Synthesis of Adamantane Derivatives. 34.[1] Synthesis of 2,4-Methanoadamantane and 2,4-Methanoprotoadamantane

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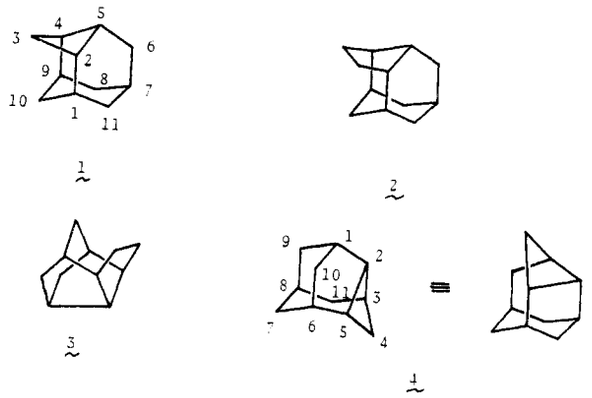
The ring contraction of 4-diazoethanoadamantan-3-one (**14**) gave 2,4-methanoadamantane-3-*endo*-carboxylic acid (**15n**) which on decarboxylation via *tert*-butyl perester (**17**) afforded 2,4-methanoadamantane (**1**). Attempted synthesis of **1** via C_4–H insertion of 2-adamantylcarbene (**5**) was unsuccessful because of occurrence of H migration and ring expansion affording methyleneadamantane (**11**) and 4-homoadamantene (**12**) as the major products. The intramolecular [2 + 2] cycloaddition of 7-*endo*-bicyclo[3.3.1]non-2-enylketene (**8**) proceeded to afford 2,4-methanoprotoadamantan-11-one (**20**) which was converted to 2,4-methanoprotoadamantane (**4**) via tosylhydrazone **21** or by the Wolff–Kishner reduction.

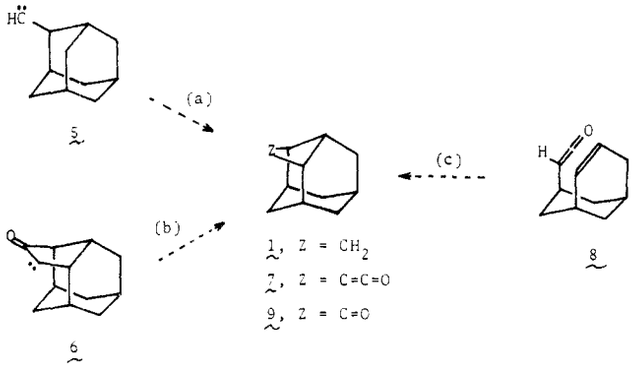
Although 2,4-methanoadamantane (tetracyclo[5.3.1.$0^{2,5}$.$0^{4,9}$]undecane, **1**) can be regarded as one of the lower homologues of 2,4-ethanoadamantane (**2**), the $C_{12}H_{18}$ tetracyclic stabilomer,[2] **1** must be a highly strained compound involving



a cyclobutane ring and a boat cyclohexane ring in the rigid tetracyclic system. Recently, Schleyer and his co-workers have shown that 2,4-ethanonoradamantane (**3**), another lower homologue of **2**, is the $C_{11}H_{16}$ stabilomer by rearrangement, synthesis, and empirical force field calculation studies.[3] The calculated strain energy of **1** is 46.22 (Engler force field)[4,5] or 46.56 kcal/mol (Allinger 1971 force field).[3,6]

We wish to report the synthesis of **1** and 2,4-methanoprotoadamantane (or 2,5-dehydrohomoadamantane, tetracyclo[4.3.1.1^{3,8}.$0^{2,5}$]undecane, **4**). The adamantane rearrangement method is obviously not applicable to the synthesis of such a thermodynamically unstable ring system[7] and we examined the following three routes (Scheme I): (a) the C–H insertion reaction of 2-adamantylcarbene (**5** → **1**); (b) the ring contraction of ketocarbene (**6** → **7** → **1**); (c) the intramolecular [2 + 2] cycloaddition of 7-*endo*-bicyclo[3.3.1]non-2-enylketene (**8** → **9** → **1**). Among the three routes, (b) was successful and (c) provided a facile route to **4**.

Scheme I



Results and Discussion

Intramolecular Reaction of 2-Adamantylcarbene (5). We have previously reported preparation of 2-adamantyldiazomethane by pyrolysis of the lithium salt (**10b**) of 2-adamantylcarboxaldehyde tosylhydrazone (**10a**) under reduced pressure.[8] However, 2-adamantyldiazomethane is very unstable at room temperature affording mainly the corresponding azine, and hence, thermal decompositions of **10b** in refluxing diglyme and at 160–170 °C without solvent were examined. Hydrocarbon mixtures obtained after sublimation were analyzed on GLC. The major products were methyleneadamantane (**11**), a hydrogen migration product, and 4-homoadamantene (**12**), a ring-expansion product based on the same retention times with authentic samples, though minor products could not be identified (Scheme II, Table I).[9] No trace amount of **1** could be detected by using the sample prepared from the ring-contraction route described below. Photodecomposition of **10c** by the method of Dauben and Willey[10] afforded also **11** as the major product. The absence of the C(4)–H insertion product **1** may be due to the somewhat longer distance between the C(4)–H bond and the carbenic center.[11] The distance measured on a Dreiding stereomodel (ca. 2.80 Å) is obviously longer than C–H- - -C: in the ring systems where the insertion is observed; the distance measured is ca. 2.5–2.55 Å.[12]

The Ring Contraction of Ethanoadamantan-3-one (13). Synthesis of 2,4-Methanoadamantane (1). Since ethanoadamantan-3-one (tetracyclo[6.3.1.$0^{2,6}$.$0^{5,10}$]dodecan-3-one, **13**) is now available readily from the insertion reaction of 2-adamantanecarbonylcarbene,[2] the ring contraction of **13** was carried out via diazotization followed by photolysis (Scheme III). The diazotization of **13** was carried out by the method of Wheeler and Meinwald,[13] i.e., treatment of **13** with isoamyl nitrite in the presence of *t*-BuOK gave the corresponding

Scheme II

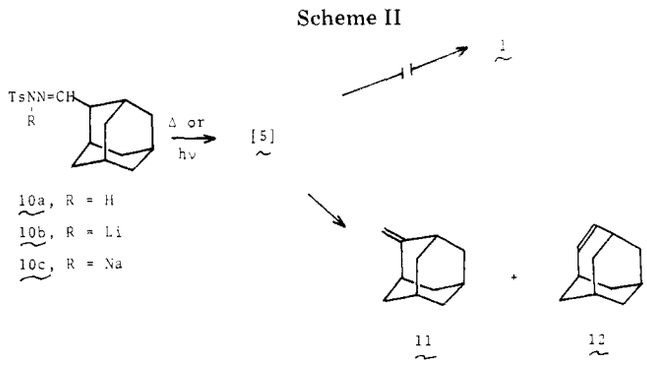


Table I. Thermal and Photodecompositions of 10b and 10c

Salt	Registry No.	Solvent	Decomposition method	Yield, %[a]	Products, %[b] 11	12	Others
10b	50782-16-6	Diglyme	Reflux	37.8	68.5	19.8	11.7[c]
10b		None[d]	160–170 °C	33.8	74.4	12.8	12.8[c]
10c	62881-86-1	0.1 N NaOMe–diglyme	Photolysis[e] (room temp)	20.3	77.6	0.5	21.9[f]

[a] The materials were sublimed at 70 °C (25 mm) and the yields are calculated as $C_{11}H_{16}$ hydrocarbons. [b] Relative peak area on GLC analysis. [c] No trace of 1 was involved. [d] Celite was used. [e] A 100-W high-pressure Hg lamp with quartz filter. [f] A trace amount of 1 was detectable.

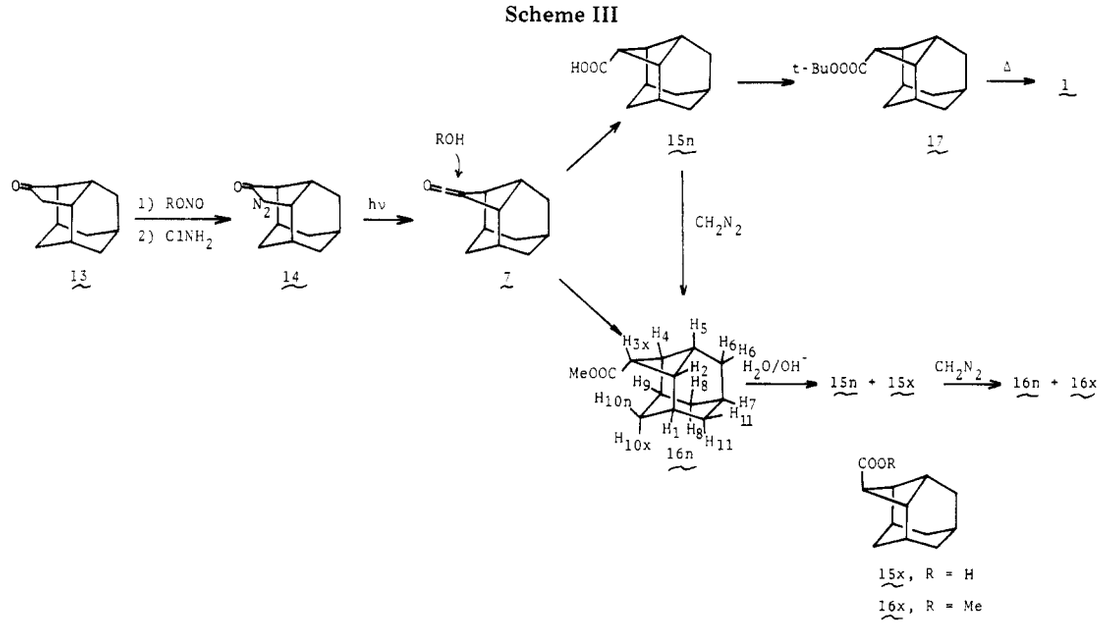
oximino ketone which was diazotized with chloramine to afford diazoketone **14** (49% from **13**) as yellowish prisms, mp 84–86 °C. The structure was supported by characteristic IR absorptions at 2070 and 1670 cm^{-1}. Photolysis of **14** in alkaline 70% aqueous tetrahydrofuran afforded 2,4-methanoadamantane-3-*endo*-carboxylic acid[14] (**15n**) (51%) as colorless crystals, mp 180–181 °C. The spectral data were compatible with the assigned structure. The endo stereochemistry of C_3–COOH was assigned based on the following facts: Treatment of **15n** with an excess amount of diazomethane afforded the corresponding methyl ester **16n** in 56% yield, which was also obtained by photolysis of **14** in methanol in 12% yield. Alkaline hydrolysis of **16n** gave a mixture of **15n** and **15x**, which afforded a 54:46 mixture of **16n** and **16x** on esterification with diazomethane as demonstrated by GLC and ^1H NMR analyses, indicating occurrence of epimerization at C(3) during the hydrolysis of **16n**. This means that photolytically produced **15n** and **16n** are thermodynamically less stable isomers, i.e., the C(3)-endo isomers where severe steric repulsion between C(3)–COOR (R = H or Me) and H(10n) should be relieved by the epimerization as suggested by stereomodel study and empirical force field calculations.[5,15] The ^1H NMR spectrum of **16n** in the presence of shift reagent, $Eu(dpm)_3$ [mole ratio of $Eu(dpm)_3$ to **16n** = 0.21], revealed signals at δ 7.28 (s, 3 H, COOMe) (the shift gradient G = 19.3),[16] 6.38 [broad d, J = 13 Hz, ca. 1 H, H(10n)] (22.0), 6.32 [t, J = 5.0 Hz, 1 H, H(3x)] (18.5), 4.30 [q, J = 5.0 Hz, 2 H, H(2), H(4)] (9.05), 3.94 [broad s, 2 H, H(1), H(9)] (9.15), 3.62 [s, 2 H, H(6) × 2] (1.10), 3.42 [s, 1 H, H(7)] (0.60), 2.96 [broad s, 1 H, H(5)] (5.75), 2.53 (d, J = 13 Hz, 1 H, H(10x)] (6.60), and 2.20 (broad m, ca. 4 H, other protons).[17] The presence of two protons having larger G values comparable to COOMe protons supported also the endo stereochemistry of **16n**. The exclusive formation of endo products rather than exo ones on the photodecomposition of **14** could be rationalyzed by addition of water or methanol to the intermediate ketene **7** from the less hindered exo side (Scheme III).

Decarboxylation of **15n** was successfully carried out via *tert*-butyl perester (**17**) followed by thermolysis in ethyl phenylacetate.[18] After chromatography and sublimations, 2,4-methanoadamantane (**1**) was obtained in 36% yield (from **15n**) as colorless crystals, mp 206–208 °C, which had correct mass spectral molecular weight and analysis. The structure of **1** was supported also by the ^{13}C NMR spectrum which revealed only eight lines due to the symmetry plane through C(3), C(5), C(6), C(7), and C(10) at δ 39.3 (d, 1 C), 38.5 (d, 2 C), 34.9 (t, 2 C), 33.7 (t, 1 C), 33.5 (t, 1 C), 29.9 (d, 2 C), 28.9 (t, 1 C), and 25.9 (d, 1 C).

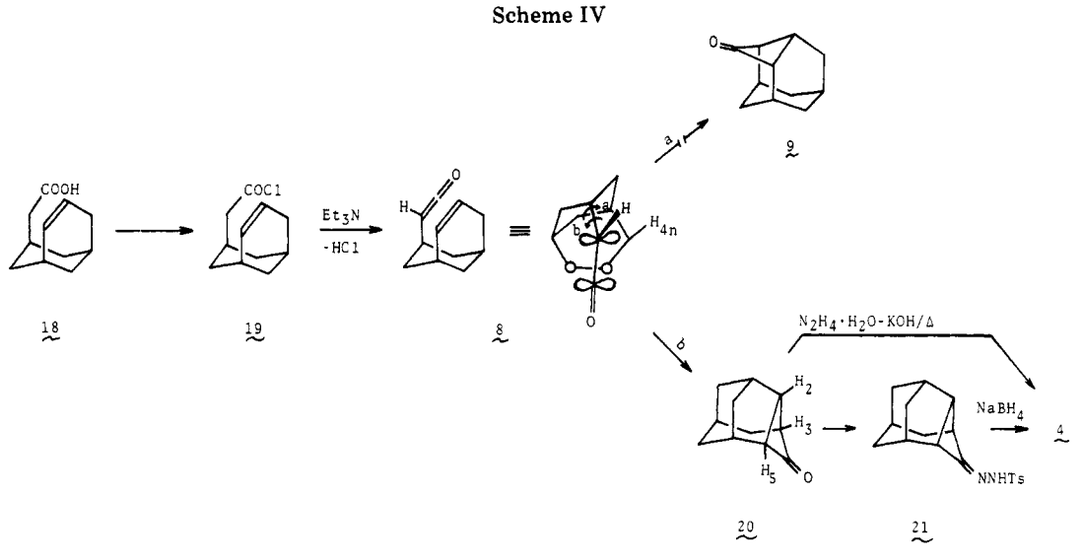
Intramolecular [2 + 2]Cycloaddition of 7-*endo*-Bicyclo[3.3.1]non-2-enylketene (8). Synthesis of 2,4-Methanoprotoadamantane (4). Thermally allowed $_\pi2_s + _\pi2_a$ cycloaddition of **8** has a possibility to afford 2,4-methanoadamantan-3-one (**9**) or 2,4-methanoprotoadamantan-11-one (**20**) depending on the rotation a or b (Scheme IV).[19,20] Bicyclo[3.3.1]non-6-ene-3-*endo*-acetic acid (**18**)[21] was converted to acid chloride (**19**) which on refluxing in benzene containing triethylamine afforded cyclobutanone derivatives, mp 224–227 °C, in 46% yield after chromatography. A strong IR absorption at 1780 cm^{-1} indicated the presence of a cyclobutanone moiety. The structure was assigned as 2,4-methanoprotoadamantan-11-one (tetracyclo[4.3.1.$1^{3,8}$.$0^{2,5}$]-undecan-4-one or 2,5-dehydrohomoadamantan-4-one, **20**) by appearance of characteristic ^1H NMR signals assignable to cyclobutanone ring protons at δ 3.58 [q, J = 7.5 Hz, 1 H, H(5)], 3.18 [d, q, J = 3.0 and 7.5 Hz, 1 H, H(3)], and 2.79 [q, J = 7.5 Hz, 1 H, H(2)]. The ^{13}C NMR data were also compatible with the assigned structure.

The selective formation of **20** via rotation b may be due to

Scheme III



Scheme IV



18 19 8 9 20 21 4

steric repulsion between ketene H and C(4)-*endo*-H on rotation a. In spite of considerable geometrical constraint in **8** for an ideal orthogonal approach of the two π moieties,[20] the formation of [2 + 2]cycloadduct **20** is of interest.

The ketone **20** gave the corresponding tosylhydrazone **21** which on reduction with $NaBH_4$ in refluxing ethanol[22] afforded tetracyclo[4.3.1.1^{3,8}.0^{2,5}]undecane (or trivial 2,4-methanoprotoadamantane or 2,5-dehydrohomoadamantane,[23] **4**) in 27% yield (from **20**) as sublimable crystals, mp 177–179 °C. The hydrocarbon **4** was also obtained by the Wolff–Kishner reduction of **20** in 64% yield. The spectral data (see Experimental Section) of **4** supported the assigned structure and furthermore different GLC retention times of **4** from 2,4-methanoadamantane (**1**) supported the structural assignment of **4** and **20**.

Experimental Section[24]

2-Adamantanecarboxaldehyde Tosylhydrazone (10a). This was prepared by refluxing crude 2-adamantanecarboxaldehyde[25] with a small excess amount of *p*-toluenesulfonylhydrazide in ethanol for 12 h. Repeated recrystallizations from methanol afforded an analytically pure sample of **10a:** mp 103–105 °C; IR (KBr) 3200, 1605, 1350, and 1160 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.81 (d, J = 8.0 Hz, 2 H), 7.48–6.85 (m, ca. 3 H), 2.51 (broad s, ca. 2 H, 1 H on shaking with D_2O), 2.42 (s, 3 H), and 2.15–0.85 (m, 14 H).

Anal. Calcd for $C_{18}H_{24}N_2O_2S$: C, 65.04; H, 7.28; N, 8.43. Found: C, 65.17; H, 7.29 N, 8.37.

Thermal Decomposition of Lithium Salt (10b) of 10a. (A). In Diglyme. To a stirred solution of **10a** (83 mg, 0.25 mmol) in tetrahydrofuran (2.0 mL) was added *n*-BuLi (0.11 mL of 15 wt % *n*-hexane solution, 0.26 mmol) at −78 °C. After stirring was continued for 0.5 h at −78 °C and for 0.5 h at 20 °C, the solvent was removed under reduced pressure (0.1 mm) to afford **10b** as a colorless solid which was further dried at ca. 45 °C for 6 h (0.1 mm). Thus, obtained **10b** was suspended in anhydrous diglyme (5 mL) and the mixture was refluxed for 2 h under an argon atmosphere. The cooled mixture was diluted with water (50 mL) and extracted with *n*-pentane (two 20-mL portions). The combined extracts were washed with water several times and dried (Na_2SO_4). Removal of the solvent gave crude products (42 mg) which were sublimed at 70 °C under an aspirator pressure (ca. 25 mm) to afford colorless solids (28 mg). The product composition was analyzed on GLC by using 2,4-methanoadamantane (**1**), methyleneadamantane (**11**),[26] and 4-homoadamantene (**12**).[27] The results are summarized in Table I.

(B) Without Solvent. The Li salt **10b** (from **10a,** 0.25 mmol) was mixed well with Celite (0.5 g) and was decomposed at 160–170 °C under reduced pressure (25 mm) by using a sublimation apparatus to afford crude products as colorless solids (25 mg) which were analyzed on GLC Table I).

Photodecomposition of Sodium Salt (10c). A suspension of **10a** (83 mg, 0.25 mmol) in 0.1 N NaOMe diglyme (10 mL) was irradiated with a 100-W high-pressure Hg lamp through a quartz filter under an argon atmosphere at room temperature for 6 h. Work-up as above gave a mixture of products (15 mg) after sublimation which was analyzed on GLC (Table I).

4-Diazotetracyclo[6.3.1.0^{2,6}.0^{5,10}]dodecan-3-one (14). To a stirred mixture of 2,4-ethanoadamantan-3-one[2,28] (**13**) (300 mg, 1.70 mmol) and potassium *tert*-butoxide (382 mg, 3.40 mmol) in *tert*-butyl alcohol (10 mL) was added a solution of isoamyl nitrite (398 mg, 3.40 mmol) in tetrahydrofuran (2.0 mL) over 0.5 h under an argon atmosphere at 20 °C. After the stirring was continued for 40 h, the mixture was diluted with water (10 mL), acidified with 10% hydrochloric acid, and extracted with ether (two 30-mL portions). The combined extracts were dried (Na_2SO_4) and evaporated to afford crude oximino ketone as an yellowish oil (0.55 g) which had IR absorptions at 3240, 1745, 1700, and 1635 cm^{-1}. The oximino ketone was dissolved in methanol (10 mL)–5% aqueous NaOH (10 mL) and filtered in order to remove a small amount of precipitate (60 mg) which was recovered **13.** To the stirred filtrate was added 28% aqueous ammonia (0.98 g) and then solid calcium hypochlorite (1.73 g of 60% purity chlorinated lime, ca. 7.2 mmol). After stirring was continued for 6 h at room temperature, the mixture was diluted with water (50 mL) and extracted with dichloromethane (two 20-mL portions). The combined extracts were washed with 20% aqueous sodium chloride and dried (Na_2SO_4). Removal of the solvent gave crude diazoketone (250 mg, ca. 72%) which was ca. 80% purity contaminated with unchanged **13.** On cooling the crude diazoketone crystallized; the crystals were washed with *n*-hexane to give an analytical sample of **14** as yellowish prisms (168 mg, 49%): mp 84–86 °C; IR (KBr) 2070 and 1670 cm^{-1}.

Anal. Calcd for $C_{12}H_{14}N_2O$: C, 71.26; H, 6.98; N, 13.85. Found: C, 71.01; H, 6.80; N, 13.76.

Tetracyclo[5.3.1.0^{2,5}.0^{4,9}]undecane-3-*endo*-carboxylic Acid (15n). A solution of the crude diazoketone (**14**) (170 mg, ca. 0.84 mmol) in tetrahydrofuran (250 mL)–0.5% aqueous sodium bicarbonate solution (100 mL) was irradiated under an argon atmosphere through a Pyrex filter with a 100-W high-pressure Hg lamp for 3 h at 25 °C. The irradiated mixture was concentrated to ca. 120 mL and diluted with 5% aqueous sodium hydroxide (30 mL) and washed with ether (20 mL). The aqueous layer was acidified with 10% hydrochloric acid and extracted with dichloromethane (five 20-mL portions). The combined extracts were dried (Na_2SO_4) and evaporated to afford crude carboxylic acid **15n** as a solid (110 mg) which was recrystallized from *n*-hexane–CH_2Cl_2 to give pure **15n** as colorless prisms (82 mg, 51%): mp 180–181 °C; IR (KBr) 3300–2300 (broad), 1680, 1615 (shoulder), 1400, 1240, and 870 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.20 (broad s, 1 H, disappeared on shaking with D_2O), 2.57 (unsymmetrical AB-q, J = ca. 5 Hz, 3 H), 2.30 (broad s, 2 H), 1.91 (broad s, ca. 2 H), 1.7–1.4 (m, 7 H), and 1.29 (unsymmetrical d, J = 13 Hz, ca. 1 H); ^{13}C NMR ($CDCl_3$) δ 181.5 (s, 1 C), 45.0 (d, 1 C), 42.0 (d, 2 C), 35.7 (d, 1 C), 35.0 (t, 1 C), 34.6 (t, 2 C), 32.9 (t, 1 C), 29.1 (d, 2 C), and 25.6 (d, 1 C); mass spectrum *m/e* (rel intensity) 193 (15.0), 192 (98.6, M$^+$), 174 (10.9, M − H_2O), 147 (20.4, M − CO_2H), 133 (29.3), 132 (40.8), 119 (20.4), 117 (17.7), 105 (40.8), 93 (54.3), 92 (40.8), 91 (76.2), 81 (22.4), 80 (37.4), 79 (100), 78 (27.2), 77 (47.6), 67 (32.7), 65 (23.8), 53 (24.5), 41 (47.6), and 39 (40.8).

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.76; H, 8.41.

Methyl Tetracyclo[5.3.1.0^{2,5}.0^{4,9}]undecane-3-*endo*-carboxylate (16n). A solution of crude diazoketone (**14**) (172 mg, ca. 0.848 mmol)

in methanol (250 mL) was irradiated as above for 7.5 h. After concentration under reduced pressure to ca. 20 mL, the irradiated mixture was diluted with water (100 mL) and extracted with ether (five 30-mL portions). The combined extracts were washed with water and saturated aqueous sodium chloride and dried (Na_2SO_4). Removal of the solvent gave crude ester (**16n**) (45 mg) as an oil which was purified on a silica gel column eluting with *n*-hexane–CH_2Cl_2. Analytically pure **16n** was obtained as a colorless oil (21 mg, 12%): $n^{18}D$ 1.5160; IR (neat) 1730, 1240, 1120, and 1025 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.68 (s, 3 H), 2.75–2.45 (m, 3 H), 2.29 (broad s, 2 H), 2.1–1.42 (m, 9 H), and 1.25 (unsymmetrical d, J = 13 Hz, 1 H).

Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.98; H, 8.58.

On treatment of the carboxylic acid **15n** (10 mg, 0.052 mmol) with diazomethane (ca. 30 mmol) in ether (50 mL) for 1 day at room temperature, the methyl ester **16n** was obtained also after chromatography on a silica gel column as an oil (6 mg, 56%) which was identical with the sample prepared from **14** by photolysis (GLC and IR spectral comparisons).

Hydrolysis of 16n and Esterification of 15n + 15x. A mixture of the endo ester **16n** (83 mg, 0.40 mmol) in ethanol (5 mL) and 51% aqueous potassium hydroxide (5 mL) was refluxed for 10 h under nitrogen atmosphere. The cooled mixture was concentrated under reduced pressure to ca. 7 mL and diluted with water (10 mL) and washed with *n*-hexane (10 mL). The aqueous layer was acidified with 10% hydrochloric acid and extracted with dichloromethane (four 10-mL portions). The combined extracts were dried (Na_2SO_4) and evaporated to afford crude carboxylic acid which was recrystallized from *n*-hexane–CH_2Cl_2 to afford a mixture of **15n** and **15x** (54:46 ratio estimated from the esterification described below) as colorless crystals (35 mg, 45%), mp 135–145 °C, with an IR spectrum (KBr) very similar to **15n** but with some extra absorptions observed at 1330, 1285, and 940 cm^{-1}.

On treatment with diazomethane (ca. 60 mmol) in ether (50 mL), the endo and exo carboxylic acid (35 mg, 0.18 mmol) afforded the corresponding methyl ester after chromatography (silica gel, *n*-hexane–CH_2Cl_2) as an oil (35 mg, 94%) which revealed two peaks in 54:46 ratio on GLC analysis (at 150 °C on a Silicone SE-30 column) and had an IR spectrum quite similar to **16n** except for bands at 990 and 745 cm^{-1}; ($CDCl_3$) δ 3.70 (s, 1.4 H, C(3x)–COOMe), 3.68 (s, 1.6 H, ^1H NMR C(3n)–COOMe), 2.83–2.1 (m, 5 H), and 2.1–1.06 (m, 10 H).

Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.83; H, 8.66.

Decarboxylation of 15n via the *tert*-Butyl Perester (17). Tetracyclo[5.3.1.$0^{2,5}$.$0^{4,9}$]undecane (1). To a stirred mixture of the acid **15n** (100 mg, 0.52 mmol) in 50% aqueous methanol (10 mL) was added 10% aqueous sodium hydroxide up to a phenolphthalein end point. After stirring for 0.5 h, the mixture was completely dried up at 80 °C under reduced pressure (0.2 mm) to afford the sodium salt of **15n**, which was suspended in benzene (6.5 mL) containing pyridine (80 mg). To the stirred suspension was added oxalyl chloride (0.2 mL, 2.4 mmol) under ice cooling and stirring was continued for 15 min at the same temperature and for 15 min at room temperature. The resulting precipitates were filtered and washed with benzene. The combined filtrate and washings were evaporated under reduced pressure to afford the corresponding acid chloride as an oil (110 mg): IR (neat) 1795 cm^{-1}.

To a stirred and ice-cooled mixture of *tert*-butyl hydroperoxide (70 mg, 0.78 mmol) and pyridine (63 mg, 0.78 mmol) in dichloromethane (5 mL) was added the acid chloride (110 mg) in dichloromethane (2 mL) and the stirring was continued for 1 h at the same temperature. After standing overnight in a refrigerator, the mixture was washed successively with cold water, 10% aqueous sulfuric acid, 5% aqueous sodium bicarbonate, and water and dried (Na_2SO_4). Removal of the solvent gave the *tert*-butyl perester **17** as an oil (170 mg), IR (neat) 1770, 1365, 1270, 1180, 1115, 980, and 800 cm^{-1}, which was pyrolyzed without further purifications.

The crude *tert*-butyl perester **17** (230 mg, from 135 mg of **15n**) was heated at 155 °C in ethyl phenylacetate (1 mL) for 2 h by the method of Ruechardt.[18] To the cooled mixture was added methanol (2 mL) and 45% aqueous sodium hydroxide, and the mixture was refluxed for 4 h under an argon atmosphere. The cooled mixture was diluted with water (10 mL) and extracted with *n*-pentane (three 10-mL portions). Crystals sublimed at the reflux condenser were washed with *n*-pentane (10 mL). The combined extracts and washings were washed with water and dried (Na_2SO_4). Removal of the solvent followed by chromatography (silica gel, *n*-pentane) and sublimation [80 °C (25 mm)] afforded **1** as colorless crystals (26 mg, 25%): mp 206–208 °C; IR (CCl_4) 2915, 2850, 1465, 1450, 1350, 1265, 1105, and 1020 cm^{-1}; ^1H NMR (CCl_4) δ 2.5–0.6 (m); ^{13}C NMR ($CDCl_3$) see text; mass spectrum *m/e* (rel intensity) 149 (10.0), 148 (62.2, M^+), 134 (13.9), 120 (11.1), 119 (23.3), 107 (16.7), 106 (23.3), 105 (30.0), 94 (14.4), 93 (24.4), 92 (44.4), 91 (52.2), 81 (20.0), 80 (44.4), 79 (100), 78 (23.3), 77 (36.7), 70 (13.3), 67 (16.7), 66 (16.6), 65 (16.5), 55 (10.0), 53 (16.7), 51 (13.3), 41 (33.3), and 39 (36.7).

Anal. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 89.09; H, 10.91.

Tetracyclo[4.3.1.$1^{3,8}$.$0^{2,5}$]undecan-4-one (20). To a suspension of the sodium salt prepared from bicyclo[3.3.1]non-6-ene-3-*endo*-acetic acid[21] (**18**) (300 mg, 1.66 mmol) as above in dry benzene (10 mL) and pyridine (0.24 mL) was added oxalyl chloride (0.42 mL, 4.96 mmol) with stirring under ice cooling. After the stirring was continued for 0.5 h at room temperature, the mixture was filtered in order to remove precipitates. The precipitates were washed with benzene (2 mL) and the combined washings and filtrate were evaporated under reduced pressure to afford acid chloride **19** as an oil (0.40 g): IR (neat) 1800 cm^{-1}.

To a refluxing mixture of triethylamine (200 mg, 1.97 mmol) and benzene (30 mL) was added the acid chloride (0.40 g) in benzene (10 mL) over 0.5 h and the refluxing was continued for 2 h. The cooled mixture was washed with water (two 10-mL portions) and dried (Na_2SO_4). Removal of the solvent gave an oily product which on purification on a silica gel column (*n*-hexane–CH_2Cl_2) afforded the ketone **20** as colorless crystals (125 mg, 46%): mp 224–227 °C (after one sublimation); IR (KBr) 1780, 1450, 1195, and 1130 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.58 (q, J = 7.5 Hz, 1 H), 3.18 (d, q, J = 3.0 and 7.5 Hz, 1 H), 2.79 (q, J = 7.5 Hz, 1 H), and 2.7–1.2 (m, 11 H); ^{13}C NMR ($CDCl_3$). Although carbonyl carbon chemical shift could not be determined, ten other carbons appeared at δ 70.9 (d), 54.6 (d), 46.3 (t), 36.1 (t), 35.2 (t), 33.8 (d), 33.7 (d), 31.9 (d), 31.0 (t), and 28.0 (d);[29] mass spectrum *m/e* (rel intensity) 162 (4.8, M^+), 135 (11.3), 134 (100), 119 (21.0), 105 (16.1), 93 (45.1), 92 (48.3), 91 (51.6), 80 (38.7), 79 (75.8), 78 (24.2), 77 (29.1), 66 (16.1), 41 (22.6), and 39 (22.5).

Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.40; H, 8.74.

As a by-product an oil (30 mg, 5.6%) supposed to be a ketene dimer was obtained: $n^{16}D$ 1.5313; IR (neat) 1820, 1745, and 1045 cm^{-1}.

Anal. Calcd for $C_{22}H_{28}O_2$: C, 81.44; H, 8.70. Found: C, 81.18; H, 8.96.

Tosylhydrazone of 20. A mixture of the ketone **20** (50 mg, 0.31 mmol) and *p*-toluenesulfonylhydrazide (100 mg, 0.54 mmol) in ethanol (5 mL) was heated under reflux for 2 h. Removal of the solvent gave a crude product which was purified by repeated recrystallizations from aqueous methanol to afford pure tosylhydrazone **21** as colorless crystals (80 mg, 79%): mp 170–172 °C; IR (KBr) 3200, 1670, 1603, 1340, and 1165 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.85 (d, J = 8.0 Hz, 2 H), 7.60 (m, 1 H, disappeared on shaking with D_2O), 7.30 (d, J = 8.0 Hz, 2 H), 3.55–3.0 (m, 2 H), 2.44 (s, 3 H), and 2.9–0.95 (m, 12 H).

Anal. Calcd for $C_{18}H_{22}N_2O_2S$: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.20; H, 6.68; N, 8.50.

Tetracyclo[4.3.1.$1^{3,8}$.$0^{2,5}$]undecane (4). (A) From Tosylhydrazone (21). To a solution of crude tosylhydrazone (**21**) (from **20**, 125 mg, 0.771 mmol and *p*-toluenesulfonylhydrazide, 215 mg, 1.15 mmol) in ethanol (5 mL) was added sodium borohydride (875 mg, 23.1 mmol) and the mixture was refluxed for 6 h. The cooled mixture was diluted with water (30 mL) and extracted with *n*-pentane (10 mL × 4). The combined extracts were dried (Na_2SO_4) and evaporated to afford crude **4** (45 mg, 40%) which was purified by passing a short silica gel column (*n*-pentane), followed by sublimation at 80 °C (25 mm) to afford pure **4** as colorless crystals (30 mg, 27%): mp 177–179 °C; IR (CCl_4) 2930, 2860, 1455, 1155, and 1065 cm^{-1}; ^1H NMR (CCl_4) δ 2.9–0.7 (m); ^{13}C NMR ($CDCl_3$) δ 43.9 (t, 2 C), 38.3 (d, 1 C), 37.8 (t, 1 C), 36.7 (d, 1 C), 35.5 (t, 1 C), 33.4 (d, 1 C), 33.1 (d, 1 C), 31.5 (d, 1 C), 29.5 (d, 1 C), and 28.2 (t, 1 C); mass spectrum *m/e* (rel intensity) 149 (26.7), 148 (44.0, M^+), 133 (20.0), 119 (20.3), 107 (21.3), 106 (25.9), 105 (37.3), 97 (26.7), 93 (29.3), 92 (46.7), 91 (53.3), 85 (25.3), 83 (25.0), 81 (34.7), 80 (44.0), 79 (100), 78 (25.3), 77 (40.0), 71 (33.3), 70 (29.3), 69 (33.5), 67 (29.0), 66 (24.0), 57 (53.3), 55 (50.6), 43 (50.7), 41 (66.7), and 39 (40.0).

Anal. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 89.15; H, 10.85.

(B) From Ketone (20). A mixture of ketone (**20**) (162 mg, 1.00 mmol), hydrazine hydrochloride (126 mg, 1.20 mmol), and 100% hydrazine hydrate (500 mg, 10.0 mmol) in diethylene glycol (12 mL) was refluxed for 3 h. To the cooled mixture was added potassium hydroxide (285 mg) and the mixture was concentrated until the temperature rises to 230 °C and then refluxed for 4 h. The cooled mixture was diluted with water and extracted with *n*-pentane (two 10-mL portions). Sublimed crystals at the reflux condenser were washed with *n*-pentane. The combined extracts and washings were washed with

water, 5% hydrochloric acid, and water successively and dried (Na_2SO_4). Removal of the solvent and sublimation afforded the hydrocarbon 4 (95 mg, 64.1%) which was identical with the sample obtained via 21 on GLC analysis.

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Registry No.—**1**, 59014-95-8; **4**, 55638-02-3; **10a**, 50782-13-3; **13**, 41171-93-1; **13** oximino ketone, 62881-87-2; **14**, 62881-88-3; **15n**, 62881-89-4; **15n** Na salt, 62959-91-5; **15n** acid chloride, 62881-90-7; **15x**, 62959-92-6; **16n**, 62881-91-8; **17**, 62881-92-9; **18** Na salt, 62881-93-0; **19**, 62881-94-1; **20**, 62881-95-2; **20** ketene dimer, 62881-97-4; **21**, 62881-96-3; 2-adamantanecarboxaldehyde, 39750-93-1; *p*-toluenesulfonylhydrazide, 1576-35-8; isoamyl nitrite, 110-46-3; oxalyl chloride, 79-37-8; *tert*-butyl hydroperoxide, 75-91-2.

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Synthesis and Absolute Configuration of Optically Active C_2-Bishomocubane (Pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane)[1]

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(−)-(1*S*,2*S*,3*S*,4*S*,5*R*,7*S*,8*S*,9*R*)-C_2-Bishomocubane (**4**) and (+)-(1*R*,2*R*,3*S*,4*R*,5*R*,7*S*,8*S*,9*S*)-C_2-bishomocuban-6-one (**14**) were prepared by photochemical ring closure of (+)-*endo*-dicyclopentadiene-1,8-dione 8-ethylene ketal (**12**) followed by successive removal of the substituent groups. Their absolute configurations were deduced from analyses of the CD spectra of (+)-C_2-bishomocuban-6-one (**14**) as well as other synthetic intermediates.

Theoretically, there are four ways to desymmetrize the highly symmetrical cubane molecule (O_h symmetry) furnishing bishomocubanes by insertion of each of two methylene groups between its eight methine groups situated on the eight corners. Among these four types of bishomocubanes (**1**,[2] **2**,[3] **3**, **4**[4]), only pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane (**4**) (C_2 symmetry) is chiral and hereafter we shall call this species C_2-bishomocubane[5] in this communication.