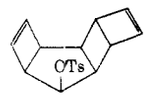
Soc., 92, 2542 (1970).
(25) These factors are roughly estimated from the rate ratios of I/13-OTs and 10-OTs/I.



I

$k = 3.54 \times 10^{-7}$ (25 °C)

K. Yano and K. Yoshida, unpublished result.
(26) S. Winstein, F. Gadient, E. J. Stafford, and P. E. Klinedinst, J. Am. Chem. Soc., 80, 5895 (1958).
(27) S. Winstein and C. Ordronneau, J. Am. Chem. Soc., 82, 2084 (1960).
(28) A rather small heat of activation and a negative entropy of activation for 10-OTs, when compared to those for 11-OTs, may also suggest a possible existence of the stabilized carbonium ion (22). However, owing to inaccuracy of these values of 11-OTs because of the narrow temperature range, it does not seem to be reasonable to discuss the possibility by comparison of those data.

Studies on $(CH)_{2n}$ Hydrocarbons. Alternative Syntheses of [3]Peristylane (Triaxane)

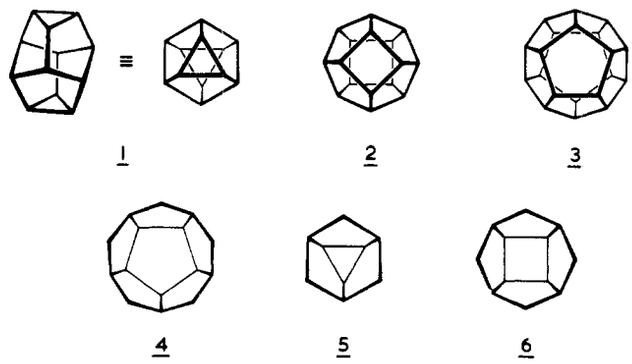
Peter J. Garratt* and John F. White

Department of Chemistry, University College London, London WC1H 0AJ, United Kingdom

Received October 20, 1976

Two routes to [3]peristylane (**5**) are described, both starting from norbornadiene. Conversion of norbornadiene to *endo*- and *exo*-3-carboxybicyclo[3.2.1]octan-6-ene (**7**) was carried out by known procedures and the acid separated into the exo and endo isomers. Reduction of the endo isomer **7a** with lithium aluminum hydride gave the corresponding alcohol, which was reoxidized with *N*-chlorosuccinimide and dimethyl sulfide to the endo aldehyde **10**. The sodium salt of the corresponding tosylhydrazone **11** was pyrolyzed to 4,5-diazatetracyclo[5.3.1.$0^{2,6}$.$0^{3,9}$]undec-4-ene (**12**), which itself on pyrolysis gave [3]peristylane (**5**). Treatment of the endo acid **7a** with thionyl chloride led to the formation of *exo*-4-chloronoradamantan-2-one (**14**), which was reduced with sodium borohydride to the corresponding alcohol **15**. Reaction of **15** with thionyl chloride gave 2,4-dichloronoradamantane (**16**) which, on treatment with disodium naphthalenide, gave **5**. Reduction of **5** with hydrogen over PtO_2 gave noradamantane.

The $(CH)_{2n}$ hydrocarbons, for reasons of symmetry, have different properties when n is an odd to those when n is an even integer. This difference has been most clearly demonstrated in the case of the annulenes, those compounds in which n is odd being aromatic whereas those in which n is even are antiaromatic.[1,2] Similarly the topology of polycyclic saturated $(CH)_{2n}$ systems will also depend on the nature of n. We have been interested in the series of molecules composed of a central n-membered ring connected by alternate carbon atoms to two $n/2$-membered rings. Such systems are only possible when n is an even integer, and this type of system can be illustrated by the first three members of the series **1**, **2**, and **3**, in which n is respectively 6, 8, and 10.[3]



1 2 3

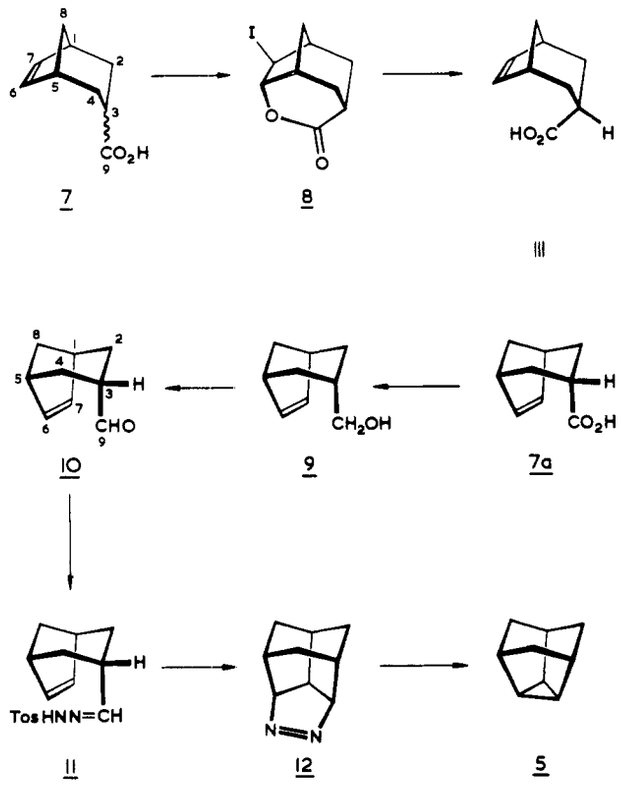
4 5 6

The only compound of this series which has received any extensive synthetic attention up to the present time has been dodecahedrane (**3**),[4,5] which has attracted interest as it represents one of the five Platonic solids, being composed entirely of planar five-membered rings.[6] Compounds **1** and **2** do not represent regular solids since the faces of the five-membered rings are not planar (see **1**). For the purpose of synthesis these systems can be dissected in a number of ways. Eaton and Mueller[4] have approached the synthesis of dodecahedrane by a route in which one of the five-membered rings is to be added in the final step, and they have prepared a derivative of the compound **4**, in which a five-membered ring is joined by alternate carbon atoms to a ten-membered ring. They have called this compound peristylane, but as it is a member of a second series of compounds in which an n-membered ring is joined by alternate carbon atoms to a $2n$-membered ring we would like to generalize their nomenclature and call this compound [5]peristylane. The related systems to **1** and **2** would then be [3]peristylane (**5**) and [4]peristylane (**6**),[6] which require the addition of a three- and a four-membered ring, respectively, to complete the $(CH)_{2n}$ system. [3]Peristylane has previously been prepared by Nickon and Pandit,[7] who called it triaxane, but we would prefer to use the peristylane nomenclature in the interest of economy of trivial nomenclature.[8] We now describe two alternative routes to **5** which we hope will be susceptible to extension to the synthesis of **1**.[9]

As **1** was our eventual synthetic goal, we wished to explore a route to **5** in which the intermediate would be capable of being modified so that substituents could be introduced at the appropriate positions. To this end, *endo*-bicyclo[3.2.1]oct-6-ene-3-carboxaldehyde (**10**) appeared to be a suitable precursor, since the preparation of compounds in which functional groups had been introduced at the 2, 4, and 6 positions, those necessary for construction of the final three-membered ring, seemed eminently feasible.

A mixture of *endo*- and *exo*-3-carboxybicyclo[3.2.1]oct-6-ene (**7**) was prepared in 14% yield from norbornadiene by the previously described route.[10,11] The exo and endo acids could be separated as previously described;[11] treatment with iodine in potassium iodide converted the endo acid into the iodolactone **8**, which could be separated and reconverted to the endo acid **7a** (ca. 70%) by treatment with zinc in ethanol. Lithium aluminum hydride reduction of **7a** gave the corresponding endo alcohol **9**, 89%, mp 30–32 °C. Oxidation of **9** by the method of Corey and Kim,[12] *N*-chlorosuccinimide and dimethyl sulfide, gave the colorless endo aldehyde **10**, mp

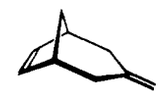
102–104 °C, 55%. In the ^{1}H NMR spectrum the aldehyde proton was at τ 0.5, and the olefinic protons appeared as a broad singlet at τ 4.22. Reaction of the aldehyde with tosylhydrazide in petroleum ether (bp 60–80 °C) in the presence of acetic acid gave the corresponding endo tosylhydrazone **11**, 98%, as colorless rods, mp 120.5–122 °C dec. In the ^{1}H NMR spectrum the azine proton appeared as a broad singlet at τ 2.9. The stereochemistry of all of these derivatives is secure since, by a parallel series of reactions, the corresponding exo compounds were also prepared. As expected, both the endo aldehyde and tosylhydrazone were readily converted to the respective exo isomers, such rearrangement partially occurring during chromatography, particularly of **11**. Both the endo aldehyde **10** and tosylhydrazone **11** show an upfield shift of the olefinic protons in the ^{1}H NMR spectrum compared to the exo isomers, presumably due to the shielding effects of the adjacent groups.



7 8 III 10 9 7a 11 12 5

Treatment of the endo tosylhydrazone **11** with sodium hydride in dry THF gave a white precipitate of the sodium salt. This was dried and then pyrolyzed at 200–250 °C at low pressure under a nitrogen atmosphere when 4,5-diazatetracyclo[5.3.1.0.^{2,6}.0^{3,9}]undec-4-ene (**12**), mp 120 °C, sublimed out of the system in 52% yield. The ^{1}H NMR spectrum showed a double doublet at τ 5.00 (2 H, H^3, H^6, J = 5, 7 Hz) and a double doublet at τ 7.20 (1 H, H^2, J = 7, 14 Hz), together with a high-field complex band (9 H). Sublimation of **12** into a vertical furnace at 500 °C gave [3]peristylane, 82%, as a colorless solid. Attempts to obtain a melting point were unsuccessful in our hands, sublimation occurring, but all the observed spectroscopic properties were identical with those reported by Nickon and Pandit.[7] Repetition of our synthesis but using lithium aluminum deuteride instead of lithium aluminum hydride to reduce the acid **7a** gave a monodeuterated [3]peristylane with the deuterium in the three-membered ring, and again in conformity with the previous observations[7] the τ 7.96 signal was diminished.

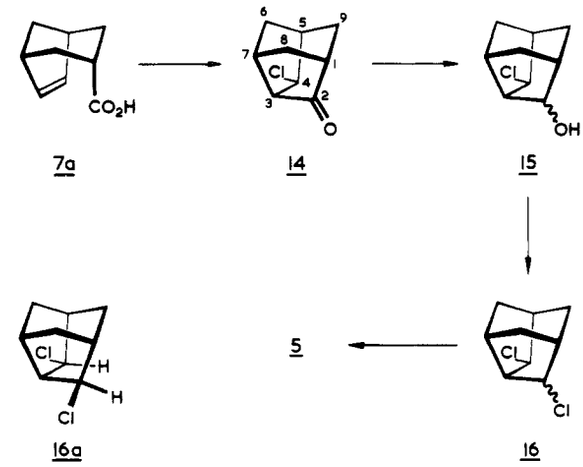
For comparison, the pyrolysis of the sodium salt of the exo tosylhydrazone isomer was examined, and it was found that 3-methylenebicyclo[3.2.1]oct-6-ene (**13**) was the major product. This compound was identified by comparison of its



13

spectral properties with those of an authentic sample.[13] The formation of **12** from **11** reflects the close proximity of the tosylhydrazone group to the double bond, but the sequence of events leading to the formation of **12** and the expulsion of the tosyl group is open to a wide variety of interpretations.

A second route to **5** from the endo acid **7a** was also explored. Baldwin and Fogelsong[11] had reported that attempts to prepare the endo acid chloride from **7a** with thionyl chloride gave instead a mixture of ketones, to one of which they tentatively assigned the *exo*-4-chloroadamantan-2-one structure. We have repeated this reaction and have obtained a ketone as a colorless solid, mp 104–105 °C. We concur with the previous structural assignment and further, on the basis of the ^{1}H NMR spectrum, substantiate the exo stereochemistry for this compound, as shown in structure **14**. Thus in **14** the H-4 proton resonates as a sharp singlet, characteristic of an endo proton and consequently an exo substituent. Treatment of **14** with sodium borohydride in anhydrous methanol gave 4-chloronoradamantan-2-ol (**15**), mp 120–126 °C, in 93% yield. The exo–endo stereochemistry shown is tentatively assigned on the basis of the ^{1}H NMR spectrum, the H-4 proton appearing as a broad singlet, whereas the H-2 proton appears as a multiplet. Reaction of the chloro alcohol **15** with neat thionyl chloride gave the dichloride **16**, a pale yellow oil, as a 2:1 mixture of the exo,exo and endo,exo isomers. When the reaction was repeated using pyridine as solvent only a low yield (10%) of the dichloride was obtained which, however, appeared to be exclusively the *exo,exo*-2,4-dichloronoradamantane (**16a**). The ^{13}C NMR spectrum of **16a** showed only six types



7a 14 15 16a 5 16

of carbon atoms, clearly demonstrating that the chlorines must have the same relative stereochemistry. The ^{1}H NMR spectrum showed a broad singlet at τ 5.85 due to the proton on the carbon bearing the chlorine, which was as expected for a derivative with an exo substituent.

Reaction of the dichloride mixture **16** with disodium naphthalenide in THF under nitrogen gave [3]peristylane (80%), identical in all observed respects with the sample prepared by the previously described route. The overall yield of **5** from the endo acid **7a** by the reaction sequence was 44%.

Nickon and Pandit[7] had reported the cleavage of [3]peristylane to noradamantol acetate by treatment with a mixture of acetic acid and sulfuric acid. Hydrogenation of **5** with PtO_2 in CCl_4 gave noradamantane, identified by comparison of the spectral properties, but a long reaction period was required. Treatment of **5** with $AlCl_3$ gave only polymeric products. Reaction of **5** with silver tetrafluoroborate in $CDCl_3$ at 70 °C

gave, in low yield, a mixture of two compounds, that in greatest amount being dimeric.

In order to develop the synthetic route forward toward **1**, functionalization of the methylene carbons in **5** is required. These carbons are derived from C-2, -4, and -8 in **7a**, and these in turn are derived from C-2, -3, and -7 in norbornadiene. Suitably substituted norbornadienes are known and we are currently exploring routes to functionalized [3]peristylanes with these.

Experimental Section

^{1}H NMR spectra were obtained on either a Varian T-60 or HA 100 spectrometer and are reported in τ units with Me_4Si as the internal standard. ^{13}C NMR spectra were obtained on a Varian CFT-20 spectrometer in $CDCl_3$, and are reported in parts per million from Me_4Si as internal standard. Mass spectra were taken on either an AEI MS-12 or MS-9 spectrometer. Infrared spectra were recorded on a Unicam SP 200 or Perkin-Elmer PE 257 recording spectrometer, and only strong and medium bands are reported. Melting points were taken on a Kofler hot stage and are uncorrected. Silica for TLC was Merck Kieselgel HF_{254}. Solvents were purified by standard methods.

Preparation of 3-Carboxybicyclo[3.2.1]oct-6-ene (7). Reduction of 3-carboxybicyclo[3.2.1]octa-2,6-diene (10 g) with potassium in liquid NH_3 by the method of Baldwin and Fogelsong gave **7** (9.9 g), with spectroscopic data in accord with those reported.[11]

Preparation of the Iodolactone 8. The mixture **7** (9.2 g), as the sodium salt, was treated with KI and I_2 to give **8** (9.4 g), mp 90–96 °C (lit.[11] 89–96 °C), recrystallized mp 97–98.5 °C (LIT/[11] 9—-9—/5 °C).

Preparation of *endo*-3-Carboxybicyclo[3.2.1]oct-6-ene (7a). The crude iodolactone (9.4 g) was reduced with zinc dust in ethanol to give **7a** (4.0 g), mp 105–115 °C (lit.[11] 121–123 °C).

Preparation of *exo*-3-Carboxybicyclo[3.2.1]oct-6-ene. The aqueous extracts from two iodolactone preparations were acidified to give the *exo*-**7** (5.8 g).

Reduction of 7a. The endo acid **7a** (2.0 g, 13 mmol) in dry ether (50 mL) was added to a stirred suspension of $LiAlH_4$ (1.0 g, 26 mmol) in ether (30 mL). The mixture was heated to reflux for 1 h and then cooled and water (1 mL), aqueous NaOH (15%, 1 mL), and water (3 mL) were added dropwise. The mixture was filtered and the filtrate was washed with aqueous NaOH (7%, 10 mL) and water (2 × 10 mL) and dried ($MgSO_4$). Removal of the solvent by evaporation and cooling the residue at −15 °C gave ***endo*-3-hydroxymethylbicyclo[3.2.1]oct-6-ene (9)**: 1.60 g (89%); mp 30–32 °C; ^{1}H NMR (CCl_4) τ 4.19 (bs, 2 H, olefin), 6.59 (d, 2 H, CH_2OH), 7.4–8.8 (m, 10 H); IR (CCl_4) 3350, 3050, 2920, 1455, and 1360 cm^{-1}.

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.46; H, 10.20.

Reduction of 7b. The exo acid was reduced with $LiAlH_4$ as described for **7a** to give ***exo*-3-hydroxymethylbicyclo[3.2.1]oct-6-ene:** 1.56 g (87%); oil; ^{1}H NMR (CCl_4) τ 4.19 (bs, 2 H, olefin), 6.65 (d, 2 H, CH_2OH), 7.3–9.0 (m, 10 H); IR (CCl_4) 3400, 3050, 2920, and 1365 cm^{-1}. The 3,5-dinitrobenzoate was prepared from 3,5-dinitrobenzoyl chloride as pale green plates, mp 105–107 °C.

Anal. Calcd for $C_{16}H_{16}N_2O_6$: C, 57.83; H, 4.85; N, 8.43. Found: C, 57.30; H, 4.77; N, 8.23.

Oxidation of 9. Dimethyl sulfide (1.6 mL) was added slowly to a stirred solution of *N*-chlorosuccinimide (2.2 g, 16 mmol) in toluene (50 mL) at 0 °C under N_2. The mixture was stirred at 0 °C for a further 30 min and then cooled to −25 °C and a solution of **9** (1.40 g, 10 mmol) in toluene (6 mL) was slowly added. Stirring was continued at −25 °C for 2 h, a solution of triethylamine (1.53 g, 15 mmol) in toluene (6 mL) was then added in one portion, and the mixture was allowed to come to room temperature. Ether (75 mL) was then added, the mixture was filtered, and the precipitate was washed with ether (25 mL). The combined ethereal layers were washed with HCl (1%, 25 mL), $NaHCO_3$ (1%, 25 mL), and water (2 × 30 mL), and dried ($MgSO_4$). Evaporation of the solvent gave a pale yellow oil which, on chromatography on silica, eluting with Et_2O and pentane, gave firstly ***endo*-3-(methylthio)methylbicyclo[3.2.1]oct-6-ene** [pale yellow oil; 0.06 g (3.0%); MS *m/e* 198 (M^+, 5%), 79 (100%); ^{1}H NMR (CCl_4) τ 4.13 (bs, 2 H), 5.53 (s, 2 H), 6.60 (d, 2 H), 7.4–8.8 (m, 12 H)] and then ***endo*-3-formylbicyclo[3.2.1]oct-6-ene (10)** [0.73 g (54%); mp 102–104 °C (petroleum ether); ^{1}H NMR (CCl_4) τ 0.50 (s, 1 H), 4.22 (bs, 2 H), 7.3–7.5 (m, 2 H), 7.5–8.7 (m, 8 H); IR (CCl_4) 2920, 2860, 2700, 1715, 1465, 1450, and 1360 cm^{-1}].

Oxidation of the Exo Alcohol 7b. The exo alcohol was oxidized by the method of Corey and Kim[12] as described above to give firstly ***exo*-3-(methylthio)methylbicyclo[3.2.1]oct-6-ene** [pale yellow oil; 0.11 g (5.6%); ^{1}H NMR (CCl_4) τ 4.18 (bs, 2 H), 5.48 (s, 2 H), 6.70 (d, 2 H), 7.5–9.1 (m, 12 H)] and then ***exo*-3-formylbicyclo[3.2.1]oct-6-ene** [0.68 g (50%); colorless oil; ^{1}H NMR (CCl_4) τ 0.50 (s, 1 H), 4.08 (bs, 2 H), 7.3 (m, 3 H), 7.4–8.8 m (6 H); IR (CCl_4) 3020, 2920, 2840, 2700, 1720, 1465, 1450, and 1360 cm^{-1}].

Preparation of the Endo Tosylhydrazone 11. Tosylhydrazine (1.20 g, 6.45 mol) and acetic acid (3 drops) were added to a solution of the endo aldehyde **10** (0.90 g, 6.6 mmol) in petroleum ether (bp 60–80 °C). The mixture was stirred at room temperature for 14 h and was then filtered to give the tosylhydrazone **11**, 1.94 g (97%), as a colorless precipitate, mp 108–110 °C. Recrystallization (ether) gave short rods: mp 120.5–122 °C dec; ^{1}H NMR ($CDCl_3$) τ 1.90 (bs, 1 H, CH=NNHTos), 2.0–2.8 (m, 5 H), 4.60 (bs, 2 H), 7.4–7.7 (m, 6 H), 8.0–8.7 (m, 6 H); IR (KBr) 3170, 2920, 2850, 1600, 1470, 1450, and 1370 cm^{-1}.

Anal. Calcd for $C_{16}H_{20}N_2SO_2$: C, 63.13; H, 6.62; N, 9.20; S, 10.53. Found: C, 62.83; H, 6.56; N, 9.16; S, 10.81.

Preparation of the Exo Tosylhydrazone. The exo tosylhydrazone was prepared from the exo aldehyde in the same manner: 61%; mp 122–124 °C; ^{1}H NMR ($CDCl_3$) τ 2.0–2.9 (m, 6 H), 4.17 (bs, 2 H), 7.3–9.0 (m, 12 H); IR (KBr) 3200, 2920, 2860, 1600, 1500, 1465, 1450, and 1355 cm^{-1}.

Anal. Calcd for $C_{16}H_{20}N_2SO_2$: C, 63.13; H, 6.62; N, 9.20; S, 10.53. Found: C, 62.66; H, 6.64; N, 9.17; S, 10.42.

Thermolysis of the Sodium Salt of 11. The endo tosylhydrazone **11** (1.0 g, 3.3 mmol) was dissolved in dry THF (15 mL) under N_2 and the solution cooled to 0 °C. Sodium hydride (0.12 g, 80%, 3.2 mmol) was added in portions with vigorous stirring. Stirring was continued for 15 min by which time a heavy white precipitate had formed. Pentane (100 mL) was then added and the precipitate was recovered by filtration and briefly dried. The salt was then put into a Schenck tube attached to a three-necked flask fitted with a N_2 inlet and an outlet connected to a flask cooled in liquid N_2. The flask was heated to 200–250 °C with a nitrogen atmosphere and the solid was then introduced. A white solid formed in the traps and this was dissolved in ether, the ethereal solution was dried ($MgSO_4$), and the solvent removed by evaporation to give a white solid. Chromatography on silica with pentane gave a fraction containing **13** and **5**, identified by GLC, and elution with ether–pentane (35:100, 700 mL) gave **4,5-diazatetracyclo[5.3.0^{2,6}.0^{3,9}]undec-4-ene (12):** 0.25 g (51%); mp ca. 120 °C (petroleum ether); MS *m/e* 148 (M^+, 24%), 120 ($M^+ - N_2$, 36%) 91 (100%); ^{1}H NMR (CCl_4) τ 5.00 (dd, J = 5, 7 Hz, 2 H), 7.20 (dd, J = 7, 14 Hz, 1 H), 7.5–9.2 (m, 9 H); IR (CCl_4) 2920, 2850, 1530, 1475, and 1345 cm^{-1}.

Anal. Calcd for $C_9H_{12}N_2$: C, 72.97; H, 8.11; N, 18.92. Found: C, 72.59; H, 8.14; N, 18.45.

Thermolysis of 12. Synthesis of [3]Peristylane (5). Compound **12** (0.06 g) was put into a 5-mL round-bottomed flask which was then attached to the bottom of a quartz tube surrounded by a cylindrical vertical furnace. Above the furnace the tube was connected to a liquid nitrogen cold finger. The apparatus was evacuated to 1 mm, the furnace heated to 500 °C (thermocouple in well), and **12** sublimed into the furnace by heating with a hot-air blower. [3]Peristylane (**5**, 0.04 g) collected on the cold finger. This was purified by sublimation (30 mm, 70 °C): MS *m/e* 120.0937 (C_9H_{12} requires *m/e* 120.0938); ^{1}H NMR (CCl_4) τ 7.52 (bs, 3 H), 7.96 (bs, 3 H, cyclopropane), 8.34 (m, 3 H), 8.70 (d, J = 11 Hz, 3 H); ^{13}C NMR 37.08, 40.25, 47.13.

Thermolysis of the Sodium Salt of the Exo Tosylhydrazone. The exo tosylhydrazone (0.70 g, 2.3 mmol) was treated with sodium hydride in THF as described for the endo isomer above. The dried salt was heated at 250 °C at 30 mm under N_2. The resulting liquid distillate showed two components on GLC, and the major component was isolated and identified as **3-methylenebicyclo[3.2.1]oct-6-ene (13):**[13] ^{1}H NMR (CCl_4) τ 4.23 (bs, 2 H), 5.42 (bs, 2 H), 7.20 (bs, 2 H), 7.7–8.8 (m, 6 H); ^{13}C NMR 146.0, 133.6, 112.3, 43.6, 39.4, 37.1.

Preparation of *exo*-4-Chlorononadamantan-2-one (14).[11] Freshly distilled thionyl chloride (3 mL) was added to **7a** (0.79 g, 5.2 mmol) and the resulting brown solution was heated under reflux for 2 h. The mixture was allowed to cool, water (10 mL) and saturated aqueous $NaHCO_3$ (10 mL) were added, and the mixture was extracted with ether (2 × 25 mL). The ethereal extracts were washed with water (10 mL) and dried ($MgSO_4$). Removal of the solvent by evaporation gave a yellow gum which, after chromatography on silica eluting with pentane–ether, gave ***exo*-4-chlorononadamantan-2-one (14):** 0.70 g (80%); mp 104–105 °C (petroleum ether), sealed tube); ^{1}H NMR (CCl_4) τ 5.80 (bs, 1 H), 7.1–8.5 (m, 10 H); IR (CCl_4) 2950, 2870, 1750, 1475, 1460, and 1450 cm^{-1}.

Anal. Calcd for $C_9H_{11}ClO$: C, 63.35; H, 6.50; Cl, 20.78. Found: C, 63.44; H, 6.50; Cl, 20.73.

Reduction of 14. The chloro ketone **14** (0.45 g, 2.6 mmol) was dissolved in methanol (25 mL), stirred, and cooled in an ice bath, and sodium borohydride (0.6 g, 15.8 mmol) was added in small portions. After completion of addition the mixture was stirred for a further 30 min and then water (100 mL) was added. The mixture was then acidified with aqueous 10% sulfuric acid and extracted with ether (4 × 50 mL). The ethereal extracts were washed with saturated aqueous $NaHCO_3$ and dried ($MgSO_4$). Evaporation of the solvent gave **4-chlorononoradamantan-2-ol (15):** 0.43 g (93%); mp 120–126 °C (petroleum ether); MS *m/e* 172, 174 (9%), 154, 156 ($M^+ - H_2O$, 100%); ^1H NMR τ 5.10 (bs, 1 H), 5.7–6.0 (m, 1 H), 7.10 (bs, 1 H), 7.3–8.7 (m, 10 H); IR (CCl_4) 3400, 2920, and 1480 cm^{-1}.

Anal. Calcd for $C_9H_{13}ClO$: C, 62.61; H, 7.59; Cl, 20.53. Found: C, 62.82; H, 7.59; Cl, 20.32.

Preparation of 2,4-Dichlorononoradamantane (16). Compound **15** (0.23 g, 1.35 mmol) was added to thionyl chloride (5 mL) and the mixture was heated under reflux for 18 h. The solution was allowed to cool, water (50 mL) was added, and the resulting mixture was extracted with ether (3 × 25 mL). The combined ethereal extracts were washed with water (25 mL) and saturated aqueous $NaHCO_3$ (2 × 25 mL) and dried ($MgSO_4$). Removal of the solvent by evaporation gave a yellow oil (0.24 g) which was chromatographed on silica eluting with ether–petroleum ether to give **16** as a 1:2 mixture of the exo,endo and exo,exo isomers: 0.18 g (70%); purified by distillation at 10^{-3} mm; MS *m/e* 190, 192, 194 (M^+, 27%), 79 (100%); ^1H NMR (CCl_4) τ 5.05 (m), 5.65–6.0 (m), 7.0–9.2 (m) (3:14:90); IR ($CHCl_3$) 2950, 2920, 2850, 1480, 1470, and 1450 cm^{-1}.

Anal. Calcd for $C_9H_{12}Cl_2$: C, 56.57; H, 6.33; Cl, 37.10. Found: C, 56.43; H, 6.08; Cl, 36.98.

Thionyl chloride (1.36 g, 11.4 mmol) in pyridine (0.95 g, 12.0 mmol) was added to **15** (0.66 g, 3.9 mmol) in $CHCl_3$ (15 mL) and the mixture heated under reflux for 21 h. The mixture was worked up as above, and gave on chromatography ***exo,exo*-2,4-dichlorononoradamantane (16a):** 0.047 g (10%); MS *m/e* 190, 192, 194 (M^+, 91%), 155, 157 ($M^+ - Cl$), 79 (100%); ^1H NMR (CCl_4) τ 5.85 (bs, 2 H), 7.0–9.2 (m, 10 H); ^{13}C NMR 69.42, 58.14, 43.34, 39.37, 35.21, 34.92.

The major product was identified as **bis(4-chlorononoradamant-2-yl) sulfite:** 0.39 g (84%); mp 112–114 °C (ether); ^1H NMR (CCl_4) τ 5.22 (bs, 4 H), 7.2–8.6 (m, 20 H); IR (CCl_4) 2920, 1480, 1450, 1385, and 1350 cm^{-1}.

Anal. Calcd for $C_{18}H_{24}Cl_2SO_3$: C, 55.24; H, 6.18; Cl, 18.12; S, 8.19. Found: C, 55.58; H, 6.21; Cl, 17.63; S, 8.61.

Some chloro alcohol (0.23 g) was also recovered, and the percent yields quoted are based on the chloro alcohol consumed.

Reaction of 2,4-Dichlorononoradamantane (16) with Disodium Naphthalenide. Synthesis of [3]Peristylane (5). A solution of **16** (0.18 g, 0.95 mmol) in dry THF (5 mL) was added slowly to a stirred solution of sodium (0.10 g, 4.4 mmol) and naphthalene (0.30 g, 2.3 mmol) in dry THF (20 mL) under N_2. After completion of addition the mixture was stirred for a further 15 min, and then poured into brine. The mixture was extracted with ether (3 × 20 mL) and the combined ethereal layers were dried ($MgSO_4$). The volume was reduced by evaporation and the [3]peristylane (**5**) was separated by chromatography on silica eluting with petroleum ether, when **5** eluted before naphthalene: 0.91 g (80%), identical in all observed respects with the previously obtained sample.

Catalytic Reduction of [3]Peristylane. A solution of **5** (0.07 g) in CCl_4 (5 mL) was added to prereduced Adam's catalyst (90 mg) in CCl_4 (1 mL), and the mixture stirred under an atmosphere of H_2 for 60 h. The catalyst was removed by filtration and the product isolated by GLC (Apiezon, 200 °C) as **noradamantane:** MS *m/e* 122 (32%), 121 (55%), 79 (100%); ^1H NMR τ 7.60 (bs, 2 H), 7.90 (bs, 2 H), 8.40 (bs, 10 H); ^{13}C NMR 44.21, 37.55, 36.80, 35.66.

Acknowledgment. We thank the Science Research Council (U.K.) for the award of a studentship to J.F.W.

Registry No.—5, 20454-87-9; **7a,** 10534-49-3; **7b,** 10531-02-9; **8,** 20831-07-6; *endo*-**9,** 61597-60-2; *exo*-**9,** 61597-61-3; *exo*-**9** 3,5-dinitrobenzoate, 61597-62-4; *endo*-**10,** 61597-63-5; *exo*-**10,** 61597-64-6; *endo*-**11,** 61597-65-7; *endo*-**11** Na salt, 61597-66-8; *exo*-**11,** 61597-67-9; *exo*-**11** Na Salt, 61597-68-0; **12,** 61597-69-1; **13,** 17782-59-1; **14,** 61597-70-4; **15,** 61597-71-5; **16a,** 61597-72-6; **16b,** 61617-16-1; 3,5-dinitrobenzoyl chloride, 99-33-2; *N*-chlorosuccinimide, 128-09-6; *endo*-3-(methylthio)methylbicyclo[3.2.1]oct-6-ene, 61597-73-7; *exo*-3-(methylthio)methylbicyclo[3.2.1]oct-6-ene, 61597-74-8; tosylhydrazide, 1576-35-8; bis(4-chlorononoradamant-2-yl) sulfite, 61597-75-9; disodium naphthalenide, 6415-62-9; noradamantane, 7075-86-7.

References and Notes

(1) See P. J. Garratt, "Aromaticity", McGraw-Hill, New York, N.Y., 1971; F. Sondheimer, *Acc. Chem. Res.*, **5,** 81 (1972).
(2) Nonbonded and angle strain intrude upon this sequence for medium rings, and at large ring size (≈30) the value of *n* becomes unimportant.
(3) The corresponding compound for $n = 4$ has two ethene bridges and is known: see J. Meinwald and H. Tsuruta, *J. Am. Chem. Soc.*, **91,** 5877 (1969); H. E. Zimmerman, J. D. Robbins, and J. Schantl, *ibid.*, **91,** 5878 (1969).
(4) P. E. Eaton and R. H. Mueller, *J. Am. Chem. Soc.*, **94,** 1014 (1972).
(5) See R. B. Woodward, T. Funkunaga, and R. C. Kelly, *J. Am. Chem. Soc.*, **86,** 3162 (1964); I. T. Jacobson, *Acta Chem. Scand.*, **21,** 2235 (1967); L. A. Paquette, S. V. Ley, and W. B. Farham, *J. Am. Chem. Soc.*, **96,** 312 (1974); L. A. Paquette and M. J. Wyvratt, *ibid.*, **96,** 4671 (1974); D. McNeil, B. R. Vogt, J. J. Sudol, S. Theodoropulos, and E. Hedaya, *ibid.*, **96,** 4673 (1974).
(6) For each member of the series the *n*-membered rings are connected to the *n*/2-membered rings by alternate carbon atoms and consequently by five-membered rings.
(7) A. Nickon and G. D. Pandit, *Tetrahedron Lett.*, 3663 (1968).
(8) The *Chemical Abstracts* name for **5** is octahydro-2,3-methanocyclopropa[*c,d*]pentalene. Nickon and Pandit[7] and ourselves considered it to be tetracyclo[3.3.1.$0^{2,4}$.$0^{3,7}$]nonane, but this name was not listed in *Chem. Abstr.*, **69** (1968), although it did appear in the 8th Collective Index. Clearly some trivial nomenclature is required, but it would be preferable to have a general name for this group of compounds rather than separate individual names.
(9) Nickon and Pandit's synthesis,[7] based on a carbene insertion reaction of noradamantane, does not appear readily capable of modification for the preparation of specifically substituted [3]peristylanes.
(10) W. R. Moore, W. R. Moser, and J. E. LaPrade, *J. Org. Chem.*, **28,** 2200 (1963).
(11) J. E. Baldwin and W. D. Fogelsong, *J. Am. Chem. Soc.*, **90,** 4303 (1968).
(12) E. J. Corey and C. U. Kim, *J. Am. Chem. Soc.*, **94,** 7586 (1972).
(13) H. M. R. Hoffmann, D. R. Joy, and A. K. Suter, *J. Chem. Soc. B,* 57 (1968).