(CCl_4) for imine, 2.64 (q, 2 H); partial NMR (CCl_4) for enamine, 5.54 (q, 1 H, J = 7 Hz), 1.70 (d, 3 H, J = 7 Hz).

Ethyl 2-iminophenylacetate (3, R = Ph) was prepared as above: yield 100%;[14] ^{1}H NMR (CCl_4) 10.5 (s, 1 H), 7.3-8.0 (m, 5 H), 4.20 (q, 2 H), 0.85 (t, 3 H).

***N*-Acetyl-2,3-dehydroalanine (7).** Imine 3 (R = Me) was prepared as above. Triethylamine (0.77 mL, 5.5 mmol) was added and the solution cooled to 0 °C. Acetyl chloride (0.54 mL, 5.5 mmol) was added dropwise. The mixture was filtered, concentrated in vacuo, and the residue purified by bulb-to-bulb distillation, giving 0.42 g (58%) of pale yellow oil; ^{1}H NMR ($CDCl_3$) 8.20 (br s, 1 H), 6.58 (s, 1 H), 5.90 (br s, 1 H), 4.40 (q, 2 H), 2.27 (s, 1 H), 1.46 (t, 3 H).

General Procedure for Preparation of α-Keto Esters (5). Ethyl 2-Oxobutanoate (5, R = Et). Ethanol (0.05 mL, 0.8 mmol) was added to *n*-butyllithium (1.6 M, 0.32 mL, 0.5 mmol) in hexane. The mixture was dissolved in 5 mL of THF and stirred at 25 °C. Ethyl 2-azidobutanoate (0.76 mL, 5.0 mmol) was added dropwise. After 20 min at 25 °C, 125 mL (5 mmol) of N_2 had evolved, and the reaction was quenched with 2 mL of 3 N HCl. The solution was extracted with two 10-mL portions of ether. The combined organic layers were dried (K_2CO_3) and concentrated in vacuo. The yield was 86% as determined by GLC: ^{1}H NMR ($CDCl_3$) 4.13 (q, 2 H), 2.70 (q, 2 H), 1.23 (t, 3 H), 1.00 (t, 3 H); 2,4-DNP, mp 139-140.5 °C (lit.[15] mp 141-142 °C); mass spectrum, m/e 310 (M^+).

Ethyl pyruvate (5, R = Me) was prepared as above: yield 50%; ^{1}H NMR ($CDCl_3$) 4.31 (q, 2 H), 2.45 (s, 3 H), 1.50 (t, 3 H); 2,4-DNP, mp 154.5-155 °C (lit.[16] mp 154.5-155 °C); mass spectrum, m/e 296 (M^+).

Ethyl α-oxoisovalerate (5, R = $(CH_3)_2CH$) was prepared as above: yield 94%; NMR ($CDCl_3$) 4.25 (q, 2 H), 3.20 (m, 1 H), 1.35 (t, 3 H), 1.17 (d, 6 H); 2,4-DNP, mp 172.5-173.5 °C (lit.[17] mp 171.5-172 °C); mass spectrum, m/e 324 (M^+).

Ethyl phenylglyoxylate (5, R = Ph) was prepared as above: yield 91%; ^{1}H NMR ($CDCl_3$) 7.20-8.00 (m, 5 H), 4.37 (q, 2 H), 1.23 (t, 3 H); 2,4-DNP, mp 161-162.5 °C (lit.[18] mp 162-163.5 °C); mass spectrum, m/e 358 (M^+).

Ethyl phenylpyruvate (5, R = $PhCH_2$) was prepared as above. The residue was purified by bulb-to-bulb distillation, affording a 94% yield of clear, light yellow oil identified as the keto ester containing a small amount of enol:[19] ^{1}H NMR ($CDCl_3$) of keto form, 7.25 (s, 5 H), 4.30 (q, 2 H), 4.15 (s, 2 H), 1.40 (t, 3 H); 2,4-DNP, mp 132.5-133 °C (lit.[20] mp 132.5-133 °C); mass spectrum, m/e 372 (M^+).

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Registry No. 3 (R = Me), 75213-99-9; **3** (R = Et), 75214-00-5; **3** (R = Ph), 75214-01-6; **4** (R = Me), 71754-74-0; **4** (R = Et), 2571-38-2; **4** (R = $(CH_3)_2CH$), 75214-02-7; **4** (R = Ph), 75214-03-8; **4** (R = $PhCH_2$), 75214-04-9; **5** (R = Et), 15933-07-0; **5** (R = Me), 617-35-6; **5** (R = Me) 2,4-DNP derivative, 17767-38-3; **5** (R = $(CH_3)_2CH$), 20201-24-5; **5** (R = Ph), 1603-79-8; **5** (R = Ph) 2,4-DNP derivative, 3602-40-2; **5** (R = $PhCH_2$), 6613-41-8; **5** (R = $PhCH_2$) 2,4-DNP derivative, 50838-93-2; **7**, 23115-42-6; ethyl 2-bromopropanoate, 535-11-5; ethyl 2-bromobutanoate, 533-68-6; ethyl 2-bromo-3-methylbutanoate, 609-12-1; ethyl α-bromobenzeneacetate, 2882-19-1; ethyl α-bromobenzenepropanoate, 39149-82-1; lithium ethoxide, 2388-07-0; **5** (R = Et) 2,4-DNP derivative, 75214-05-0; **5** (R = $CH_3)_2CH$) 2,4-DNP derivative, 50838-92-1.

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Synthesis of Triamantane

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Triamantane, the third member of the diamondoid hydrocarbon series, has been synthesized efficiently in five easy stages from norbornadiene. Acid-catalyzed rearrangement of the norbornadiene [4 + 4] dimer, binor S (5), either in solution using silver perchlorate or in the gas phase on silica gel, gives two hexacyclic olefins (**13** and **14**) suitable (without separation) for further elaboration: [4 + 2] cycloaddition with butadiene gives C_{18} adducts whose hydrogenated forms (**26** and **27**) are converted by aluminum chloride catalyzed rearrangement into triamantane in 60% yield. By use of isoprene instead of butadiene in the cycloaddition stage the synthesis can be modified to produce 9-methyltriamantane. The mechanism of the binor S rearrangement is discussed.

The diamondoid hydrocarbons adamantane (**1**)[1] and diamantane (**2**)[2,3] are best prepared by Lewis acid catalyzed rearrangement of tetrahydrodicyclopentadiene (**3**) and tetrahydrobinor S (**4**), respectively.[4,5] These precursors are readily available, the former from hydrogenation of cyclopentadiene dimer and the latter from hydrogenolytic opening of the cyclopropane rings of the [4 + 4] norbornadiene dimer, binor S (**5**).[6] Although triamantane (**6**), the third member of the diamondoid series, has also been synthesized by rearrangement routes, the polycycles (**7**)[7]

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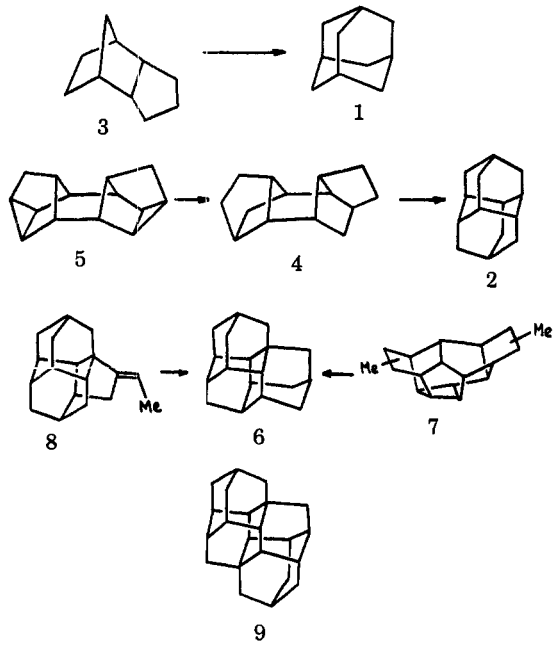
and (8),[8,9] used as precursors, are not easily prepared and the overall yield in both cases is very low (<1%). *anti*-Tetramantane (9), the fourth member of the series, has been synthesized in the gas phase by double homologation of diamantane.[9]

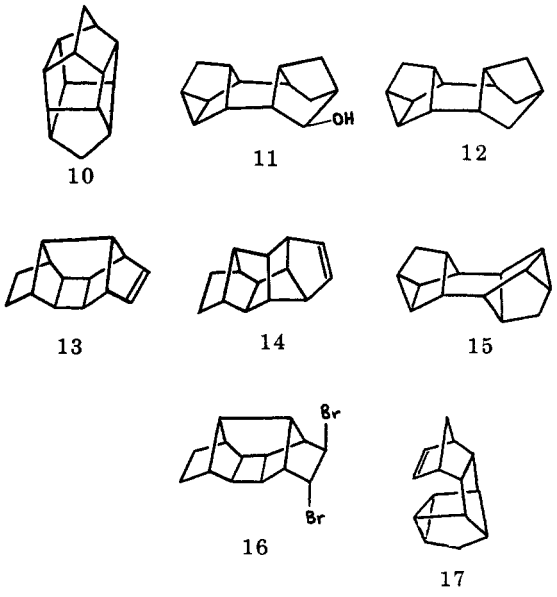


In seeking to devise an improved synthesis of triamantane, we were struck by the remarkable ease with which diamantane is produced from tetrahydrobinor S (>80% yield with aluminum chloride in dichloromethane[3]). Clearly, this precursor possesses to a high degree the requirements necessary for efficient rearrangement: it is a multiple-bridged system isomeric with, but appreciably more strained than, diamantane, and its structure is such that carbonium ion intermediates encounter no serious mechanistic obstacles on route to the product.[10] Accordingly, we investigated ways of modifying the binor S structure so as to make it an efficient precursor for triamantane also, and we now describe a new rearrangement of the dimer which renders this approach feasible.[11]

This elaboration of binor S into a triamantane precursor requires the addition of four carbon atoms. Futhermore, for preservation of the isomeric relationship between the two, this change must be brought about without an increase in the total number of rings since binor S and triamantane are both heptacycles. Ideally, we wished to rearrange binor S into a hexacyclic olefin which could be raised to the C_{18} heptacyclic level by addition of butadiene in a Diels–Alder reaction and thence to the required $C_{18}H_{24}$ level by hydrogenation. Apart from the fact that binor S undergoes catalytic hydrogenolysis at ordinary temperatures, little was known about the chemistry of this highly strained molecule. However, the susceptibility of strained, small-ring polycycloalkanes to metal-catalyzed bond reorganization is well-known[12] and so a further study of the chemistry of binor S was undertaken.

Since the cyclopropane rings of binor S open so readily on platinum in the presence of hydrogen we examined initially the effect of the catalyst in the absence of hydrogen. A platinum–silica catalyst and a gas-phase procedure were used. When binor S was vaporized in a stream of nitrogen and passed over the catalyst at 250 °C, a product mixture was obtained, consisting of two major components (ratio 1:1) and two minor components (ca. 5% of the total). The major products which were separable by preparative GLC and spinning-band distillation (though separation was found later to be unnecessary on route to triamantane), were isomeric with binor S. Both isomers were monoolefins, though without cyclopropane rings, and ^{13}C NMR data suggested that one isomer was highly symmetrical (8 lines) whereas the other was not (12 lines). Both isomers formed crystalline adducts with silver nitrate and crystalline dibromides with bromine. That the latter products were formed without rearrangement was established by exposing a mixture of the two to potassium iodide in methanol whereupon the olefins were regenerated. An X-ray diffraction study[13] of the trans dibromide (16) of the more symmetrical olefin revealed its structure to be 13. The second olefin was assigned structure (14) after consideration of the spectral data and likely mechanisms for its formation (vide infra).

Later solution studies revealed that binor S in benzene containing silver perchlorate, a metal salt known to cause rearrangement of other strained polycycles,[14] behaved in exactly the same way as it did in the gas phase on platinum–silica, furnishing 13 and 14 in 60% yield with trace amounts of the other two products. However, the precise role of the silver ion in the rearrangement was soon questioned when it was discovered that perchloric acid in benzene also promoted the formation of 13 and 14, though



the yield on isolation was poor. Futhermore, when a carefully dried sample of silver perchlorate was used in dry benzene the rearrangement was almost totally inhibited. This doubt about silver ion catalysis led us to reconsider

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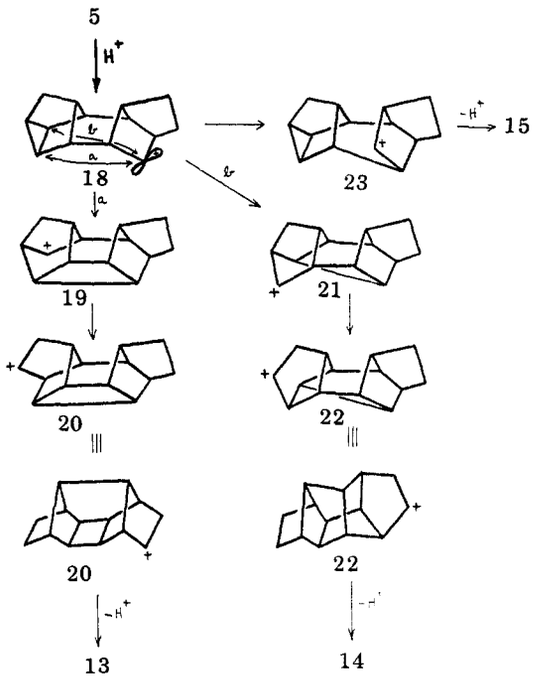
the gas-phase reaction of binor S on platinum–silica, in particular the role of the silica support. And indeed when binor S was passed in nitrogen over silica alone at 250 °C in the gas phase, fused in silica at 200 °C, or boiled with a suspension of silica gel in decalin, olefins **13** and **14** were obtained in up to 45% yield after isolation by distillation. With the gas-phase procedure the first material to break through the silica bed in the flow system was the heptacyclotetradecane (**10**). However, the surface of the catalyst aged quickly from coking and olefins **13** and **14** soon became the predominant products. Formation of the heptacyclotetradecane in this fashion parallels our previous observation of its formation from the Katz dimer (**17**) in the gas phase at elevated temperatures on silica alumina.[15] These observations all suggest that the rearrangement of binor S under these various conditions is in fact a proton-initiated process. Use of silver perchlorate in benzene, without exclusion of moisture, gave better yields than perchloric acid in benzene, due simply to the fact that olefins **13** and **14** form particularly stable adducts with silver ion which precipitate from solution as soon as they are formed whereas in perchloric acid the olefins are free to react further with the solvent, giving products of alkylation which could be detected. It is possible that at least some of the many rearrangements of strained, small-ring hydrocarbons involving apparent silver ion catalysis, reported over the years, may have been caused by Brønsted activity and not by the metal ion as supposed.

A proposal for the mechanism of the binor S rearrangement is summarized in Scheme I. Protonation of one of the cyclopropane rings produces cation **18**, the vacant orbital of which should be favorably disposed in distance and dihedral angle toward interaction with the inside edge of the second cyclopropane ring (X-ray analysis of a binor S derivative confirms that the inside edges of the cyclopropane rings are held in close proximity[16]). Cyclopropyl participation in cation **18** along pathway a produces a second cation (**19**) which cannot easily eliminate a proton but which can undergo a 1,2-bond shift to cation **20**. Proton loss from **20** produces olefin **13** of established structure. Although the structure of the second olefin is less secure, we propose formulation **14** on the grounds that there is a second, equally accessible pathway for cyclopropyl participation in cation **18** along direction b, leading to a comparable set of cations (**21** and **22**) and terminating after proton loss in olefin **14**. The ^{13}C NMR data for olefins **13** and **14** are consistent with the conclusion that reaction pathway b should lead to a less symmetrical product than pathway a. Furthermore, the structure of olefin **14** is such that hydrogenation of the double bond should produce a hexacyclotetradecane having a C_2 symmetry axis. Such a polycycle should exhibit seven resonances in its ^{13}C NMR spectrum as was found to be the case. We also explored the binor S rearrangement in the presence of water in the expectation that one or more of the cationic intermediates in Scheme I might be intercepted. After 6 h in 1:1 50% sulfuric acid–ether at room temperature, binor S was converted into the crystalline alcohol **11** in 50% yield. The structural assignment is based on the spectral data for **11** and for the hydrocarbon **12** obtained from it by successive oxidation and Wolff–Kishner reduction. However, the cationic precursor to alcohol **11** appears not to be directly implicated in Scheme I. Under conditions leading to olefins **13** and **14**, this cation

Scheme I



may be reversibly formed from binor S.

The fact that olefins **13** and **14** complex strongly with silver ion made possible the isolation of one of the minor products of the binor S rearrangement in silver perchlorate. In practice the rearrangement product was distilled, then dissolved in petroleum ether, and shaken with aqueous silver nitrate whereupon olefins **13** and **14** were almost completely removed from the organic phase. The residual solution was then processed by preparative GLC, yielding a liquid hydrocarbon, isomeric with binor S, whose spectral properties (^{13}C and ^{1}H NMR) all pointed to the structure of the hitherto unknown anti form of the [4 + 4] norbornadiene dimer, binor A (**15**). Like olefins **13** and **14**, binor A may also be derived from cation **18** in a formal sense if, instead of cyclopropyl participation, a 1,2-bond shift occurs to form cation **23** which then suffers a 1,3-proton elimination.

The remaining stages in the triamantane synthesis were conducted by using **13** and **14** separately or ca. 1:1 mixtures of the two, with comparable results. A Diels–Alder reaction with butadiene at 180 °C furnished the crystalline polycycles **24** and **25** in high yield. Catalytic hydrogenation of **24** and **25** gave the dihydro compounds **26** and **27**, which on exposure to aluminum chloride is hot cyclohexane for 5 days gave triamantane (**6**) in 60% yield. This conversion into triamantane was also observed in the gas phase, using our chlorinated platinum alumina–hydrogen chloride procedure.[17] The mechanism of this remarkable transformation has not yet been subjected to the type of graphical analysis used to illuminate the formation of adamantane,[18] methyladamantane,[19] and diamantane[10] by rearrangement. Numerous intermediates can be observed by GLC analysis of the reaction mixture at intermediate times; thus far none has been isolated or identified. Production of a graphical analysis of manageable size

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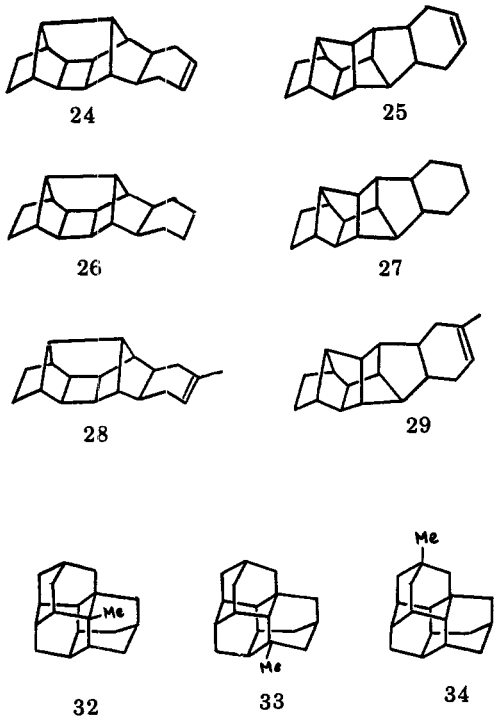

would require numerous approximations on the possible cationic pathways and severe restrictions on the number of intermediates involved. There are tens of thousands of heptacyclooctadecane isomers and there may be literally hundreds of energetically and mechanistically accessible pathways operating between **26**, **27**, and triamantane, but cursory examination of the structures does not reveal any obvious preferred pathway. An intriguing aspect of the mechanism is the fact that although precursors **26** and **27** are structurally quite different in character they are transformed into triamantane with equal ease.

This triamantane synthesis is easily modified to allow the introduction of methyl substituents. Thus Diels–Alder addition of isoprene to olefins **13** and **14** gave adducts **28** and **29**. Hydrogenation of these adducts produced the corresponding dihydro compounds **30** and **31** which on exposure to aluminum chloride in boiling cyclohexane produced 2-, 3-, and 9-methyltriamantane (32, 33, and 34) in the ratio <0.1:1.0:10.0 in 60% yield. Molecular models and steric considerations suggest that the substituent is most encumbered in the 2-methyl isomer and least encumbered in the 9 isomer. The product ratio observed is in fact the equilibrium ratio, confirming that 9-methyltriamantane is thermodynamically the most stable of the three isomers. Treatment of 2-methyltriamantane (**33**) with aluminum chloride caused isomerization, leading eventually to the three isomers in the same ratio. The three methyltriamantanes were identified by independent synthesis from the appropriate bromotriamantane[20,21] and methylmagnesium bromide, using a coupling procedure.[22] 2-Methyltriamantane (**32**) possesses the remarkably high melting point of 313–314 °C.

Experimental Section

Melting points were determined for samples sealed in capillary tubes and are uncorrected. ^{1}H Nmr data were measured at 60 and 90 MHz and ^{13}C NMR data at 22.63 MHz, using tetramethylsilane as internal standard. Mass spectrometric data were obtained at 70 eV with an AE1 MS902 instrument. GLC refers to analysis on one of the following columns: (A) 2-m Silicone Gum Rubber on Chromosorb G (2.5% w/w); (B) 5-m Silicone Gum Rubber on Chromosorb G (30% w/w, preparative); (C) 5-m Silicone Gum Rubber on Chromosorb G (10% w/w); (D) 2-m CyanoEthylMethylSilicone on Chromosorb G (2% w/w). The drying agent employed was magnesium sulfate. Binor S was prepared according to a literature procedure.[3]

Rearrangement of Binor S in the Gas Phase on Platinum–Silica. The catalyst was prepared as described previously.[9] Binor S (0.5 g) was vaporized in a stream of nitrogen and passed slowly through the catalyst bed (10 g) at 250 °C. Products (0.3 g) were condensed from the effluent gas stream in a cold trap at −78 °C. GLC analysis on column A at 120 °C showed the presence of about equal amounts of two major components and two trace components, one of which corresponded to binor S in retention time. Preparative GLC on column B at 100 °C gave olefin **13** [^{1}H NMR ($CDCl_3$) τ 3.8 (2 H), 7.5–9.2 (14 H); ^{13}C NMR ($CDCl_3$) 26.3, 34.7, 36.5, 37.4, 42.8, 44.8, 52.9, 134.9 ppm; mass spectrum, *m/e* 184 (83%, M^+). Anal. Calcd for $C_{14}H_{16}$: C, 91.31; H, 8.69. Found: C, 91.51; H 8.87] and olefin **14** [^{1}H NMR ($CDCl_3$) τ 4.1 (2 H), 7.7–8.9 (14 H); ^{13}C NMR ($CDCl_3$) 24.1, 27.2, 40.6, 42.4, 45.7, 47.4, 48.0, 48.7, 50.2, 54.1, 65.1, 133.7 ppm; mass spectrum *m/e* 184 (80%, M^+). Anal. Calcd for $C_{14}H_{16}$: C, 91.31; H, 8.69. Found: C, 91.20; H, 8.71].

Bromination of Olefin 13. Bromine (10% in CCl_4) was added dropwise to olefin **13** (0.2 g) in CCl_4 (0.5 mL) until the red color persisted. Evaporation of the solvent followed by crystallization of the residue from methanol gave the dibromide **16** (91%): mp 102–104 °C; mass spectrum, *m/e* 347, 345, 343 (<5%, M^+). Anal. Calcd for $C_{14}H_{16}Br_2$: C, 48.83; H, 4.67; Br, 46.50. Found: C, 48.71; H, 4.70; Br, 46.54.

Bromination of Olefin 14. Bromination of **14** exactly as described above for **13** yielded, the dibromide: mp 80–81 °C (from methanol); mass spectrum, *m/e* 347, 345, 343 (<5% M^+). Anal. Calcd for $C_{14}H_{16}Br_2$: C, 48.83; H, 4.67; Br, 46.50. Found: C, 48.79; H, 4.70; Br, 46.49.

Debromination of Dibromides from 13 and 14. A 1:1 mixture of the dibromides (0.5 g) was heated under reflux in dry methanol (50 mL) containing potassium iodide (10 g) while the progess of the reaction was monitored by GLC analysis on column A at 150 °C. After 5 days the dibromides were completely converted into olefins **13** and **14**.

Hydrogenation of Olefin 14. The olefin (0.5 g) in dichloromethane (5 mL) containing platinum oxide (0.1 g) was hydrogenated at atmospheric pressure. The mixture was then filtered, the solvent was removed by evaporation, and the residue was distilled at 115–117 °C (9 mmHg), yielding the dihydro compound: mass spectrum, *m/e* 186 (88%, M^+); ^{13}C NMR ($CDCl_3$) 24.2, 27.3, 40.8, 41.3, 43.6, 49.7, 52.3 ppm.

Rearrangement of Binor S on Silica Gel. Silica gel (60–85 mesh) (100 g) was heated at 200 °C under vacuum for 3 h and then cooled in nitrogen. Binor S (50 g) was added and the mixture was heated at 180 °C under nitrogen with stirring. After 4 days the mixture was cooled and washed several times with chloroform. The combined washings were concentrated and the residue was distilled, yielding olefins **13** and **14** (ratio 1:1, 24 g, 45%).

Rearrangement of Binor S in Decalin Containing Silica Gel. Silica gel (200 g), pretreated as described above, was added in 25-g portions to a stirred solution of binor S (110 g) in boiling decalin (300 mL) under nitrogen. After 6 days the mixture was cooled and filtered. Concentration of the filtrate followed by distillation of the residue gave olefins **13** and **14** (37 g, 35%).

Rearrangement of Binor S with Silver Perchlorate in Benzene. Silver perchlorate (20 g) was added in portions with stirring over 4 h to a boiling solution of binor S (80 g) in benzene (500 mL). The mixture was heated under reflux for a further 15 h and most of the benzene was then removed at reduced pressure. Concentrated ammonium hydroxide (200 mL) was added to the residue and the mixture was stirred at room temperature for 2 h and then extracted (3 × 100 mL) with light petroleum. The combined extracts were washed with water, dried, and concentrated to an oil which on distillation at 110–115 °C (9 mmHg) gave a 1:1 mixture of olefins **13** and **14** (51 g, 64%). Redistillation

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of the mixture using a spinning-band fractionating column gave pure samples of olefin **13**, bp 118–120 °C (9 mmHg), and olefin **14**, bp 112–114 °C (9 mmHg).

Reaction of Binor S with Sulfuric Acid. Binor S (5 g) in diethyl ether (25 mL) was stirred with 50% sulfuric acid (10 mL) at room temperature for 6 h. The reaction mixture was diluted with water (100 mL) and the ether layer and ethereal extracts of the aqueous layer were combined, washed with aqueous sodium bicarbonate and water, and dried. Removal of the solvent followed by crystallization of the residue from acetone gave alcohol **11** (2.8 g, 50%): ^{1}H NMR ($CDCl_3$) τ 6.05 (1 H), 9.2–7.8 (17 H); ^{13}C NMR ($CDCl_3$) 15.2, 15.5, 16.2, 30.6, 32.4, 33.9, 34.8, 35.2, 36.9, 40.2, 41.8, 46.6, 47.5, 78.3 ppm; mass spectrum, m/e 202 (24, M^+). Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.26; H, 9.18.

Conversion of Alcohol 11 to Hydrocarbon 12. Jones reagent was added dropwise with stirring to a solution of the alcohol (4 g) in acetone (100 mL) until oxidation was complete. The reaction mixture was diluted with water and extracted with chloroform (3 × 25 mL). The combined extracts were washed with water, dried, and concentrated to an oil which was placed on a column of silica gel (100 g). Elution with ether–light petroleum (1:20) gave the ketone (2.7 g, 66%): mp 64–66 °C (from pentane): ^{1}H NMR ($CDCl_4$) τ 7.4–9.2; ^{13}C NMR ($CDCl_3$) 14.7, 14.9, 15.2, 32.4, 33.5, 34.6, 31.1, 38.9, 41.6, 48.2, 52.8, 219.8 ppm; mass spectrum, m/e 200 (37%, M^+). Anal. Calcd for $C_{14}H_{18}O$: C, 83.96; H, 8.05. Found: C, 84.04; H, 7.98.

The ketone (1 g), hydrazine hydrate (4 mL), and acetic acid (2 mL) were heated at 80–90 °C in triethylene glycol (25 mL) under nitrogen for 24 h. Potassium hydroxide (10 g) was then added and the mixture was heated at 200 °C for 6 h. The cooled reaction mixture was diluted with water (250 mL) and extracted with ether (3 × 50 mL). The combined extracts were washed with water, dried, and concentrated. Distillation of the residue gave hydrocarbon **12** as an oil (0.7 g): ^{1}H NMR (CCl_4) τ 7.4–9.6; ^{13}C NMR ($CDCl_3$) 14.9, 15.2, 33.6, 34.0, 34.4, 35.4, 38.0, 38.6, 39.3, 41.7 ppm; mass spectrum, m/e 186 (100%, M^+). Anal. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C, 90.34; Hd, 9.87.

Isolation of Binor A. The product of rearrangement of binor S (10 g) with silver perchlorate in benzene was subjected to initial purification by distillation and the distillate (6.2 g) was dissolved in light petroleum (10 mL). A solution of silver nitrate (8.0 g) in water (10 mL) was added and the mixture was stirred for 6 h at room temperature. The silver nitrate complexes of olefins **9** and **10** were removed by filtration and the filtrate was extracted with light petroleum (7 × 10 mL). The combined extracts were dried and concentrated to an oil (0.4 g). Preparative GLC on column A at 120 °C gave binor A (**15**): ^{1}H NMR ($CDCl_3$) τ 9.02 (6 H), 8.80 (4 H), 8.20 (2 H), 7.87 (4 H) (cf. ^{1}H NMR spectrum of binor S, τ 8.95 (6 H), 8.72 (4 H), 8.40 (2 H), 8.12 (4 H)); ^{13}C NMR ($CDCl_3$) 13.6, 15.5, 32.9, 42.5 ppm; mass spectrum, m/e 184 (100%, M^+). Anal. Calcd for $C_{14}H_{16}$: C, 91.30; H, 8.70. Found: C, 91.21; H, 8.80.

Conversion of Mixture of 13 and 14 into Triamantane. A mixture of **13** and **14** (30 g) and butadiene (50 mL) was heated in a stainless steel autoclave at 160 °C for 24 h. Distillation of the product at bp 140–145 °C (0.05 mmHg) gave the adducts **24** and **25** (27 g, 70%). Anal. Calcd for $C_{18}H_{22}$: C, 90.70; H, 9.30. Found: C, 90.45; H, 9.29.

Adducts **24** and **25** were hydrogenated in dichloromethane (100 mL) in the presence of Adam's catalyst (0.5 g), using 3 atm of hydrogen pressure. The catalyst was removed by filtration and the filtrate evaporated, yielding the dihydro compounds **26** and **27** in quantitative yield.

A mixture of **26** and **27** (5 g) and anhydrous aluminum chloride (2 g) in cyclohexane (250 mL) was heated under reflux with stirring for 5 days. The cooled mixture was poured on ice and the organic layer and light petroleum extracts (3 × 50 mL) of the aqueous layer were combined, dried, and concentrated to an oil which on addition of acetone produced crystals of triamantane (**6**, 3 g, 60%). A sample recrystallized from acetone had mp 225–225. 5 °C (lit.[7] mp 221–221.5 °C).

Conversion of Olefin 13 into Triamantane. Olefin **13** (39 g) was treated with butadiene exactly as described above, yielding the adduct **24** (35 g, 68%): bp 145–147 °C (0.05 mmHg), which solidified; mp 92–94 °C (from methanol); mass spectrum, m/e 238 (100%, M^+). Anal. Calcd for $C_{18}H_{22}$: C, 90.70; H, 9.30. Found: C, 90.4; H, 9.30.

Adduct **24** was hydrogenated in quantitative yield to the dihydro derivative **26**: mp 117–119 °C (from methanol); mass spectrum, m/e 240 (100%, M^+). Anal. Calcd for $C_{18}H_{24}$: C, 89.94; H, 10.06. Found: C, 90.12; H, 10.24. Treatment of the dihydro derivative **26** with aluminum chloride in cyclohexane exactly as described above gave triamantane in ca. 60% yield.

Conversion of Olefin 14 into Triamantane. A similar sequence was used to prepare adduct **25** from olefin **14**. The pure adduct had bp 143–145 °C (0.05 mmHg); mass spectrum, m/e 238 (62%, M^+). Anal. Calcd for $C_{18}H_{22}$: C, 90.70; H, 9.30. Found: C, 90.57; H, 9.26.

Hydrogenation of **25** gave the dihydro derivative: mp 61–63 °C (from methanol); mass spectrum, m/e 240 (100%, M^+). Anal. Calcd. for $C_{18}H_{24}$: C, 89.94; H, 10.06. Found: C, 39.70; H, 10.02. Treatment of **27** with aluminum chloride in cyclohexane gave triamantane in 60% yield.

Preparation of Isoprene Adducts 28 and 29. A 1:1 mixture of olefins **13** and **14** (50 g) and isoprene (34 g) containing hydroquinone (0.5 g) was heated in an autoclave at 180 °C for 20 h. The reaction mixture was taken up in light petroleum and passed through a column of silica gel. Distillation gave unreacted starting material followed by adducts **28** and **29**, bp 98–100 °C (0.04 mmHg) (33.5 g, 55%). Crystallization of the adduct mixture from acetone gave needles: mp 64–68 °C; mass spectrum, m/e 252 (100%, M^+). Anal. Calcd for $C_{19}H_{24}$: C, 90.42; H, 9.58. Found: C, 90.54; H, 9.50.

Hydrogenation of Adducts 28 and 29. A 1:1 mixture of these adducts was hydrogenated exactly as described earlier for adducts **26** and **27**, giving products **30** and **31** as colorless plates: mp 77–79 °C (from acetone); mass spectrum, m/e 254 (100%, M^+). Anal. Calcd for $C_{19}H_{26}$: C, 89.70; H, 10.30. Found: C, 90.00; H, 10.33.

Aluminum Chloride Catalyzed Rearrangement of 30 and 31. A 1:1 mixture of hydrogenated adducts **30** and **31** (5 g) and aluminum chloride (2 g) in cyclohexane (250 mL) was heated under reflux for 5 days after which time GLC analysis on column B at 150 °C showed no further change. The cooled mixture was poured onto ice and the products were isolated by extraction. Distillation at 90–100 °C (0.04 mmHg) gave the rearrangement product (3 g, 60%) as a colorless liquid. GLC analysis on column B at 150 °C showed that the product consisted of 2-, 3-, and 9-methyltriamantane (32, 33, and 34) in the ratio <0.1:1.0:10.0 by coinjection with authentic samples.

2-Methyltriamantane (32). 2-Bromotriamantane[20] (1.13 g) and methylmagnesium bromide (from 1.0 g of magnesium and 4 mL of methyl bromide) were heated at 100 °C for 20 min in a pressure bottle according to the procedure in ref 22. 2-Methyltriamantane was obtained as a white solid (0.55 g, 61%), mp 313–314 °C (from acetone). Anal. Calcd for $C_{19}H_{26}$: C, 89.70; H, 10.30. Found: C, 89.37; H, 10.00.

3-Methyltriamantane (33). This isomer, prepared from 3-bromotriamantane[20] exactly as just described for the 2-methyl isomer, had mp 158–159 °C (from acetone). Anal. Calcd for $C_{19}H_{26}$: C, 89.70; H, 10.30. Found: C, 89.92; H, 10.21.

9-Methyltriamantane (34). This isomer was prepared in 74% yield from 9-bromotriamantane,[20] mp 28–29 °C (from acetone). For a discussion of the NMR spectra of 2-, 3-, and 9-methyltriamantane see ref 21.

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Registry No. 5, 13002-57-8; **6**, 13349-10-5; **11**, 74999-09-0; **11** ketone, 74999-10-3; **12**, 74999-11-4; **13**, 62870-26-2; **14**, 38589-62-7; **14** dihydro, 74999-12-5; **15**, 75044-21-2; **16**, 62870-25-1; **24**, 75044-22-3; **25**, 62870-28-4; **26**, 74999-13-6; **27**, 74999-14-7; **28**, 74999-15-8; **29**, 75010-82-1; **30**, 67615-83-2; **31**, 67615-84-3; **32**, 70950-41-3; **33**, 71548-04-4; **34**, 67615-85-4; butadiene, 106-99-0; isoprene, 78-79-5; 2-bromotriamantane, 67613-53-0; 3-bromotriamantane, 67613-55-2; 9-bromotriamantane, 67613-54-1.