



I

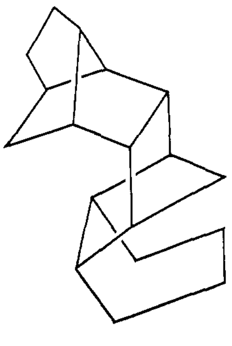


III

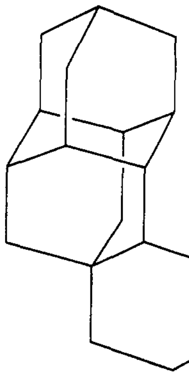
All chemical shifts of I except those of C_7, C_{14}, C_{15}, and C_{17} are derived from the shifts of III and VII, leaving the signal at 37.5 ppm for the remaining methylenes. The assignment supports strongly the [2]-diadamantane structure I.

The proton nmr spectrum was particularly distinctive. Theory predicts 14 signals, including three AB quartets, from the eight different proton types present. As was observed for III,[5b] the chemical shift differences of the protons in I are surprisingly large for an unsubstituted, saturated hydrocarbon. All 14 absorptions are clearly resolved in the 220-MHz spectrum of I.

Integration, spin decoupling, and comparison with model compounds allowed assignment of the signals of I to bridgeheads and AB pairs. The pentuplet ($J \sim 3$ Hz) at δ 1.13 (2 H) was due to the bridgehead protons on C_2 and C_9. A broad singlet at δ 1.99 (4 H, $W_{1/2} \cong 11$ Hz) corresponds to the other group of equivalent bridgehead protons (C_4, C_6, C_{11}, and C_{13}). The methylene protons gave rise to three AB quartets (all $J_{AB} \sim 12$ Hz). Being most remote in the molecule, the geminal protons at C_5 and C_{12} are expected to have the smallest chemical shift difference. The doublet pairs at δ 1.63 (2 H) and 1.71 (2 H) were assigned to these protons. Assignment of the other AB systems was made by analogy to the 220-MHz spectrum of 2,2-dimethyladamantane (VII) and [1]diadamantane (III).[5b] The protons on C_3 (and C_{10}, C_{16}, C_{18}) in I and the C_4 protons in VII and in III have a similar environment. The AB doublets in VII were centered at δ 1.50 and 2.05 ($J_{AB} \sim 12$ Hz) and in III at δ 1.54 and 2.04 ($J_{AB} \sim 12$ Hz). Thus, we assign the doublet pairs at δ 1.49 (4 H) and 2.16 (4 H) in the spectrum of I to the protons on C_3, C_{10}, C_{16}, and C_{18}. The remaining AB doublet pairs in I at δ 1.03 (4 H) and 2.52 (4 H) were assigned to the C_7, C_{14}, C_{15}, and C_{17} protons.



VIII



IX

We have also attempted to obtain I by isomerization of hexacyclo$[11.3.1.1^{4,11}.0^{2,14}.0^{3,12}.0^{5,10}]$octadecane (VIII), mp 114.9–115.8°, prepared by Diels–Alder addition of butadiene to Katz's dimer,[10] followed by hydrogenation. Under various rearrangement conditions, no [2]diadamantane (I) was detected by glc among the several products. The major component (~70%), collected by preparative glc, was shown by its mass spectrum (P^+ m/e 242 = $C_{18}H_{26}$) to be an isomerization and not a disproportionation product. Structure IX, the most stable cyclohexanodiamantane, appeared to be an attractive possibility for the major component as molecular mechanics calculations[11] actually predict IX ($\Delta H_f°$ calcd = −50.4 kcal/mol) to be appreciably more stable than I ($\Delta H_f°$ calcd = −42.6 kcal/mol). However, the ^{13}C nmr spectrum excluded IX from consideration, and the correct structure has not yet been established. This experiment demonstrates again that synthesis of higher diamondoid molecules by isomerization can be dependent on the choice of starting material.

We have already prepared [2]diamantane (I) in large quantity and are exploring its chemistry.

Acknowledgments. This research was supported at Princeton by grants from the National Institutes of Health (GM-19134), the National Science Foundation, and Hoffmann La Roche, Inc., Nutley, N. J.

(10) J. J. Mrowca and T. J. Katz, *J. Amer. Chem. Soc.*, **88**, 4012 (1966).

(11) Performed by E. Engler using a force field essentially that described by J. L. Fry, E. M. Engler, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **94**, 4628 (1972).

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Reaction of Alkenylboronic Acids with Iodine under the Influence of Base. A Simple Procedure for the Stereospecific Conversion of Terminal Alkynes into *trans*-1-Alkenyl Iodides *via* Hydroboration

Sir:

trans-1-Alkenylboronic acids, readily prepared *via* the hydroboration of 1-alkynes with catecholborane fol-