mostated oil bath, and NMR measurements were made periodically after quenching the tube in water. The kinetics were followed by the disappearance of the bicyclobutane signals relative to an assumed constant aromatic region.

Kinetics of 2a to 1a. A solution of **2a** (6.7×10^{-3} M) in cyclohexane was placed in a visible–uv cell equipped with a graded seal and ground glass joint. The tube was sealed in vacuo. The cell was heated in a thermostated oil bath and measurements were made periodically after quenching the cell in the water. The kinetics were followed by the appearance of **1a** in the visible; an infinity reading was taken after heating the cell at >190 °C for 10 h.

Preparation of 3b. To a solution of 300 mg (1.69 mmol) of **3a** in 50 ml of ether under nitrogen was added 3.0 ml of 2.0 N *n*-butyllithium (6.0 mmol) in hexane. The resulting dark orange solution was stirred at room temperature for 1 h after which it was quenched with D_2O. Workup afforded an almost quantitative yield of **3b.** Mass spectral and NMR analysis revealed an 83% incorporation of deuterium into the bridgehead positions with less than 2% incorporation into the benzylic positions.

Preparation of 1b and 2b. These were prepared by the literature method used to prepare **1a** and **2a** only beginning with the **3b** described above.

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Registry No.—**1a,** 208-20-8; **2a,** 30736-79-9; **3a,** 40480-63-5.

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Stepwise Elaboration of Diamondoid Hydrocarbons. Synthesis of Diamantane from Adamantane

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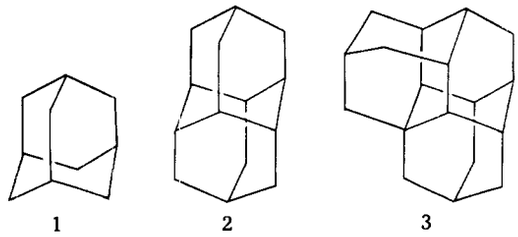
Diamantane (**2**) has been synthesized in a stepwise manner starting with adamantane (**1**). The key steps involve functionalization, ring closures by diazo ketone-derived carbene insertions (**7** → **8** and **23** → **24** + **25**), and rearrangement to give the diamantane skeleton (**13, 14** → **2**). This method is general, and could in principle be used to elaborate any lower diamondoid hydrocarbon to a higher one.

Polycycloalkanes with diamond lattice structure generally possess ultimate thermodynamic stabilities.[2] Consequently, Lewis acid catalyzed carbocationic isomerizations provide remarkably successful syntheses of many molecules of this type,[2] e.g., adamantane (**1**),[3] diamantane (**2**),[4] and, in lower yield, triamantane (**3**).[5]



1 2 3

However, an attempt to prepare a tetramantane by this route failed; instead, isomerization of a $C_{22}H_{28}$ precursor led to "bastardane", a compound with an irregular rather than a diamondoid structure.[6] This result demonstrates that thermodynamic control cannot always be realized, owing evidently to high barriers for certain of the rearrangement steps when the dihedral angles are unfavorable[7] or to the required involvement of high-energy intermediates.

A viable synthetic alternative might be to elaborate a more readily available lower diamondoid hydrocarbon (e.g., adamantane, **1**) to a higher one (e.g., diamantane, **2**) by adding four new carbons and two new rings. We have developed such a general procedure which should permit the synthesis of unknown higher polyamantanes.[8]

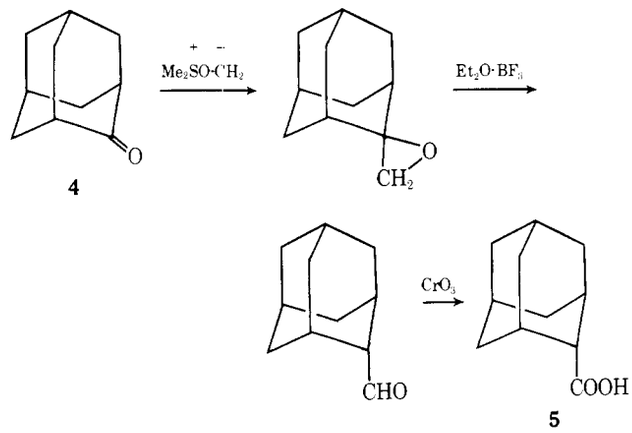
Synthetic Design and Results

Our objective was to convert adamantane (**1**) to diamantane (**2**) in a stepwise manner. The first part of the synthesis [ac-

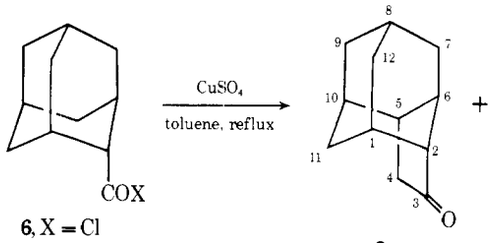
tually starting from adamantanone[9] (4)] was reported in preliminary form in connection with the study of the corresponding hydrocarbon, ethanoadamantane (tetracyclo-[6.3.1.$0^{2,6}$.$0^{5,10}$]dodecane).[10] We give here the pertinent details.

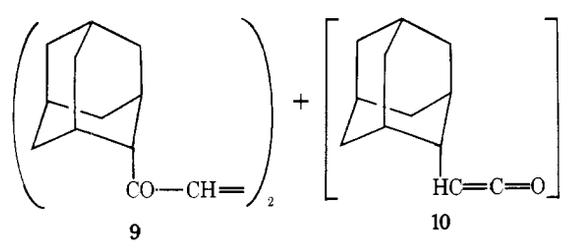
After development of a simple method which produced 2-adamantanecarboxylic acid (5) (Chart I),[11] the corresponding acid chloride (6) and diazo ketone (7) could be prepared easily on a reasonably large scale. However, the ketocarbene insertion[12] performed as described[12b] gave less than 10% yield of tetracyclo[6.3.1.$0^{2,6}$.$0^{5,10}$]dodecan-3-one (8). The main product (42%) was the enedione (9) formed by the dimerization of the ketocarbene (or more probably of its complex with the metal ions[13]). The yield of 8 was increased to over 55% (based on the acid chloride, 6) by using a high-dilution apparatus designed for thermally unstable reactants.[14] At the same time the yield of 9 dropped to 1–2% (the balance appeared to consist of oligomers of ketene 10).[15]

Chart I



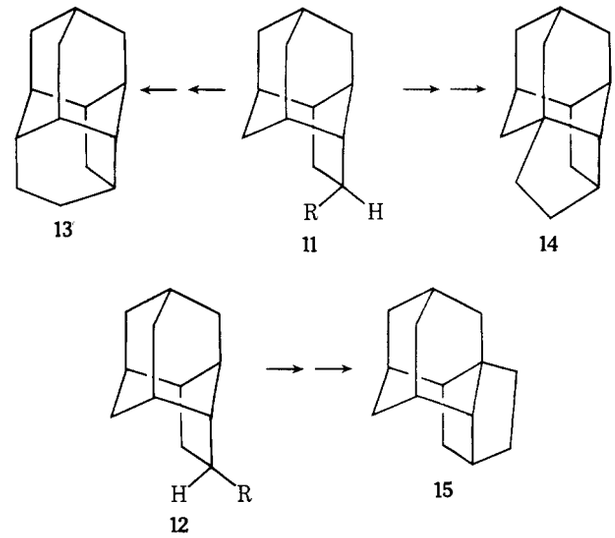
4 5





9 10

Continuing from the tetracyclic ketone 8, the synthetic sequence needs to be repeated, the second bridge being anchored in the place of the carbonyl group. The product of such a synthesis must have a nondiamondoid structure, but we expected that an acid-catalyzed rearrangement would correct this defect easily and cleanly. The new carbon chain should be introduced in the endo (11) rather than in the exo configuration (12) (exo and endo isomers are defined as indicated in ref 28b). If the last two-carbon bridge was built from 11, 13 or 14 should result, while the same operation starting with 12 would lead to 15. Both 13 and 14 should be convertible to diamantane (2) by simpler rearrangement processes (fewer steps and less strained intermediates) than 15. Structure 13 is especially appealing, since it represents a "protodiamantane",[16] just one Wagner–Meerwein shift away from 2.



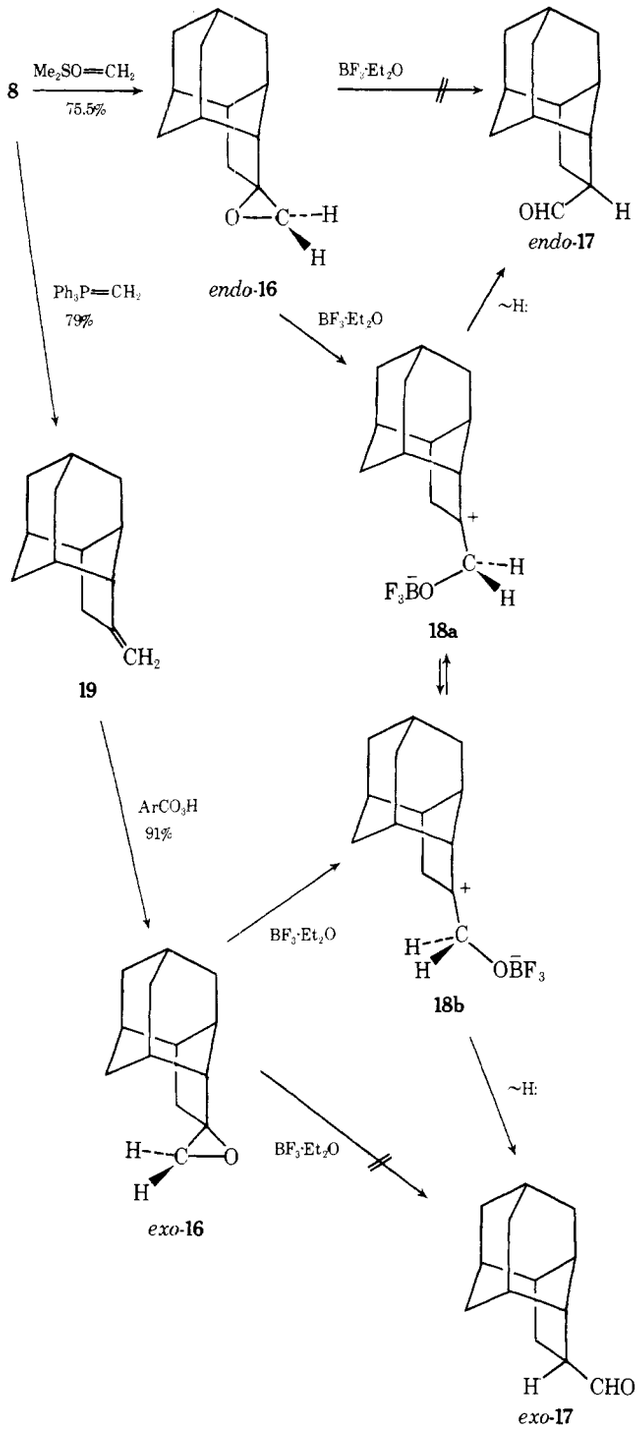
13 11 14 12 15

Examination of molecular models indicated the endo side of the two-carbon bridge in 8 to be shielded by a hydrogen atom at C-11. A reactant can be expected to attack this ketone from the exo side. Therefore, the synthesis had to achieve the introduction of an endo substituent by exo attack. We hoped at first to achieve this goal by a duplication of the sequence shown in Chart I. The reaction of 8 with dimethylsulfoxonium methylide[11,17] was expected to give predominantly the *endo*-3-(epoxymethylene)ethanoadamantane (*endo*-16) (Chart II). There are literature examples of the formation of carbonyl compounds from epoxides in which a 1,2 shift is concerted (or nearly so) with the ring opening.[18] If this were the case, isomerization of *endo*-16 should lead to the aldehyde *endo*-17. The same result would be achieved via the carbocation 18 if the carbon–carbon bond rotation in the latter (18a $\rightleftarrows$ 18b) is much slower than the hydride shift.

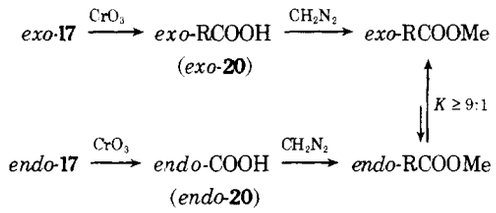
The first assumption (stereoselectivity of attack at C-3 of 8) was tested by preparing the two stereoisomeric epoxides 16. The epoxide obtained by the reaction of 8 with dimethylsulfoxonium methylide exhibited an AB pattern in the NMR spectrum ($\Delta\ \delta$ 0.07 ppm, J = 5 Hz) centered at 2.62 ppm, for the CH_2O group, and was assigned the endo configuration (*endo*-16, Chart II). On the other hand, 3-methyleneethanoadamantane (19), prepared[19] from 8 by a Wittig reaction, gave on Prilezhayev (peracid) oxidation[20] an epoxide which showed a sharp singlet at δ 2.68 ppm for the $-CH_2O-$ group in the NMR spectrum, and was assigned the exo configuration (*exo*-16, Chart II). No mutual contamination was detected in either case.

However, on treatment with boron trifluoride etherate[11,21] both epoxides gave aldehyde mixtures, exhibiting two aldehyde proton signals at δ 9.56 and 9.58. These were assigned to *exo*- and *endo*-17, rather than to a splitting due to H–H coupling (no coupling was seen, for instance, in the spectrum of 2-adamantanecarboxaldehyde[11]). The peaks had similar intensity, but the chemical shifts were too close to allow accurate integration. Therefore, the mixture was oxidized[11] and the resulting acids were esterified with diazomethane. The signals for the carbomethoxy groups (δ 3.60 and 3.63 ppm) were sharp, and integrated for 1.2 and 1.8 protons, respectively (2:3 molar ratio of isomers). The same ratio was found for the esters originating from *exo*-16, as for the esters originating from *endo*-16. (Since the aldehyde mixtures from *exo*- and *endo*-16 also exhibited identical NMR spectra, it was concluded that

Chart II



no epimerization took place during chromic acid oxidation of the aldehydes.) The 2:3 ratio did not represent an equilibrium mixture, since boiling the esters with 0.08 M methanolic sodium methoxide for 90 h changed the peak intensity ratio to ca. 9:1 (it was not established if final equilibrium was reached). Therefore, the downfield methoxy peak was assigned to the endo (least stable) isomer.



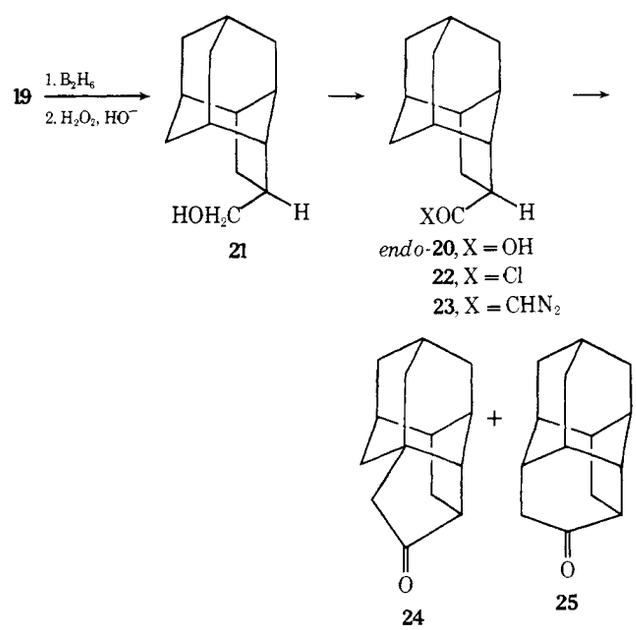
The epimerization by BF_3 of the aldehydes *after* their formation is unlikely, because identical mixtures (by NMR) were obtained from *endo*-**16** with an epoxide to BF_3 ratio of 1.35 or 1.75. Thus the 2:3 ratio, favoring the less stable isomer, should be kinetically controlled and reflect the ratio of hydride shift taking place in conformation **18a** and **18b**, respectively (Chart II).

The shielding of the endo side in the ethanoadamantane system was also indicated by the large difference in the rates of air oxidation of *exo*- and *endo*-**17**. On standing (neat or in carbon tetrachloride solution) only exo acid was formed and could be isolated in pure (NMR) form from the mixture. While this reaction could in principle be used to separate the two isomers, it was of no use to us, since for our synthetic plan the exo acid was merely lost material.

The above observation of stereoselective attack on the double bond of **19** was used in the synthesis of the endo alcohol **21** by hydroboration–oxidation.[22] Subsequent treatment of **21** with chromic acid gave virtually pure *endo*-**20**, in 60% yield based on olefin **19**. (The NMR spectrum of the methyl ester indicated that about 0.5% exo isomer might be present.)

Duplication of the reaction sequence used for the synthesis of **8**, starting from *endo*-**20**, led to a mixture of ketones **24** and **25** (separated from other products and from each other by column chromatography) in ca. 3:1 ratio. As in other cases,[12c,23] the five-membered ring ketone **24** ($\nu_{C=O}$ 1750 cm^{-1}), albeit more strained, was favored over the six-membered ring isomer **25** ($\nu_{C=O}$ 1715 cm^{-1}) (Chart III). The yield of the last

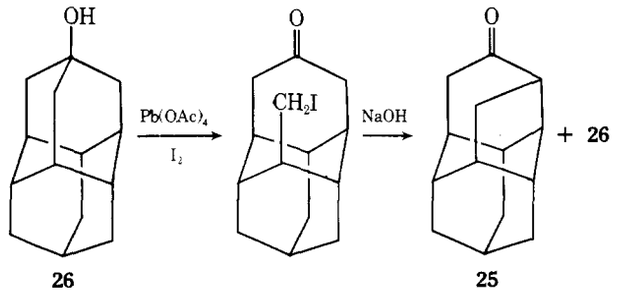
Chart III



step was unexpectedly low (20–25%, based on the acid chloride **22**), although competitive dimerization of the ketocarbene was minimized by use of the high-dilution technique.[14] (The ir spectrum of the crude reaction mixture exhibited a very weak peak at 1670 cm^{-1} which can be attributed to the enedione dimer, based on analogy with **9**.) Possibly, the larger part of the product consisted of oligomers of the ketene formed by Wolff rearrangement. Also, some four-membered ring insertion product[24] could not be ruled out, since a peak at a 1780 cm^{-1} was also seen in the ir spectrum of the reaction mixture. Variations of the catalyst[25] and the reaction conditions[25b] might possibly increase the yield of **24** and **25** significantly.

In order to secure these structural assignments, protodiamantanone **25** was synthesized independently. Treatment of 4-diamantanol (**26**)[26] with lead tetracetate and iodine, then

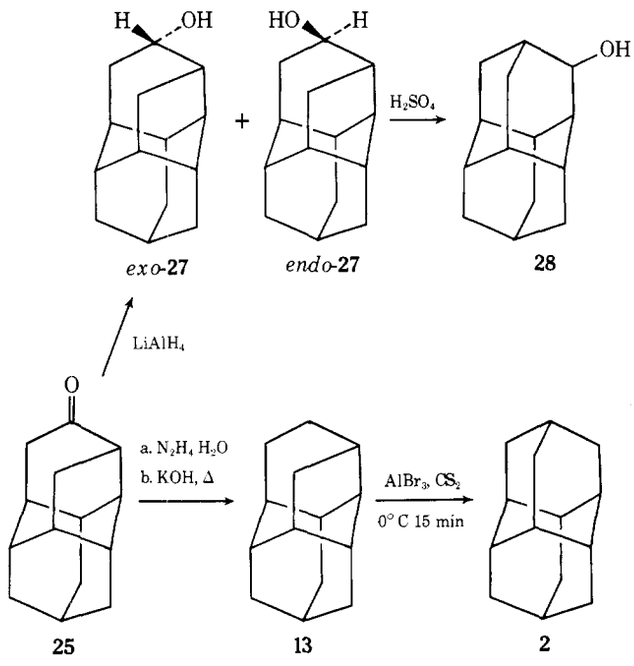
with base,[27] gave a ketone identical with the second product of ketocarbene insertion:



26 25

As expected, rearrangement of the protodiamantane to the diamantane skeleton was very easy.[28] Thus, lithium aluminum hydride reduction of **25** produced a mixture of two alcohols (*exo*- and *endo*-**27**), which were converted to 3-diamantanol (**28**)[26] by dilute sulfuric acid at room temperature with unequal speed, but in very high yield. On the other hand, Wolff–Kishner reduction of **25** led to protodiamantane (**13**), quantitatively converted to diamantane (**2**) by aluminum bromide at 0 °C (Chart IV).

Chart IV

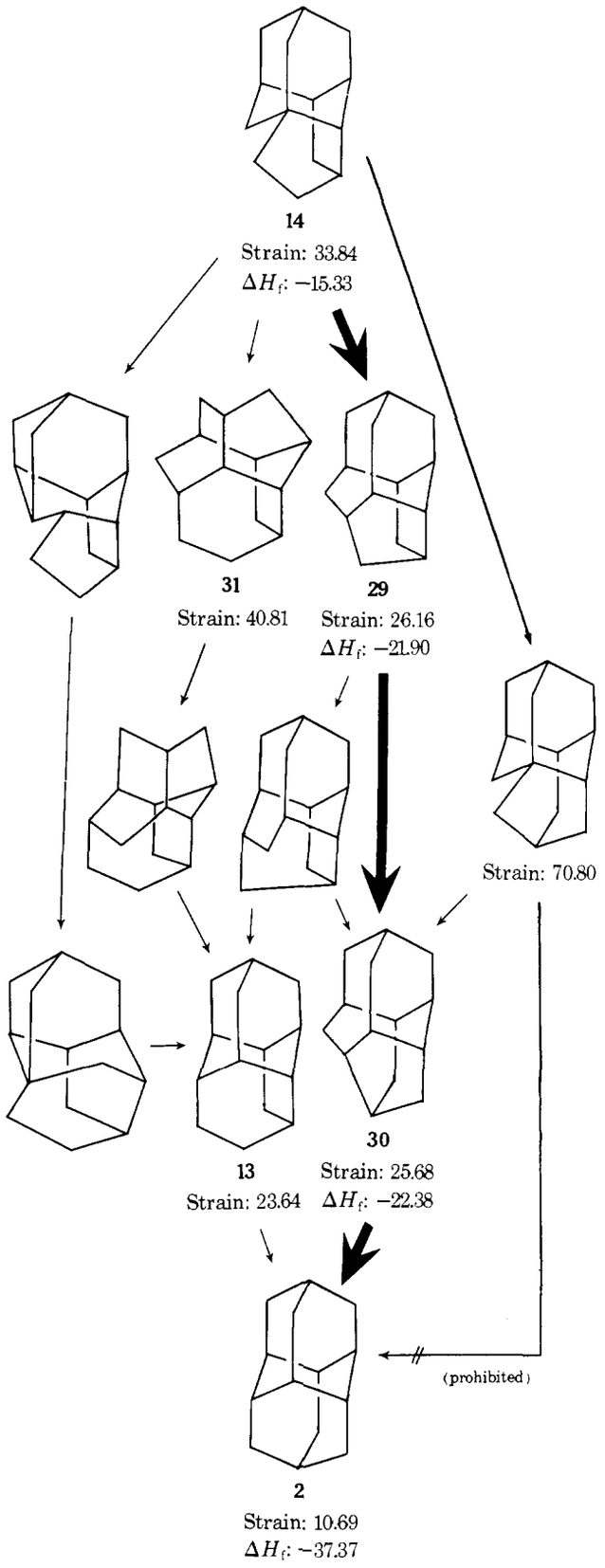


The conversion to diamantane of the hydrocarbon **14**, corresponding to the ketone **24**, might be expected to be less smooth. **14** contains a tetrasubstituted carbon[4b] and therefore is relatively strained. This might result in an increased tendency toward fragmentation and disproportionation[10] on treatment with isomerization catalysts. However, an examination of the portion of the $C_{14}H_{20}$ rearrangement graph[4b] which contains **14** and **2** has shown that there is at least one path (**14** → **29** → **30** → **2**) for which each step is exothermic and no shift is difficult on stereoelectronic grounds (Chart V).[29]

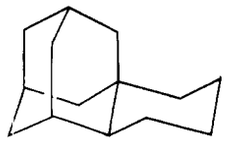
Indeed, treatment of **14** with aluminum bromide in boiling cyclohexane led to over 95% diamantane (**2**) (by GLC) with a mere trace of the disproportionation product, **32**.[19] The isolated yield was only 60%, but the small quantities used probably resulted in manipulation losses. The same reaction in carbon disulfide at reflux was slow and gave a less pure product, with a ratio **2**:**32** of about 19:1.

In conclusion, the successful completion of the synthesis of diamantane (**2**) from adamantane (**1**) has demonstrated the feasibility of the stepwise building of a diamondoid skeleton. The synthetic scheme used for **2** should be applicable to higher members of the series (e.g., **3**, or tetramantane). The regioselectivity in construction of a bridge (as shown by **13** + **14**

Chart V. Partial Representation of the $C_{14}H_{20}$ Rearrangement Graph[a]



[a] Strain energies and heats of formation[29] are given in kcal/mol.



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vs. 15) based on the stereoselectivity in introducing a substituent (*endo*-**20** vs. *exo*-**20**) has been used subsequently for the synthesis of the three isomeric ethanonoradamantanes.[30]

Experimental Section

General. Melting points (Mettler FPI apparatus) are uncorrected. Elemental analyses were performed by Hoffmann-La Roche, Inc. The NMR spectra were taken at 60 MHz (Varian A-60A instrument). Mass spectra were determined at 70 eV (AEI-MS9 instrument).

2-Adamantanecarboxylic Acid Chloride (6).[31] The acid[11] (24 g, 0.133 mol) was treated with thionyl chloride (50 ml) for 3 h at room temperature and for 7 h at 95–100 °C. Evaporation of the excess reactant and distillation of the residue gave **6** (25.6 g, 96% yield) as a colorless liquid, bp 99–100 °C (0.9 mm).

2-Adamantyl Diazomethyl Ketone (7). An alcohol-free solution of diazomethane in ether, prepared[32] from 119 g of Diazald (Aldrich), was dried on two portions of potassium hydroxide pellets (1 h each), then over sodium (2 h) at 0 °C. To this solution, vigorously stirred at −5 °C and protected from moisture, a solution of 9.18 g (46 mmol) of **6** in 100 ml of anhydrous ether (containing 5 drops of thionyl chloride) was added during 1 h. The solution was stirred for another 2 h at 0–3 °C, then left at room temperature overnight. Filtration through glass wool and evaporation of solvent left a shiny yellow solid which was used directly in the next step.

3-Ethanoadamantanone (8). Anhydrous copper sulfate (38 g, 238 mmol) was suspended in dry toluene (750 ml) in a 3-l. three-necked flask and refluxed for 12 h using a Dean-Stark trap to remove the last traces of water. The high dilution installation[14] was then mounted on the flask and a solution of **7** (from 9.18 g, 46 mmol, of acid chloride) in 1100 ml of toluene was added from a cooled (below 0 °C) dropping funnel into the mixing chamber[14] maintained at 0 °C. Drying tubes were placed at the top of the reflux condenser and dropping funnel. The rate of dropping was adjusted to maintain a dilution ratio of 10–15; addition took 16 h. The copper tubing[14] was cooled by an air stream; vigorous stirring was maintained at all times. The mixture was refluxed for another 8 h, then cooled and filtered. The filtrate was extracted once with water, twice with 10% sodium hydroxide solution (50 ml each), then twice with water. (On acidification of the basic washings very little acid precipitated, and this was not investigated further.) The dried (Na_2SO_4) organic solution was concentrated under vacuum and the part of the residue which was soluble both in methanol and in pentane was chromatographed on silica gel (600 g). Elution sequentially with hexane (700 ml), hexane–benzene mixtures (750 ml), and then with benzene produced a number of fractions with $\nu_{C=O}$ 1700–1810 cm^{-1}, then virtually pure **15** (mp 178–182 °C) (4.56 g, 56% yield). For analysis **8** was sublimed at 110 °C (12–14 mm) (mp 184–185 °C); NMR and ir spectra have been published.[10]

Anal. Calcd for $C_{12}H_{16}O$: C, 81.76; H, 9.15. Found: C, 81.70; H, 9.20.

1,2-Bis(2-adamantylcarbonyl)ethylene (9). The diazo ketone (**7**) prepared from 7.5 g (37.7 mmol) of acid chloride, dissolved in 250 ml of cyclohexane, was added to the stirred suspension of 4 g (26 mmol) of anhydrous copper sulfate in 500 ml of boiling cyclohexane during 5 h. After cooling, filtering, and washing as above, the material *in*soluble both in methanol and pentane was collected (2.83 g, 42% yield), mp 220.3–222.6 °C dec (from benzene). For analysis **9** was sublimed at 175–180 °C (0.15 mm): ir (KBr disk) 3024, 1670, 1640 cm^{-1} (vw); NMR ($CDCl_3$) δ 1.79 and 1.94 (two broad, overlapping signals, 24 H), 2.42 (broad, 4 H), 2.80 (broad, 2 H), and 7.22 ppm (s, 2 H); M *m/e* 352 (mass spectrometry).

Anal. Calcd for $C_{24}H_{32}O_2$: C, 81.76; H, 9.15. Found: C, 81.82; H, 9.36.

***endo*-3-(Epoxymethylene)ethanoadamantane (*endo*-16).** Treatment of **8** (1.34 g, 7.5 mmol) with dimethylsulfoxonium methylide[17] (from 9.55 mmol of trimethylsulfoxonium iodide and 9.25 mmol of 41% sodium hydride) as described[11] gave a mixture of *endo*-**16** and starting material (by ir). Repetition of the treatment for 1 h at room temperature and 4 h at 50–55 °C gave an almost complete conversion into epoxide (liquid, 1.075 g, 75% yield): ir 3030 cm^{-1} (neat); NMR (CCl_4) δ 0.71–2.38 (complex, 16 H) and 2.62 ppm (2 H, AB system, Δδ 0.07 ppm, J = 5 Hz).

***exo*-3-(Epoxymethylene)ethanoadamantane (*exo*-16).** To the alkene (**19**)[19] (0.8 g, 4.6 mmol) dissolved in methylene chloride (5 ml), *m*-chloroperbenzoic acid (1.15 g, 85% peracid, 5.65 mmol) in methylene chloride (12 ml) was added over a period of 30 min at 15 °C, with stirring. The mixture was stirred for 5 more h at 25 °C and extracted twice with aqueous sodium sulfite, then once with sodium carbonate solution. After drying ($MgSO_4$), evaporation of the solvent left 0.8 g (91%) of *exo*-**16**, as a solid: ir (CS_2) 3022 cm^{-1}, NMR (CCl_4) 1.05–2.35 (complex, 16 H) and 2.68 ppm (2 H, s).

***exo*- and *endo*-Ethanoadamantane-3-carboxaldehyde (17).** Treatment of either *exo*- or *endo*-**16** with 0.56, 0.74 (for *endo*-**16**), or 1.01 equiv (for *exo*-**16**) of boron trifluoride etherate as described[11] led to the same mixture of aldehydes (liquid): ir (neat) 1722 cm^{-1}; NMR (CCl_4) 9.56 and 9.58 ppm (CHO), and an envelope between 1.1 and 3.0 ppm, with a strong band centered at 1.80 ppm. The ir spectrum indicated the presence of some carboxylic acid, by the bands at 3600–2500 and 1696 cm^{-1} (weak, growing in time), which disappeared after washing with base, then reappeared on longer standing.

***exo*-Ethanoadamantane-3-carboxylic Acid (*exo*-20).** The aldehyde mixture (*exo*- + *endo*-**17**) prepared from 1.07 g of *endo*-**16** was left for 24 h at room temperature, then diluted with ether and extracted with aqueous sodium carbonate. Acidification of the aqueous layer, extraction with chloroform, drying (Na_2SO_4), and evaporation of solvent gave 0.199 g (17%) of *exo*-**20**: mp 119.3–121.0 °C (from aqueous methanol); NMR (CCl_4) complex absorption between 1.25 and 2.87 ppm (17 H) with a strong peak at 1.76 ppm; also 11.9 ppm (1 H, COOH).

Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.72; H, 8.90.

***exo*- and *endo*-Ethanoadamantane-3-carboxylic Acids (*exo*- and *endo*-20), and Methyl Esters.** Oxidation of the mixture of *exo*- and *endo*-**17**, obtained from *exo*- or *endo*-**16**, with chromic acid as described[11] gave a mixture of acids (melting over a range of temperature) in 65–75% yield based on the epoxide. The NMR spectrum of the product can be accounted for as a mixture of *exo*- and *endo*-**20**. Treatment with an excess of diazomethane in ether solution gave the methyl esters in quantitative yield. (In the NMR spectrum the carboxyl proton was replaced by two carbomethoxy signals at δ 3.60 and 3.63, integrating for ca. 1.2 H and 1.8 H, respectively.)

Methyl Ester of *exo*-Ethanoadamantane-3-carboxylic Acid (*exo*-20 Methyl Ester) by Epimerization. The mixture of esters prepared above (0.12 g) was boiled under reflux with a solution of sodium methoxide (from 0.03 g of sodium and 15 ml of anhydrous methanol) for 90 h. Neutralization with acetic acid followed by evaporation of solvent under vacuum with addition of benzene to ensure the complete removal of methanol gave a slightly yellow liquid: NMR δ 3.60 (ca. 2.85 H), 3.63 ppm (ca. 0.15 H). The remainder of the spectrum was almost identical with that of *exo*-**20** obtained from the air oxidation of the aldehyde.

An attempt to epimerize the acids directly by heating with 7.5 N aqueous potassium hydroxide[33] (5 ml for 0.103 g of acid) on an oil bath of 130 °C for 69 h was unsuccessful (no significant change of the NMR spectrum of the acid was noticed).

***endo*-3-(Hydroxymethyl)ethanoadamantane (21).** To a solution of 6.1 g (35 mmol) of **19** (obtained from **8** in 79% yield[19]) in dry tetrahydrofuran (55 ml), water cooled and magnetically stirred under nitrogen, 39 ml of a 1 M diborane solution in THF was injected through a rubber septum during 25 min. The mixture was stirred for another 3.5 h at room temperature and for 0.5 h at 35 °C. Aqueous sodium hydroxide (3 N, 9 ml) was added slowly with water cooling, followed by 30% hydrogen peroxide (18 ml). The mixture was warmed to 50 °C and stirred for 3 h at this temperature, then at room temperature overnight. The THF was distilled off, solid sodium chloride was added, and the water solution was extracted five times with ether. Drying (Na_2SO_4) and evaporation of solvent gave an oil which solidified several days later: NMR ($CDCl_3$) δ 3.86 (2 H, d, J = 7 Hz, CH_2O), 2.60 (1 H, OH), 1.0–2.3 ppm (complex, 16 H). The material was used directly in the next step.

***endo*-Ethanoadamantanone-3-carboxylic Acid (*endo*-20).** To the crude alcohol (**21**) (prepared from 35 mmol of **19**) dissolved in acetone (65 ml), Jones reagent[11] (55 ml) was added during 1 h with stirring. Intermittent ice cooling maintained the temperature between 18 and 21 °C. The mixture was stirred for another 4.5 h at room temperature, rinsing the walls of the reaction flask with acetone (55 ml) occasionally; the mixture was then poured onto 300 ml of ice–water, and thoroughly extracted with chloroform. The residue from the chloroform solution was treated with 500 ml of 5% aqueous sodium hydroxide (in two portions) and the solid washed twice with water (100 ml each). The combined water solution was acidified (H_2SO_4), satu-

rated with KSO_4H, and extracted with chloroform (eight times). Evaporation of the dried (Na_2SO_4) chloroform solution gave 4.4 g of *endo*-**20** (60% yield based on **19**): mp 148.8–151.0 °C (from aqueous methanol); NMR (CCl_4) complex absorption between δ 1.1 and 3.3 ppm (17 H) with sharp peaks at 1.85 (very strong) and 2.07, and a much weaker one at 1.77 ppm; also 11.43 ppm (1 H, COOH).

Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.70; H, 8.76.

The methyl ester, obtained with diazomethane, exhibited a carbomethoxy peak at δ 3.63 ppm with a mere trace (perhaps 0.5%) of the δ 3.60 ppm isomer (*exo*-**20**).

***endo*-3-Ethanoadamantanecarboxylic acid chloride (22)** was prepared as described for **6**, from 4.3 g (20.86 mmol) of *endo*-**20**, yield 90% (4.21 g), bp 139–140 °C (0.9 mm).

Pentacyclo[5.5.1.1^{1,5}.0^{3,8}.0^{10,13}]tetradecan-11-one (24) and Pentacyclo[8.3.1.0^{2,8}.0^{4,13}.0^{7,12}]tetradecan-5-one (25). The acid chloride **22** (4.18 g, 18.7 mmol) was treated with diazomethane, as shown for **7**. The crude diazo ketone (**23**, yellow solid) was dissolved in 500 ml of toluene and added to a predried suspension of 21 g (131 mmol) of $CuSO_4$ in 350 ml of toluene, during 13 h, using the high-dilution apparatus.[14] After refluxing another 10 h, the reaction mixture was worked up as described for **8**; very little carboxylic acid and 0.4 g (ca. 10%) of material insoluble both in pentane and methanol were obtained as by-products. Column chromatography (250 g of silica gel, with benzene as eluent) of the fraction soluble in both pentane and methanol gave a sizable amount of (mostly oily) material, $\nu_{C=O}$ 1700–1810 cm^{-1}. Then, 0.585 g (15.5%) of **24** and 0.169 g (4.5%) of **25** were eluted in this order. (In another run, starting with a mixture of *exo*- and *endo*-**20** in a ratio of 2:3, a combined yield of 15% **24** and **25** was obtained, i.e., 25% based on the endo isomer.)

Pentacyclo[5.5.1.1^{1,5}.0^{3,8}.0^{10,13}]tetradecan-11-one (24): mp 118–121 °C (softening around 105 °C); ir (CCl_4) 2890, 1750 (vs), 1490, 1463, 1452, 1405, 1220, 1190, 1160, 1103, 1078, 1048 cm^{-1}; NMR (CCl_4) complex absorption between 1.10 and 2.55 ppm, with a strong peak at 1.84 ppm.

Anal. Calcd for $C_{14}H_{18}O$: M, 202.1358. Found: M, 202.1357 (by high-resolution mass spectrometry).

Pentacyclo[8.3.1.0^{2,8}.0^{4,13}.0^{7,12}]tetradecan-5-one (Protodiamantanone, 25): mp 113–116 °C (softening around 110 °C); ir (CCl_4) 2890, 1720 (vs), 1460, 1436, 1412, 1228 cm^{-1} (all weak); NMR (CCl_4) 1.50–2.08 (broad, 15 H) with a peak at 1.87 ppm, and 2.12–2.62 (broad, 3 H), with peaks at 2.22 and 2.53 ppm.

Anal. Calcd for $C_{14}H_{18}O$: M, 202.1358. Found: M, 202.1353.

Synthesis of Protodiamantanone (25) from 4-Diamantanol (26).[27] A mixture of 2.7 g (13.2 mmol) of **26** and 5.75 g (13.2 mmol) of lead tetraacetate in 100 ml of dry benzene, containing 3.5 g (13.2 mmol) of iodine, was heated to reflux for 2 h. The cooled mixture was filtered and the filter paper washed with 50 ml of ether. The combined ether solution was washed with two portions, 50 ml each, of 5% sodium bisulfite, then twice with 5% $NaCO_3H$, and finally with water. (GLC of the reaction mixture on a 3 m, 10% Carbowax 20M column at 190 °C indicated a 22% conversion of **26**.)

The entire mixture was refluxed with ethanol (50 ml) containing NaOH (1 g) for 3 h. The mixture was diluted with water and extracted twice with ether (100 ml each), then dried ($MgSO_4$) and concentrated. The residue, dissolved in cyclohexane (10 ml), was chromatographed on a neutral alumina (activity I) column, eluting with a 1:1 cyclohexane–ethyl acetate mixture. **25** was eluted first (0.51 g, 21% yield) and recrystallized from hexane to yield 0.48 g (19%, crude mp ca. 91 °C). A further purification by preparative GLC gave a material exhibiting identical spectral properties (ir, NMR) and GLC retention time with the product obtained from the diazo ketone **23**.

Reduction of 25 with Lithium Aluminum Hydride. To 400 mg (2 mmol) of **25** in 10 ml of ether, lithium aluminum hydride (0.2 g) was added and the mixture was refluxed for 2 h. The mixture was then hydrolyzed by the addition of water (10 ml) and 2 drops of HCl. The ether layer was extracted with 3 × 20 ml of water, dried ($MgSO_4$), and concentrated, yielding 380 mg (95%) of a mixture of endo and exo protodiamantanols (*endo*- and *exo*-**27**) in the ratio of 41:59 (mp 121–125 °C). A sample of this mixture isolated by GLC had the following spectral properties: ir (CCl_4) 3600, 3400, 2880, 1465, 1445, 1250 cm^{-1}; NMR (CCl_4) δ 4.0 (b, 0.4 H), 3.15 (b, 0.6 H), 2.1 (b, 1 H), 1.8 (m, 17 H), 1.3 (s, 1 H), 0.9 ppm (m, 1 H); mass spectrum *m/e* 204, 187, 186.

Anal. Calcd for $C_{14}H_{20}O$: C, 82.36; H, 9.87. Found: C, 82.12; H, 10.21.

Rearrangement of the Mixture of Protodiamantanols (27) with Sulfuric Acid. A mixture of 200 mg (0.00096 mol) of the protodiamantanols and 5% H_2SO_4 in 50% water–acetone solution was stirred for 2 h at room temperature. Analysis by GLC of the reaction products at 0.5-h intervals indicated that the initial products were disappearing and that diamantan-3-ol[26] was being formed. At the end of the reaction the mixture was diluted with water (10 ml) and the product extracted with ether (30 ml). The ether layer was washed with water (30 ml) and 5% Na_2CO_3 (20 ml), dried, and concentrated, yielding 190 mg of a crude product, which, when purified by GLC, had the same melting point and ir spectrum as diamantan-3-ol. (A second component of this mixture corresponded in retention time to the 59% component in the original protodiamantanol mixture and presumably[28] was the endo isomer.)

Preparation of Protodiamantane (13).[34] A solution of 180 mg (0.00089 mol) of **25** in 0.25 ml of 85% hydrazine hydrate, 2 drops of acetic acid, and 4 ml of glycerine was heated to between 80 and 90 °C for 24 h under an atmosphere of dry nitrogen. At the end of this period, 2 g of dry potassium hydroxide was added to the mixture and the solution was heated to 190 °C for 5 h under nitrogen. During this period, the protodiamantane sublimed on the Claisen head. The collected product was resublimed to give 140 mg (87%), mp 136–136.5 °C.

Anal. Calcd for $C_{18}H_{20}$: C, 89.29; H, 10.17. Found: C, 89.60; H, 10.36.

Rearrangement of Protodiamantane (13) with Aluminum Bromide. A solution containing 100 mg (0.53 mmol) of protodiamantane in 15 ml of carbon disulfide was stirred at 0 °C with 10 mg of freshly sublimed aluminum bromide. The rearrangement to diamantane was monitored by GLC (Carbowax 20M, 1.2 m, 130 °C). The formation of diamantane was complete within 15 min. No intermediates were revealed by GLC nor were any other final products observed.

Pentacyclo[5.5.1.1^{1,5}.0^{3,8}.0^{10,13}]tetradecane (14). Ketone **24** (0.4625 g, 2.29 mmol) dissolved in 30 ml of triethylene glycol containing 25 drops of acetic acid was treated with 3 ml of 97% hydrazine hydrate at 84–86 °C for 48 h under nitrogen. Solid potassium hydroxide (3.5 g) was added, the solution was heated to 195 °C in 1 h, then to 200 °C in another 0.5 h, and stirred at 200–205 °C for 6 h.

After cooling, the product was extracted with pentane; the pentane solution when dried (Na_2SO_4) and concentrated gave 0.43 g of solid, which was chromatographed on 26 g of silica gel (eluent pentane). **14** was obtained as a transparent solid (0.3355 g, 78%): mp 101–104 °C (from ethanol) after becoming a glassy mass at ca. 70 °C; NMR (CS_2) broad absorption from 1.00 to 2.22 ppm, with peaks at 1.17, 1.24, 1.71, and 1.90 ppm.

Anal. Calcd for $C_{14}H_{20}$: M, 188.1565. Found: M, 188.1576.

The chromatographed product was 95% pure; ethanoadamantane (ca. 5%) was a possible impurity.

Rearrangement of 14 with Aluminum Bromide. A solution of 0.048 g (0.25 mmol) of **14** in cyclohexane (0.5 ml) was stirred with 0.1995 g of aluminum bromide at 65 °C for 4 h and at 85 °C for 8 h, then left overnight at room temperature. The reaction mixture was extracted several times with boiling cyclohexane and the extract was neutralized (KOH). GLC of the solution showed complete conversion of **14** into **2**, with six other peaks, amounting to a fraction of a percent each. (Less than 1% of **32** was present.)

Evaporation of solvent gave 0.029 g of material: mp 234–237 °C (after pressing on a filter paper); NMR 1.75 ppm (s); MS *m/e* 189 (M + 1, 15.2), 188 (M, 100), 187 (16.0), 159 (6.4), 131 (7.5), 91 (10.2), 79 (7.4). The NMR and mass spectra verified the structure of the product **2**.[4a]

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Registry No.—**2**, 2292-79-7; **6**, 40079-92-3; **7**, 53803-41-1; **8**, 41171-93-1; **9**, 60526-50-3; **13**, 60526-51-4; **14**, 60526-52-5; *endo*-**16**, 60526-53-6; *exo*-**16**, 60562-35-8; *exo*-**17**, 60526-54-7; *endo*-**17**, 60562-36-9; **19**, 41171-89-5; *exo*-**20**, 60526-55-8; *exo*-**20** Me ester, 60526-56-9; *endo*-**20**, 60562-37-0; *endo*-**20** Me ester, 60562-38-1; *endo*-**21**, 60526-57-0; *endo*-**22**, 60526-58-1; *endo*-**23**, 60526-59-2; **24**, 60526-60-5; **25**, 60526-61-6; **26**, 30651-03-7; *exo*-**27**, 60526-62-7; *endo*-**27**, 60562-39-2; diazomethane, 334-88-3; dimethylsulfoxonium methylide, 5367-24-8; lithium aluminum hydride, 16853-85-3.

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Photochemistry of 17β-Hydroxyestra-5(10),9(11)-dien-3-one. Synthesis of AB Spiro Steroids[1,2]

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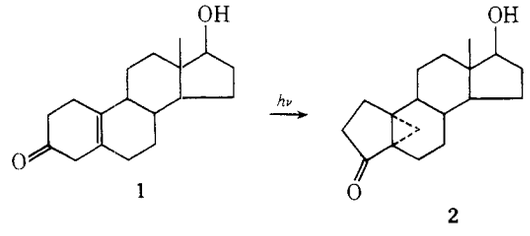
17β-Hydroxyestra-5(10),9(11)-dien-3-one (**3**) was photoisomerized via a 1,3 acyl shift to (10*S*)-17β-hydroxy-3,10-cyclo-3,4-seco-10α-estra-4,9(11)-dien-1-one (**4a**) whose structure was proven by x-ray analysis. Irradiation of **4a** caused photodecarbonylation to 2,10-cyclo-2,3-seco-*A*-norestra-3(5),9(11)-dien-17β-ol (**5a**) plus photoisomerization back to **3**. Acetone photosensitization of **3** did not yield any isolable photoproducts.

Several years ago the unusual spectroscopic properties of β,γ-unsaturated cyclic ketones caused us to investigate their photochemistry.[3-7] It was found that upon direct irradiation 17β-hydroxyestra-5(10)-en-3-one (**1**) afforded 17β-hydroxy-5α,19-cyclo-*A*-nor-10β-androstan-3-one (**2**) via a 1,2 acyl



1 2

shift.[5,6] Since direct irradiation of cyclic β,γ-unsaturated ketones usually afforded products resulting from 1,3 acyl shifts, rather than 1,2,[8] it was thought that the "semiplanar" A ring conformation[9] led to this unusual reaction pathway. To test this hypothesis 17β-hydroxyestra-5(10),9(11)-dien-3-one (**3**) was irradiated since **3** contains a similar "semiplanar" A-ring conformation[9] which is now part of a β,γ,δ,ε dienone chromophore.

Results and Discussion

Direct irradiation of **3** in benzene with a medium pressure mercury arc (Hanovia 450W) through a Pyrex filter gave two products plus recovered **3** (53%) which were separated by chromatography on alumina. The first photoproduct (**4a** 36%) was acetylated to aid in crystallization and yielded 17β-acetoxy-3,10-cyclo-3,4-seco-10α-estra-4,9(11)-dien-1-one (**4b**) on the basis of the following data. Elemental analysis of the acetate **4b** indicated that the alcohol **4a,** from which it was derived, was isomeric with **3.** The infrared spectrum of **4a** showed a hydroxyl band at 3610 cm^{-1}, and **4a** showed an ester carbonyl at 1725 cm^{-1}. Both spectra contained absorption