was recrystallized from MeOH to give long, clear spar crystals: mp 200–204 °C; TLC (EtOAc–hexane, 1:1) R_f 0.33; IR ($CHCl_3$) ν 3520 (NH_2), 3405 (NH_2), 2900, 1680 (C=O), 1588 (C=C) cm^{-1}; ^1H NMR δ ca. 1.7 (br, 1 H), ca. 2.1 (s, 4 H), ca. 2.3 (br, 2 H), 3.40 (s, 3 H, OCH_3), 3.88 (d, 2 H, J = 8 Hz, CCH_2O), 4.40 (s, 1 H, acetal proton), 5.63 (s, 2 H, vinyl protons); mass spectrum, m/e (rel intensity) 211 (M^+, 10), 191 (9), 189 (14), 179 (40), 72 (100). Anal. ($C_{11}H_{17}O_3N$) C, H, N.

Acyl Hydrazide of 7b (10). A sample of **9** (200 mg, 0.95 mmol) was mixed with hydrazine hydrate (6 mL, 99%) and poured into a 20-mL, thick-walled Pyrex tube equipped with a stirring bar. After the tube was sealed under a water-aspirator vacuum, it was refluxed for 36 h in an oil bath at 160 °C. After the tube was opened, TLC (EtOAc–EtOH, 8:1) indicated that there was a 90% conversion of **9** and **10**. The solvent was removed by rotary evaporation at 75 °C, and the residue was dissolved into $CHCl_3$ (60 mL). This solution was transferred to a 125-mL separatory funnel and washed with brine (40 mL). The brine was then back-extracted with CH_2Cl_2 (2 × 50 mL), and the organics were combined and dried. After filtration, removal of the solvent gave **10** (176 mg, 82%) as a glassy liquid: TLC (EtOAc–EtOH, 8:1) R_f 0.50; IR ($CHCl_3$) ν 3440 (NH), 3320 (NH), 2959, 1668 (C=O), 1620 (C=C), 1500 cm^{-1}; ^1H NMR δ 1.80–2.90 (m, 9 H), 3.48 (s, 3 H, OCH_3), 4.03 (d, 2 H, J = 7 Hz, CCH_2O), 4.38 (d, 1 H, J = 7 Hz), 5.49 (s, 1 H, $NHNH_2$), 5.65 (s, 2 H, vinyl protons); mass spectrum, m/e (rel intensity) 210 (7), 194 (100), 179 (12), 163 (22), 69 (100). Anal. ($C_{11}H_{18}O_3N_2$) C, H.

***cis*-1β-Methoxy-4β-carbomethoxy-4a,5,8,8a-tetrahydroisochroman (3b).** Freshly cut sodium metal (60 mg, 0.0024 g-atom) was added to anhydrous MeOH (35 mL) in a dry, 100-mL, two-necked flask equipped with a stirring bar and protected by a N_2 atmosphere. Freshly prepared Cu^ICl[19] (240 mg, 2.4 mmol) was added to the mixture after complete solubilization of the sodium. The solution immediately turned blue. This solution was stirred for about 5 min, and a bubbler, connected to an oxygen tank, was inserted through the vertical neck of the flask. Into the side neck of the flask was placed a 25-mL, pressure-equalizing dropping funnel charged with **10** (333 mg, 1.47 mmol) dissolved in anhydrous methanol (15 mL). This solution was dripped into the reaction flask over a 30-min period, during which time the vessel was well stirred and a vigorous stream of O_2 bubbled through it. After the addition, the reaction flask was swept with O_2 for 1 h more. The solvent was removed, and the resulting residue was dissolved in Et_2O (75 mL). This solution was poured into a 250-mL separatory funnel and washed with brine (80 mL). The brine solution was back-extracted with Et_2O (2 × 60 mL), and the organic extracts were combined and dried. After filtration, most of the solvent was removed by rotary evaporation and the concentrated solution put onto a 30 × 1.5 cm silica gel column and eluted with an Et_2O–hexane (1:3) solvent system. Evaporation of the fractions containing the product gave **3b** (168 mg, 50%) as a clear glasslike material. Despite repeated attempts, **3b** could not be recrystallized: TLC (Et_2O–hexane, 1:3) R_f 0.85; IR ($CHCl_3$) ν 2900, 1725 (C=O), 1512, 1440 cm^{-1}; ^1H NMR δ 2.10 (m, 4 H), 2.50–2.80 (m, 3 H), 3.38 (s, 3 H, OCH_3), 3.68 (s, 3 H, CO_2CH_3), 3.78 (m, 2 H, CCH_2O), 4.38 (s, 1 H, acetal proton), 5.60 (s, 2 H, vinyl proton); mass spectrum, m/e (rel intensity) 226 (M^+, 19), 211 (4), 194 (30), 164 (14), 79 (100). Anal. ($C_{12}H_{18}O_4$) C, H.

Acknowledgment. This research was supported in part by a grant from the National Institutes of Health (CA 17127). We are indebted to Professor B. Fraser-Reid, University of Guelph/Waterloo, for the model experimental procedure used to make **5b** by a Lewis acid catalyzed Diels–Alder reaction. We thank Jim Blackbourn and Gary Girdaukas, School of Pharmacy, for NMR and MS analyses and Professor H. Schnoes and W. A. Gibbons, Department of Biochemistry, for high-resolution MS and NMR analyses.

Registry No. 3b, 71117-60-7; **4b**, 60249-17-4; **5b**, 71117-61-8; **7a**, 71117-62-9; **7b**, 71117-63-0; **9**, 71117-64-1; **10**, 71097-05-7; 2,5-dimethoxy-2,5-dihydrofurfuryl alcohol, 19969-71-2; butadiene, 106-99-0; tosylmethyl isocyanide, 36635-61-7.

Synthesis and Chemistry of 2,11-Dehydro-5-homoadamantanone

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Tiffeneau–Demjanov ring expansion of 8,9-dehydro-2-adamantanone gives 2,11-dehydro-5-homoadamantanone (**9**). Wolff–Kishner reduction of **9** provides 2,11-dehydrohomoadamantane. Alternatively, this hydrocarbon can be prepared by photoreduction of 5-acetoxy-2,11-dehydrohomoadamantane. Treatment of the tosylhydrazone of **9** with methyllithium affords 2,11-dehydro-4-homoadamantene which undergoes a thermal vinylcyclopropane–cyclopentene rearrangement to give tetracyclo[5.3.1.$0^{2,6}$.$0^{3,9}$]undec-4-ene. Perchloric acid catalyzed addition of acetic acid to **9** provides 2-*endo*-acetoxy-5-homoadamantanone (**17**). The structure proof of **17** follows in part from the photoisomerization of 2-*endo*-hydroxy-5-homoadamantanone to 3-oxa-*endo*-tricyclo[6.3.1.$0^{2,6}$]dodecan-4-one. Addition of bromine to **9** gives 2,11-*diendo*-dibromo-5-homoadamantanone.

The carbon skeleton of homoadamantane (**1**) allows for five "non-bridgehead" dehydrohomoadamantanes, **2–6** (Scheme I). Three of these hydrocarbons have been synthesized: 2,4-dehydrohomoadamantane[2] (**2**), 2,5-dehydrohomoadamantane[3] (**3**), and 2,9-dehydrohomoadamantane[4] (**4**). We now wish to report the preparation of 2,11-dehydro-5-homoadamantanone (**9**) and some of the aspects of its chemistry, including the synthesis of the parent hydrocarbon **6**.

Results and Discussion

Cyclopropyl ketone **9** was readily generated by Tiffeneau–Demjanov ring expansion of 8,9-dehydro-2-adamantanone[5] (**7**). Treatment of **7** with trimethylsilyl

(1) Recipient of a Camille and Henry Dreyfus Teacher–Scholar Grant Award, 1976–1981.

(2) (a) Z. Majerski, S. H. Liggero, and P. v. R. Schleyer, *J. Chem. Soc., Chem. Commun.*, 949 (1970); (b) R. Yamaguchi, T. Katsushima, and M. Kawanisi, *Bull. Chem. Soc. Jpn.*, **47**, 2830 (1974); (c) R. K. Murray, Jr., K. A. Babiak, and T. K. Morgan, Jr., *J. Org. Chem.*, **40**, 2463 (1975).

(3) T. Sasaki, S. Eguchi, and Y. Hirako, *J. Org. Chem.*, **42**, 2981 (1977).

(4) R. K. Murray, Jr., D. L. Goff, and R. E. Ratych, *Tetrahedron Lett.*, 763 (1975).

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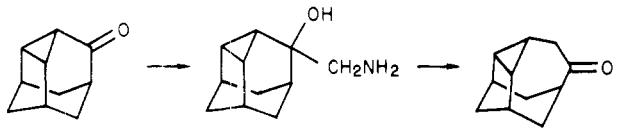

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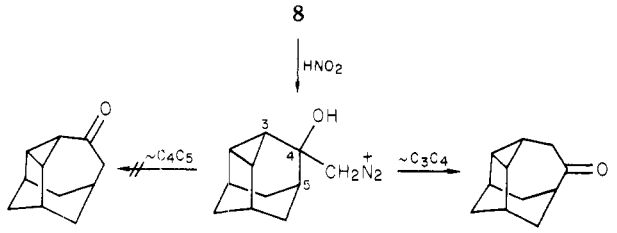
cyanide,[6] followed by reduction of the resulting trimethylsilyl cyanohydrin ether with lithium aluminum hydride, gave β-amino alcohol **8**. Treatment of **8** with nitrous acid provided **9** in ca. 70% overall yield from **7**. Consistent with the assigned structure, **9** shows a nonconjugated carbonyl absorption in the infrared at 1698 cm^{-1} and a two-proton doublet at δ 3.09 in its ^1H NMR spectrum. Moreover, the ^{13}C NMR spectrum of **9** contains only eight signals with one of the three signals for methylene carbons being twice as intense as the others and two of the four signals for methine carbons also being twice as intense as the others. Since **8** gives exclusively **9**, it follows that



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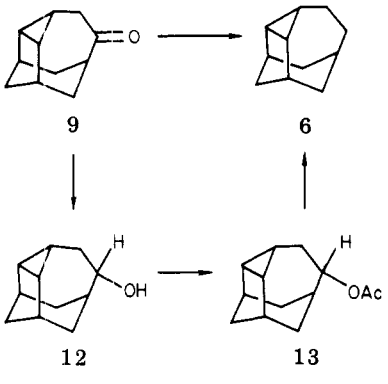
bond C_3–C_4 in intermediate **10** migrates in strong preference to bond C_4–C_5. This behavior parallels earlier observations that homologation of conjugated cyclic cyclopropyl ketones under analogous conditions affords the ring-expanded nonconjugated cyclopropyl ketones.[7]

Wolff–Kishner reduction of **9** provided 2,11-dehydrohomoadamantane[8] (**6**) in 35% yield. Although the hydrocarbon analyzed well for $C_{11}H_{16}$, gave a correct exact mass spectroscopic determination for the parent ion, and showed no resonance below δ 2.9 in its ^1H NMR spectrum, the ^{13}C NMR spectrum of **6** contained only six signals. Attempts to resolve the apparent accidental coincidence of signals in the ^{13}C NMR spectrum of **6** were unsuccessful. Consequently, in order to ensure the structure assignment of **6**, it was prepared from **9** by an alternative route.



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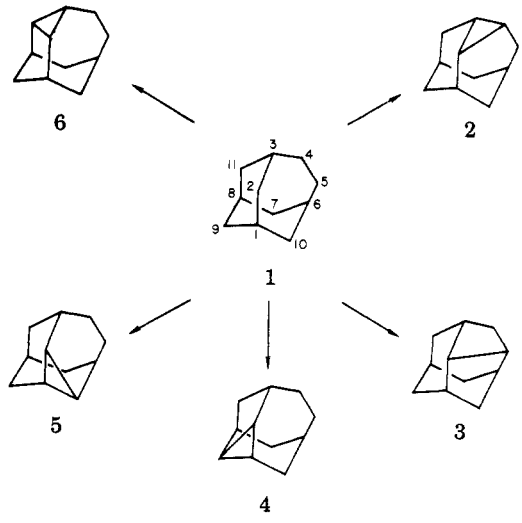
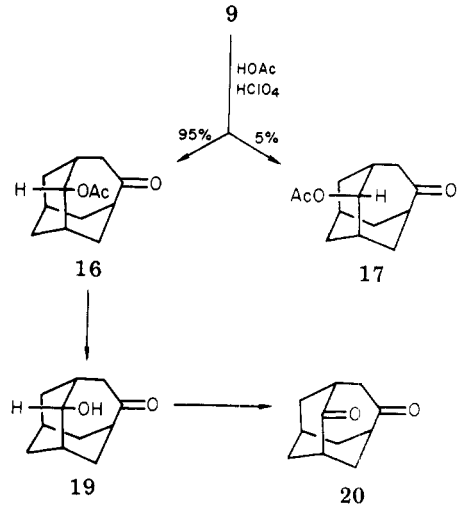
Scheme I



Scheme II



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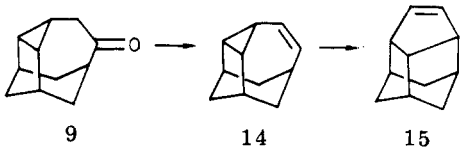
Sodium borohydride reduction of **9** provided alcohol **12** which was converted to acetate **13** with sodium acetate and acetic anhydride. Irradiation of a solution of **13** in a 95:5 mixture of hexamethylphosphoric triamide–water[9] gave **6** exclusively.

We have also prepared vinylcyclopropane **14** from **9**.



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Treatment of the tosylhydrazone of **9** with an excess of methyllithium afforded 2,11-dehydro-4-homoadamantene (**14**) in 59% yield. Consistent with the presence of a plane of symmetry in **14**, the ^{13}C NMR spectrum of **14** contains only eight signals with one of the two signals for methylene carbons being twice as intense as the other and two of the four signals for methine carbons being twice as intense as the others. The olefinic carbons in **14** show a chemical shift difference of 13.4 ppm in its ^{13}C NMR spectrum, and the olefinic protons in **14** appear as a complex multiplet from δ 6.19 to 5.47 in its ^1H NMR spectrum. Hydrocarbon **14** readily undergoes a vinylcyclopropane–cyclopentene thermal rearrangement.[10] Heating a neat sample of **14**

(5) J. E. Baldwin and W. D. Foglesong, *J. Am. Chem. Soc.*, **90**, 4303 (1968); R. K. Murray, Jr., T. K. Morgan, Jr., and K. A. Babiak, *J. Org. Chem.*, **40**, 1079 (1975); G. Karlovic and Z. Majerski, *J. Org. Chem.*, **43**, 746 (1978).

(6) D. A. Evans, G. L. Carroll, and L. K. Truesdale, *J. Org. Chem.*, **39**, 914 (1974).

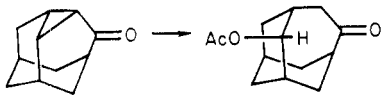
(7) J. T. Lumb and G. H. Whitham, *Tetrahedron*, **21**, 499 (1965); R. R. Sauers, J. A. Beisler, and H. Feilich, *J. Org. Chem.*, **32**, 569 (1967); W. v. E. Doering, B. M. Ferrier, E. T. Fossel, J. H. Hartenstein, M. Jones, Jr., G. Klumpp, R. M. Rubin, and M. Saunders, *Tetrahedron*, **23**, 3943 (1967).

(8) By IUPAC nomenclature **6** is tetracyclo[5.3.1.$0^{2,4}$.$0^{3,9}$]undecane.

(9) H. Deshayes, J.-P. Pete, C. Portella, and D. Scholler, *J. Chem. Soc., Chem. Commun.*, 439 (1975); H. Deshayes, J.-P. Pete, and C. Portella, *Tetrahedron Lett.*, 2019 (1976).

at 200 °C afforded tetracyclo[5.3.1.$0^{2,6}$.$0^{3,9}$]undec-4-ene (**15**) in 50% yield. The ^{1}H NMR spectrum of **15** features an apparent singlet for the olefinic protons at δ 5.70, and the enantiotopic olefinic carbons in **15** give rise to a single resonance in its ^{13}C NMR spectrum. Moreover, the ^{13}C NMR spectrum of **15** consists of only seven signals with four of the signals being twice as intense as the others.

The cyclopropane ring in **9** can easily be opened with electrophilic reagents. Perchloric acid catalyzed addition of acetic acid to **9** gave an ca. 90% yield of a 95:5 mixture of 2-*endo*-acetoxy-5-homoadamantanone (**16**) and 2-*exo*-acetoxy-5-homoadamantanone (**17**), respectively (Scheme II).[11,12] The minor product was obtained earlier by the perchloric acid catalyzed acetolysis of 2,4-dehydro-5-homoadamantanone (**18**).[2c] The skeletal framework of the



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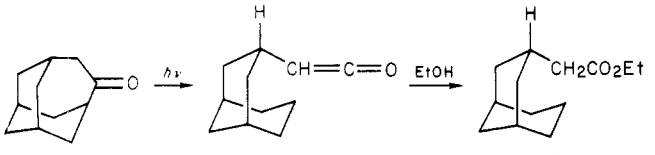
major product and the skeletal positions of the substituents in **16** follow from the conversion of **16** to 2,5-homoadamantanedione (**20**).[2c] Hydrolysis of **16** provided 2-*endo*-hydroxy-5-homoadamantanone (**19**), and Sarett oxidation of **19** afforded **20**. Previously, we noted that the ^{1}H NMR signal of the C-2 endo hydrogen in a 2-exo-substituted homoadamantane appears as a broad singlet, whereas the C-2 exo hydrogen in a 2-endo-substituted homoadamantane appears as a doublet of doublets.[2c] Since the C**H**(OAc) signal in **16** is an apparent triplet, it follows that the acetoxy substituent in **16** is endo. The photochemistry of keto alcohol **19** supports this conclusion. Earlier it was shown that irradiation of a solution of 4-homoadamantanone (**21**) in ethanol affords **23**.[13] The



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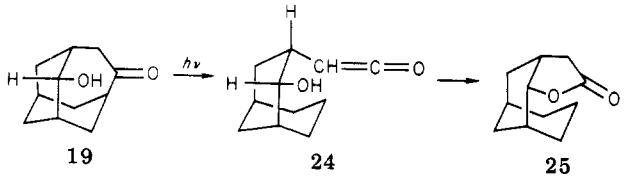
reaction is rationalized as proceeding by the initial formation of ketene **22** which then reacts with the solvent. By contrast, irradiation of a solution of **19** in ether with a Hanovia L 450-W high-pressure mercury lamp gave a 25% yield of 3-oxa-*endo*-tricyclo[6.3.1.$0^{2,6}$]dodecan-4-one (**25**) which shows a characteristic carbonyl absorption at



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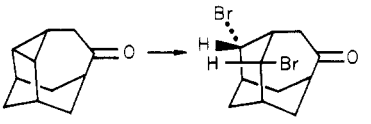
1783 cm^{-1} in the infrared. Apparently, photolysis of **19** provides ketene **24** which is trapped intramolecularly by the C-2 endo hydroxyl substituent to give lactone **25**.

The reaction of **9** with bromine was also investigated. Examination of the crude reaction mixture by ^{13}C NMR indicated that greater than 90% of the material consisted of a single product which possessed a plane of symmetry because the ^{13}C NMR spectrum contained only eight signals with three of the signals being twice as intense as the others. Since the CHBr signals in the ^{1}H NMR spectrum of **26** are an apparent triplet, it follows[2c] that the



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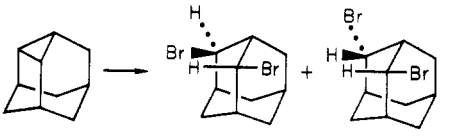
reaction product is 2,11-*diendo*-dibromo-5-homoadamantanone (**26**). In contrast, it is striking that the addition of bromine to 2,4-dehydroadamantane (**27**) is reported to give a 60:40 mixture of **28**:**29**.[14]



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Experimental Section

Melting points were obtained in sealed capillary tubes using a Thomas-Hoover melting point apparatus and are uncorrected. Infrared spectra were obtained on Perkin-Elmer 180 or 337 spectrophotometers. Proton magnetic resonance spectra were recorded with a Perkin-Elmer R-12B 60 MHz spectrometer and are referenced to an internal standard of tetramethylsilane. Apparent splittings are reported in all cases. Carbon magnetic resonance spectra were taken at an operating frequency of 22.63 MHz on a Brüker HFX-90 spectrometer equipped for Fourier transform pulsed NMR with a Nicolet 1085 data acquisition system and are referenced to an internal standard of tetramethylsilane. Electron-impact mass spectra were obtained with a duPont CEC 21-110B mass spectrometer. Unless noted otherwise, yields were obtained by integration of appropriate signals in the ^{1}H NMR spectrum of the product(s) vs. the signal of a predetermined amount of an added standard (generally chloroform or trichloroethylene) and are regarded as being accurate to ca. ±10%. Elemental analyses were performed by Micro-Analysis, Inc., Wilmington, Del.

2,11-Dehydro-5-homoadamantanone (9). Zinc iodide (10 mg) was added to a solution of 8,9-dehydro-2-adamantanone[5] (1.0 g, 6.7 mmol) in freshly distilled trimethylsilyl cyanide (1.56 g, 15.8 mmol) which was maintained at ca. 5 °C under nitrogen. The resulting pale yellow solution was allowed to warm to room temperature, and the reaction mixture was stirred at this temperature under nitrogen for 48 h. The excess trimethylsilyl cyanide present was removed from the reaction mixture by evaporation at reduced pressure to give a viscous oil which showed no carbonyl absorption in the infrared. The resulting unpurified α-siloxynitrile was dissolved in anhydrous ether (10 mL) and added dropwise under nitrogen to a stirred slurry of lithium aluminum hydride (2.5 g, 67 mmol) in anhydrous ether (100 mL) at a rate sufficient to maintain a gentle reflux of the reaction mixture. After the addition was completed, the reaction mixture was stirred for 16 h at room temperature. At this point, the excess lithium aluminum hydride present was destroyed by the dropwise addition of 2.5 mL of water, followed by 2.5 mL of 15% sodium hydroxide and 7.5 mL of water. Stirring was continued until a granular white precipitate formed. The precipitate was filtered and then washed with methylene chloride. The filtrates were combined, and the solvent was evaporated at reduced pressure to provide the crude amino alcohol as a white crystalline solid.

A solution of sodium nitrite (700 mg, 10.0 mmol) in water (4 mL) was added dropwise to a stirred solution of the crude amino alcohol in acetic acid (2 mL) and water (11 mL) which was maintained at 0 °C. The resulting reaction mixture was stirred

(10) For a review of the thermal rearrangements of vinylcyclopropanes see: E. M. Mil'vitskaya, A. V. Tarakanova, and A. F. Plate, *Russ. Chem. Rev.*, **45**, 469 (1976).

(11) Perchloric acid catalyzed addition of acetic acid to the parent hydrocarbon 6 gave a more complex mixture of products.

(12) We have adopted the convention that a substituent is designated as endo if it is oriented toward the larger ring of a polycyclic skeleton and exo if it faces the smaller ring.

(13) T. Sasaki, S. Eguchi, and M. Mizutani, *Synth. Commun.*, **3**, 369 (1973).

(14) A. C. Udding, J. Strating, and H. Wynberg, *Tetrahedron Lett.*, 1345 (1968).

at 0 °C for 3 h and then at room temperature for 12 h. The reaction mixture was then diluted with brine (50 mL) and extracted with ether (3 × 35 mL). The combined ether extracts were washed with saturated aqueous sodium bicarbonate (5 × 10 mL) and brine and then dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure gave an oil which was Kugelrohr distilled (100 °C (0.1 mm)) to provide 770 mg (70% overall yield) of **9**. Final purification by GLC (10 ft × 0.25 in. SE-30 column, 225 °C) afforded **9** as a white solid: mp 115–116 °C; ^{1}H NMR δ (CCl_4) 3.09 (d, J = 3.5 Hz, 2 H, $-CH_2CO-$), 2.68–2.0 (br m, 4 H), 1.95–1.03 (br m, 8 H); ^{13}C NMR δ ($CDCl_3$) tentative assignments 212.4 (C-5), 52.4 (C-9),[15] 44.3 (C-6), 38.9 (C-4), 33.2 (C-1 and C-8), 29.1 (C-3), 28.9 (C-7 and C-10), 27.4 (C-2 and C-11); IR ν ($CHCl_3$) 3015, 2935, 2865, 1698, 1450, 1405, 1230, 1150, 940 cm^{-1}.

Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.50; H, 8.62.

2,11-Dehydrohomoadamantane (6). A solution of potassium hydroxide (1.0 g), 95% hydrazine (0.75 g), and **9** (97 mg, 0.6 mmol) in diethylene glycol (3 mL) was heated with stirring at 100 °C for 0.5 h and then at 185 °C for 16 h. While the solution was being heated and stirred, a white solid appeared on the water-cooled condenser. The system was cooled, and the material on the condenser was dissolved in pentane. The cooled reaction mixture was also extracted with pentane (3 × 15 mL). The combined pentane extracts were washed with water (5 mL) and brine (5 mL) and then dried over anhydrous magnesium sulfate. Removal of the solvent by atmospheric distillation provided a colorless oil which by GLC analysis (10 ft × 0.25 in. SE-30 column, 150 °C) was homogeneous. Sublimation (100 °C (760 mm)) of this material gave **6** (31 mg, 35% yield) as a colorless solid: mp 119–121 °C; ^{1}H NMR δ (CCl_4) 2.9–1.1 (br m); ^{13}C NMR δ (C_6D_6) 54.3 (t), 37.0 (t), 36.6 (d), 35.2 (d), 28.9 (d), 24.0 (t); IR ν (CCl_4) 3010, 2915, 2860, 1460, 1350, 1200, 1175, 1100, 1065, 1050, 1030 cm^{-1}. Exact mass calcd for $C_{11}H_{16}$: 148.125. Found: 148.128.

Anal. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 89.31; H, 10.89.

5-Hydroxy-2,11-dehydrohomoadamantane (12). Sodium borohydride (250 mg, 5.3 mmol) was added to a stirred solution of **9** (200 mg, 1.23 mmol) in methanol (10 mL) at 0 °C. The reaction mixture was stirred for 6 h at room temperature, and then 10 mL of water was added. The resulting solution was saturated with sodium chloride and then extracted with ether (2 × 25 mL). The combined ether extracts were dried over anhydrous magnesium sulfate, and the solvent was evaporated at reduced pressure. Analysis of the residue by ^{1}H NMR indicated that **12** was obtained in ca. 85% yield. GLC analysis (10 ft × 0.25 in. SE-30 column, 225 °C) showed a single component to be present, and purification of **12** by GLC (above conditions) gave a white solid: mp 99–100 °C; ^{1}H NMR δ ($CDCl_3$) 3.82 (br t, J = 8 Hz, 1 H, CHOH), 3.10–1.07 (complex m, 15 H); IR ν (CCl_4) 3630, 3365, 3015, 2915, 2865, 1455, 1350, 1225, 1210, 1100, 1070, 1040, 1020 cm^{-1}.

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.49; H, 9.78.

5-Acetoxy-2,11-dehydrohomoadamantane (13). A reaction mixture consisting of **12** (161 mg, 1.03 mmol), sodium acetate (320 mg), and acetic anhydride (4 mL) was stirred at 95 °C for 2 h, then cooled, and diluted with water (20 mL). The resulting mixture was neutralized with solid sodium bicarbonate and extracted with ether (2 × 20 mL). The combined ether extracts were washed with saturated aqueous sodium bicarbonate (25 mL) and dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure gave a pale yellow oil which by ^{1}H NMR analysis contained an ca. 80% yield of **13**. Isolation by GLC (10 ft × 0.25 in. SE-30 column, 225 °C) provided **13** as a colorless oil: ^{1}H NMR δ (CCl_4) 4.78 (t, J = 7.8 Hz, 1 H, $CHOCOCH_3$), 2.9–1.1 (complex m, 17 H, containing $CHOCOCH_3$ singlet at δ 1.92); IR ν (CCl_4) 3020, 2930, 2865, 1734, 1365, 1245, 1020, 975 cm^{-1}.

Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79. Found: C, 75.95; H, 9.03.

Photoreduction of 13. A nitrogen-purged solution of **13** (160 mg) in hexamethylphosphoric triamide (14.25 mL) and water (0.75 mL) was irradiated through a Quartz filter with a Hanovia L 450-W high-pressure mercury lamp for 25 h. At this point the reaction mixture was diluted with water (100 mL) and then extracted with ether (4 × 15 mL). The combined ether extracts were washed successively with 5% hydrochloric acid (2 × 10 mL), saturated aqueous sodium bicarbonate (10 mL), and saturated aqueous sodium chloride (10 mL) and then dried over anhydrous magnesium sulfate. Removal of the solvent by atmospheric distillation provided a residue which by GLC analysis (10 ft × 0.25 in. SE-30 column, 150 °C) contained a single component. Isolation of the product by GLC (above conditions) gave a white solid whose IR spectrum was identical with that of **6** prepared from **9**.

2,11-Dehydro-4-homoadamantene (14). A solution of **9** (178 mg, 1.1 mmol) and *p*-toluenesulfonylhydrazine (97%, 211 mg, 1.1 mmol) in methanol (3 mL) was refluxed for 2 h. Evaporation of the solvent at reduced pressure left a yellow solid residue which was recrystallized from methanol at −10 °C to give **2,11-dehydro-5-homoadamantanone tosylhydrazone (30)** as a white crystalline solid: mp 142–144 °C; ^{1}H NMR δ ($CDCl_3$) 8.29–7.28 (4 H, d of d, aromatic protons), 3.3–1.2 (complex m, 14 H, containing CH_3 signal at δ 2.46).

A slurry of **30** (755 mg, 2.3 mmol) in anhydrous ether (20 mL) was treated at room temperature under nitrogen with ca. 4 equiv of methyllithium. The reaction mixture was stirred at room temperature for 6 h, and then the excess methyllithium present was quenched by the cautious addition of water (20 mL). The aqueous layer was separated and extracted with ether (3 × 20 mL). The combined ether extracts were washed with water (3 × 5 mL) and brine (10 mL) and then dried over anhydrous magnesium sulfate. Removal of the solvent by atmospheric distillation afforded a colorless oil which was Kugelrohr distilled to provide 217 mg (59% yield) of **14**: ^{1}H NMR δ (CCl_4) 6.19–5.47 (complex m, 2 H, $-CH=CH-$), 2.96–0.68 (complex m, 12 H); ^{13}C NMR δ ($CDCl_3$) tentative assignments 139.8 (C-4), 126.4 (C-5), 54.5 (C-9),[15] 38.0 (C-1 and C-8), 33.7 (C-3 or C-6), 30.9 (C-7 and C-10), 29.8 (C-3 or C-6), 25.7 (C-2 and C-11); IR ν (CCl_4) 3025, 2925, 2855, 1500, 1470, 1450, 1350, 1260, 1080, 1060, 1050, 1020 cm^{-1}. Exact mass calcd for $C_{11}H_{14}$: 146.110. Found: 146.111.

Tetracyclo[5.3.1.0^{2,6}.0^{3,9}]undec-4-ene (15). A neat sample of **14** was heated in a sealed ampule at 200 °C for 2.5 h. Analysis of the residue by ^{1}H NMR indicated that the product was obtained in ca. 50% yield. Purification by GLC (10 ft × 0.25 in. SE-30 column, 180 °C) provided **15** as a white solid: mp 165–168 °C; ^{1}H NMR δ (CCl_4) 5.70 (s, $W_{1/2}$ = 4 Hz, 2 H, $-CH=CH-$), 3.34–1.32 (complex m, 12 H); ^{13}C NMR δ ($CDCl_3$) 130.2, 59.6, 55.3, 45.2, 35.5, 35.0, 31.7 in the ratio of 2:1:2:2:1:2:1, respectively; IR ν (CCl_4) 3060, 2935, 2870, 1350, 1305, 1090, 720 cm^{-1}.

Anal. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.62; H, 9.42.

2-*endo*-Acetoxy-5-homoadamantanone (16). A solution containing **9** (97 mg, 0.6 mmol) and 70% perchloric acid (50 μL) in acetic acid (4 mL) was stirred at 100 °C for 4 h. The cooled reaction mixture was poured into water (100 mL), neutralized with solid sodium bicarbonate, and extracted with ether (3 × 20 mL). The combined ether extracts were washed successively with saturated aqueous sodium bicarbonate (10 mL) and brine (10 mL) and then dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure provided a yellow oil which by ^{1}H NMR analysis contained an ca. 90% yield of a 95:5 mixture of **16**:**17**. Purification by GLC (10 ft × 0.25 in. SE-30 column, 235 °C) gave **16** as a colorless oil: ^{1}H NMR δ ($CDCl_3$) 5.16 (apparent t, J = 4.7 Hz, 1 H, $CHOCOCH_3$), 3.18–1.43 (complex m, 17 H, containing $CHOCOCH_3$ singlet at δ 2.06); IR ν (CCl_4) 2920, 2860, 1736, 1690, 1445, 1370, 1245, 1110, 1035, 940 cm^{-1}.

Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.25; H, 8.16. Found: C, 70.09; H, 8.13.

2-*endo*-Hydroxy-5-homoadamantanone (19). A reaction mixture containing **16** (115 mg), potassium hydroxide (100 mg), methanol (2.5 mL), and water (2.5 mL) was refluxed for 4 h. The resulting solution was cooled, diluted with water (15 mL), and extracted with ether (3 × 10 mL). The combined ether extracts were washed with brine (5 mL) and dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure

(15) This assignment follows from the observation that the ^{13}C NMR spectra of **7** and **27** contain signals for unique methylene carbons at δ 50.8 and 52.4, respectively.

afforded a pale yellow solid (108 mg). Purification by GLC gave **19** as a white solid: mp 288–293 °C; ^{1}H NMR δ ($CDCl_3$) 4.11 (apparent t, J = 3.7 Hz, 1 H, CHOH), 3.41–1.37 (complex m, 15 H); IR ν (CCl_4) 3625, 3435, 2915, 2855, 1697, 1450, 1050, 930, 915 cm^{-1}.

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.94. Found: C, 73.26; H, 8.86.

2,5-Homoadamantanedione (20). Chromium trioxide (336 mg, 3.36 mmol) was added in small portions to a mixture of pyridine (530 mg, 6.72 mmol) in methylene chloride (9 mL). To this complex was added a solution of **19** (50 mg, 0.28 mmol) in methylene chloride (0.5 mL). The reaction mixture was stirred at room temperature for 15 min, and the resulting inorganic precipitates were removed by filtration. The filtrate was washed successively with 5% aqueous sodium hydroxide, 10% aqueous hydrochloric acid, saturated aqueous sodium bicarbonate, and brine and then dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure gave crude **20** which was purified by GLC (10 ft × 0.25 in. SE-30 column, 225 °C). The IR spectrum of this material was identical with that of **20** prepared by an alternative procedure.[2c]

3-Oxa-*endo*-tricyclo[6.3.1.0^{2,6}]dodecan-4-one (25). A solution of 20 mg of **19** in 2 mL of nitrogen-purged diethyl ether was irradiated through a Vycor filter with a Hanovia L 450-W high-pressure mercury lamp. Monitoring the photolysis by GLC (10 ft × 0.25 in. SE-30 column, 235 °C) indicated a gradual disappearance of **19** with the concomitant formation of a photoproduct. After irradiation for 2 h, ca. 85% of **19** had reacted. Evaporation of the solvent at reduced pressure provided an oil which by ^{1}H NMR analysis contained an ca. 25% yield of the photoproduct. Purification by GLC (above conditions) gave **25** as a colorless oil: ^{1}H NMR δ (CCl_4) 4.97–4.59 (br m, 1 H, –CHO–), 2.76–0.96 (complex m, 15 H); IR ν (CCl_4) 2930, 2880, 1783, 1465, 1180, 1160, 1010, 975, 920 cm^{-1}.

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.94. Found: C, 73.44; H, 8.68.

2,11-*diendo*-Dibromo-5-homoadamantanone (26). Bromine (8 μL, 0.15 mmol) was added to a stirred solution of **9** (25 mg, 0.15 mmol) in carbon tetrachloride (2 mL) at room temperature. The reaction mixture was stirred for 0.5 h and then diluted with ether (25 mL). The resulting solution was washed with 10% aqueous sodium bisulfite (2 × 10 mL) and brine (10 mL) and then dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure gave an orange oil which was shown by ^{13}C NMR to contain >90% of a single product: δ ($CDCl_3$) 207.6, 57.4, 46.8, 42.3, 41.3, 36.5, 34.8, 26.3 in the ratio of 1:2:1:1:1:1:2:2, respectively. Sublimation provided **26** as a white waxy semisolid: ^{1}H NMR δ ($CDCl_3$) 4.69 (apparent t, J = 4.7 Hz, 2 H, CHBr), 3.16 (d, J = 4.0 Hz, 2 H, $-CH_2CO-$), 2.82–1.50 (complex m, 10 H); IR ν ($CHCl_3$) 3010, 2920, 2860, 1700, 1465, 1445, 1400, 1360, 1300, 1280, 1240, 1150, 1050 cm^{-1}; m/e 322/324 = 2.13. Exact mass calcd for $C_{11}H_{14}Br_2O$: 319.941. Found: 319.942.

Registry No. **6**, 71129-58-3; **7**, 10497-56-0; **9**, 71129-59-4; **12**, 71129-60-7; **13**, 71129-61-8; **14**, 71129-62-9; **15**, 59159-18-1; **16**, 71183-74-9; **17**, 55638-06-7; **19**, 71183-75-0; **20**, 55638-09-0; **25**, 71129-63-0; **26**, 71129-64-1; **30**, 71129-65-2; *p*-toluenesulfonylhydrazine, 1576-35-8.

Synthesis of Substituted Cyclooctatetraenide Dianions

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Dilithioalkyl and -aryl monosubstituted cyclooctatetraenide dianions ($Li_2C_8H_7R$; R = methyl, *n*-butyl, *sec*-butyl, *tert*-butyl, phenyl, and benzyl) were synthesized by reaction of the appropriate organolithium reagent with cyclooctatetraene in diethyl ether or tetrahydrofuran. The reaction occurred cleanly and with a good yield of the dilithio monosubstituted cyclooctatetraenide dianion at ambient or lower temperature for all alkyl or aryl organolithium reagents studied except *tert*-butyllithium. (TMEDA is needed as an activator for CH_3Li.) A two-step mechanism for the reaction is proposed that involves addition of the organolithium reagent to cyclooctatetraene followed by proton removal to yield the appropriate dianion.

Organolithium reagents are known to readily add to conjugated olefins and styrenes.[1] Reaction of cycloheptatriene with organolithium reagents yields lithium 6-substituted cycloheptadienide.[2] In a similar way, reaction of organolithium reagents with cyclooctatetraene (**1a**) might be expected to yield lithium 8-substituted cyclooctatrienide. Hydrolysis of this anion would yield the monosubstituted cyclooctatriene. Cope et al.[3a] in an early study of **1a** with *sec*-butyllithium observed monosubstituted cyclooctatrienes on hydrolysis. However, on reaction of **1a** with *n*-butyl- and phenyllithium,[3] monosubstituted cyclooctatetraenes as well as monosubstituted cyclooctatrienes were observed on hydrolysis. In fact, this method has been used to prepare the monosubstituted cyclooctatetraenes, but the yields are low and the cyclooctatetraenes and cyclooctatrienes must be separated by a time-consuming $AgNO_3$ extraction.[4,5] Here we show

Table I. Reaction Data for Monosubstituted Cyclooctatetraenide Dianions

compd	temp, °C	solvent	reacn time[c]	% yield[a]
methylcyclooctatetraene[b] (**2a**)	25	Et_2O	18 h	60
n-butylcyclooctatetraene (**3a**)	25	Et_2O	45 min	70
sec-butylcyclooctatetraene (**4a**)	0	Et_2O	30 min	51
tert-butylcyclooctatetraene (**5a**)	−78	Et_2O/pentane	5 min	45
phenylcyclooctatetraene (**6a**)	25	Et_2O	36 h	76
benzylcyclooctatetraene (**7a**)	0	THF	5 min	60

[a] Based on O_2 oxidation to the monosubstituted cyclooctatetraene followed by hydrolysis. All yields are based on VPC data. [b] 1.2 TMEDA/CH_3Li molar ratio. [c] Time for complete reaction.

(1) B. J. Wakefield, "The Chemistry of Organolithium Compounds", Pergamon Press, New York, 1974, Chapter 7.
(2) K. Haffner and W. Rellensmann, *Chem. Ber.*, **95**, 2567 (1962); R. B. Bates, S. Brenner, and B. I. Mayall, *J. Am. Chem. Soc.*, **94**, 4765 (1972).
(3) (a) A. C. Cope and H. O. Van Orden, *J. Am. Chem. Soc.*, **74**, 175 (1952); (b) A. C. Cope and M. R. Kinter, *ibid.*, **73**, 3424 (1951); (c) A. C. Cope and W. R. Moore, *ibid.*, **77**, 4939 (1955).

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