were placed in quartz photolysis tubes and purged with nitrogen. Tubes were then irradiated with a Hanovia 450-W high-pressure mercury lamp, using a "merry-go-round" apparatus to ensure equal amounts of light incident on each tube. Analysis was conducted by GC using aniline as internal standard for **2** and **7** (UCW column described above at 90°) and naphthalene as internal standard for **8** and **10** (UCW column described above, temperature-programmed run, 150–250°).

Acknowledgment. We thank the Research Corporation and the Faculty Research Fund of the University of Denver for support of this research.

Registry No.—**1**, 1074-06-2; **2**, 1462-92-6; **3**, 767-92-0; **5**, 76-09-5; **6**, 109-05-7; **7**, 22023-64-9; **8**, 700-91-4; **9**, 54276-78-7; **10**, 2211-66-7; *N*-propyl-2-aminopropane, 21968-17-2.

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Synthesis of 2-Substituted 8,9-Dehydroadamantanes[1]

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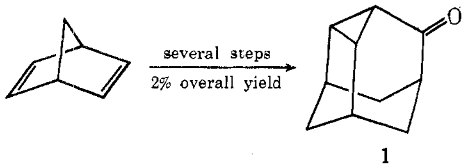
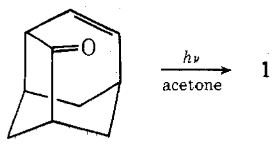
Acetone-sensitized photoisomerization of 2-protoadamantenone gives 8,9-dehydro-2-adamantanone (1). Several new 2-substituted 8,9-dehydroadamantanes have been prepared from 1. A general route for the introduction of alkyl substituents at the C-8 bridgehead of 1 has been devised and is illustrated by the synthesis of 8-methyl-8,9-dehydro-2-adamantanone.

In view of the considerable interest in the properties and chemistry of adamantane derivatives,[2] it is striking that 8,9-dehydro-2-adamantanone (**1**), a structurally rigid conjugated cyclopropyl ketone which contains a plane of symmetry and is potentially of significant synthetic utility, has received only modest attention.[3–8] It would appear that this has been the case because it simply has not been convenient to employ **1** in synthesis. The only reported preparation of **1** involves a multistep reaction sequence which converts norbornadiene to **1** in an overall yield of 2%.[3] We now wish to report (a) an alternative and improved procedure for the synthesis of **1**, (b) the preparation of several 2-substituted 8,9-dehydroadamantanes from **1**, and (c) a synthetic route for introducing alkyl substituents at C-8 of **1**.



1

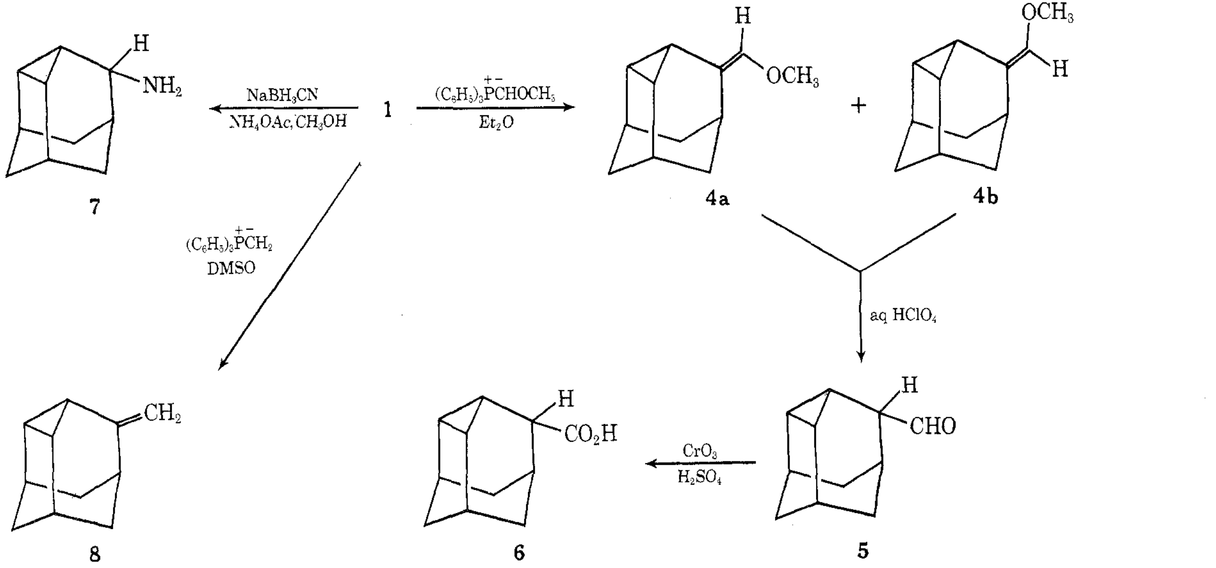
Results and Discussion



2

It is well established that the triplet-sensitized photorearrangement of a β,γ-unsaturated ketone can lead to a formal [1,2] shift of the acyl group and the formation of an isomeric conjugated cyclopropyl ketone (the oxa-di-π-methane photorearrangement).[9] Thus, by analogy, **1** should be accessible by the photoisomerization of 2-protoadamantenone (**2**). The availability of **2**[10] led us to examine its photochemistry. Irradiation of a nitrogen-purged 0.5% solution of **2** [λ_{max}(EtOH) 296 nm (ϵ 230)] in acetone through a Pyrex filter with a Hanovia L 450-W lamp proceeds smoothly to give **1**.[11] Under these conditions **1** [λ_{max}(EtOH) 277 nm (ϵ 40)] undergoes slow photodecomposition, but this reaction does not effectively compete with the photo-

Scheme I

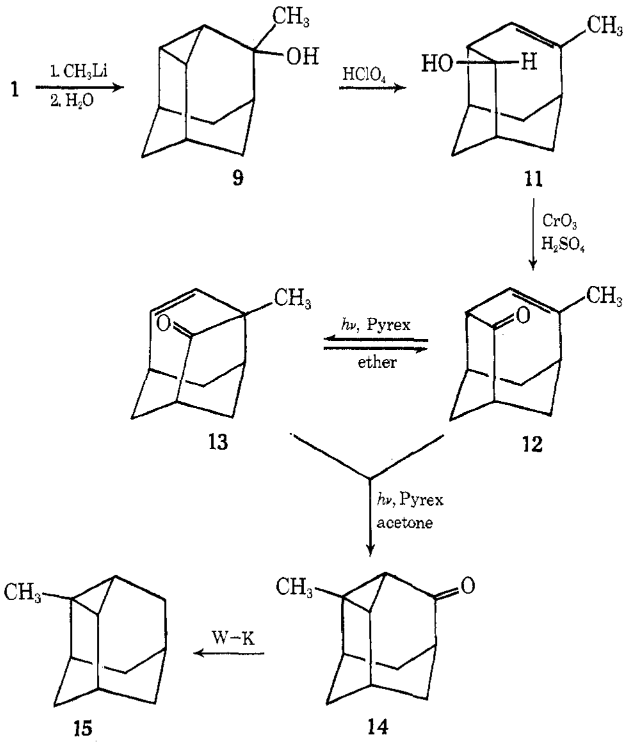


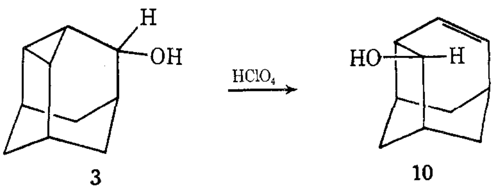
isomerization of **2** to **1**. Thus, irradiation of **2** to 80% conversion affords **1** in ca. 70% yield.

The only 2-substituted 8,9-dehydroadamantanes which have been reported are ketone **1**, 8,9-dehydro-2-adamantanol (**3**), and some derivatives prepared from **3**.[3,6] Routes to several new 2-substituted 8,9-dehydroadamantanes are summarized in Scheme I. Reaction of **1** with methoxymethylenetriphenylphosphorane[12] affords a 55:45 mixture of **4a**:**4b**. The isomer assignments follow from the relative ^1H NMR chemical shifts of the $CH(OCH_3)$ protons. Reichardt et al. have prepared a series of 1-cycloalkyl-2-alkoxyethylenes and have found that the ^1H NMR chemical shifts of the $CH(OCH_3)$ proton in the Z isomers consistently appear upfield relative to the corresponding proton in the E isomers.[13] Treatment of the mixture of enol ethers with aqueous perchloric acid gives 8,9-dehydro-2-adamantanecarboxaldehyde (**5**), which can be oxidized with Jones reagent to provide 8,9-dehydro-2-adamantanecarboxylic acid (**6**). By this sequence of reactions, **6** was prepared from **1** in an overall yield of 20%.[14] 2-Amino-8,9-dehydroadamantane (**7**) is readily obtained from **1** by the reductive amination procedure of Borch et al.[15] Treatment of **1** with sodium cyanohydridoborate and ammonium acetate in methanol affords amine **7** in ca. 40% yield. 2-Methylene-8,9-dehydroadamantane (**8**) can be prepared from **1** by Corey's modification[16] of the Wittig reaction.[17] The structures of **4**–**8** follow from their spectral and analytical properties (see Experimental Section) and their mode of formation.

It has previously been recognized that adamantanes, owing to their rigid skeletons and undistorted chair conformations, offer ideal models to investigate the influence of substituents on chemical shifts.[18] As is apparent from Table I, the CHX protons of 2-substituted 8,9-dehydroadamantanes consistently appear ca. 0.2–0.4 ppm downfield from the corresponding protons of 2-substituted adamantanes. As might be expected, this influence is diminished as the sensor group is moved farther from the cyclopropyl moiety. Thus, in 2-methyl-8,9-dehydro-2-adamantanol (**9**), which is readily prepared by treatment of **1** with methyllithium, the methyl protons appear at δ 1.41, whereas the chemical shift of the methyl protons in 2-methyl-2-adamantanol is δ 1.31.[18a]

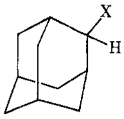
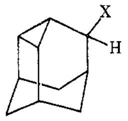
Scheme II





Although 2,4-dehydroadamantane[19] and ketone **1** have been known for some time, no *bridgehead substituted* 2,4-dehydroadamantanes have been reported. In view of the successful photoisomerization of **2** to **1**, 8-substituted 8,9-dehydro-2-adamantanones should be accessible if substituents can be introduced at the 3 or 5 positions of **2**. A general route for preparing 5-alkyl-substituted 2-protoadamantenones is summarized in Scheme II. Recently, we have shown that treating alcohol **3** with dilute perchloric acid in refluxing 80% aqueous acetone affords 2-*exo*-protoadamantenol (**10**).[6] Similar treatment of methyl alcohol **9** gives 5-methyl-2-*exo*-protoadamantenol (**11**), which can be oxidized with Jones reagent to the corresponding ketone (**12**). Since the organic alkyllithium reagent that is employed in the initial step of this sequence can be varied considerably,

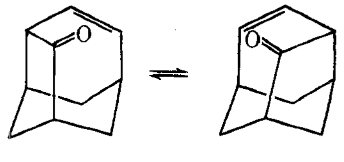
Table I
^{1}H NMR Chemical Shifts of C$\underline{H}$X in 2-Substituted Adamantanes and 2-Substituted 8,9-Dehydroadamantanes[a]

x		
CHO	2.40[b]	2.64[c]
CO_2H	2.69[d]	2.87[c]
NH_2	2.98[e]	3.18[c]
OCH_3	3.30[f]	3.67[g]
OH	3.75[e] 3.80[h]	4.15[i]
Cl	4.30[j] 4.39[e]	4.70[g]

[a] Chemical shifts are given in δ units relative to TMS. [b] J. Scharp, H. Wynberg, and J. Strating, *Recl. Trav. Chim. Pays-Bas*, **89**, 18 (1970). [c] Present report. [d] G. Snatzke and D. Marquarding, *Chem. Ber.*, **100**, 1710 (1967). [e] Reference 18b. [f] A. C. Udding, J. Strating, and H. Wynberg, *Tetrahedron Lett.*, 1345 (1968). [g] Reference 6. [h] Reference 18a. [i] Reference 3. [j] W. Hoek, J. Strating, and H. Wynberg, *Recl. Trav. Chim. Pays-Bas*, **85**, 1045 (1966).

this set of reactions offers a route for the preparation of a variety of 5-alkyl-substituted 2-protoadamantenones.

Several β,γ-unsaturated ketones are known to undergo a formal [1,3] shift of the acyl group to give isomeric β,γ-unsubstituted ketones on direct irradiation, whereas triplet-sensitized photolysis of these enones leads to a formal [1,2] shift of the acyl group and the formation of isomeric cyclopropyl ketones.[20] Such is the photochemical behavior of enone **12**. Irradiation of an ether solution of **12** through a Pyrex filter with a Hanovia L 450-W lamp produces an approximately 1:1 photoequilibrium mixture of **12** and 3-methyl-2-protoadamantenone (**13**).[21] Irradiation of **13** under identical conditions also affords a ca. 1:1 photostationary mixture of **12** and **13**. Of course, this aspect of the photochemistry of 2-protoadamantenones is not detected in **2**, as the analogous photoisomerization in **2** is degenerate.



Irradiation of an acetone solution of **12** through a Pyrex filter gives 8-methyl-8,9-dehydro-2-adamantanone (**14**) in ca. 65% yield. Enone **13** is also detected in the early stages of this photolysis, but **13** disappears on continued irradiation, and irradiation of the photostationary mixture of **12** and **13** under these conditions provides only **14**.[22] Treatment of **14** under the conditions of the normal Huang-Minlon modification of the Wolff–Kishner reduction[23] gives 2-methyl-2,4-dehydroadamantane (**15**).[24] Ketone **14** and hydrocarbon **15** thus provide the first reported examples of bridgehead substituted 2,4-dehydroadamantanes.

Experimental Section

All melting points were obtained in sealed capillary tubes using a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were obtained on Perkin-Elmer 180 or 337 spectrophotometers and proton magnetic resonance spectra were recorded with Varian A-60A or Perkin-Elmer R-12B 60-MHz spectrometers. Apparent splittings are given in all cases. 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 added standard (generally trichloroethylene) and are regarded as being accurate to ca. ±10%. Mass spectra were obtained on a CEC 21-110B instrument at an ionization potential of 70 eV. Ultraviolet spectra were determined on a Cary 14 spectrophotometer. Elemental analyses were performed by Micro-Analysis Inc., Wilmington, Del.

8,9-Dehydro-2-adamantanone (1). A nitrogen-purged solution of 294 mg of 2-protoadamantenone[10] (**2**) in 35 ml of acetone was irradiated through a Pyrex filter with a Hanovia L 450-W high-pressure mercury lamp. Monitoring the photolysis by GLC (5 ft × 0.25 in. FFAP column, 175°) showed a gradual disappearance of **2** and the appearance of a photoproduct of longer retention time. After irradiation for 24 hr, no starting material remained and only the photoisomer was present. Irradiation for considerably longer periods of time produced a small decrease in the concentration of the initial photoproduct and the formation of a trace of a photoproduct with a shorter GLC retention time. This latter reaction was not investigated further. Evaporation of the solvent at reduced pressure gave a yellow oil which was chromatographed on silica gel with benzene as eluent to give 206 mg of **1** (70% yield). The physical and spectral properties of **1** are in complete agreement with those previously reported for this compound.[3]

(*E*)- and (*Z*)-2-Methoxymethylene-8,9-dehydroadamantane (4a and 4b). Sodium-dried ether (100 ml) and methoxymethyltriphenylphosphonium chloride (1.568 g, 4.58 mmol) were added under nitrogen to a thoroughly dried flask.[12] The mixture was cooled in an ice bath and an equimolar quantity of *n*-butyllithium (2.0 ml of 21.8 wt % in hexane) was added with stirring. The resulting red solution was stirred for 15 min. To this solution was added **1** (243 mg, 1.64 mmol) and the reaction mixture was stirred overnight. Finally, zinc chloride (1 g) was added with vigorous stirring, and the resulting precipitate was filtered and washed with ether. The filtrate and ether washings were combined and the solvent was evaporated at reduced pressure to give an oil. Chromatography of this oil on silica gel with pentane as eluent provided 113 mg (39% yield) of a ca. 55:45 mixture (by ^{1}H NMR) of **4a** and **4b**, respectively. Purification of **4** by GLC (5 ft × 0.25 in. FFAP column, 135°) afforded a clear oil: $\delta_{TMS}(CDCl_3)$ 1.4–3.1 (br m, 12 H), 3.53 and 3.56 (each s, 3 H together, OCH_3), and 5.80 and 6.00 [each s, 1 H together, $CH(OCH_3)$ of **4b** and **4a**, respectively]; $\nu(CHCl_3)$ 3035, 3005, 2930, 2855, 1675, 1455, 1385, 1245, 1200, 1115, 1060, 1030, 985, and 860 cm^{-1}.

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 82.00; H, 9.08.

8,9-Dehydro-2-adamantanecarboxaldehyde (5). To 10 ml of ether was added 52 mg (0.3 mmol) of **4** and 1 ml of 35% perchloric acid.[12] The resulting solution was stirred at reflux for 1 hr and then poured into water (20 ml). Additional ether (75 ml) was added, the aqueous layer was separated, and the ether layer was washed with water (2 × 10 ml) and dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure provided 45 mg of an oil which by ^{1}H NMR analysis contained a ca. 35% yield of **5**. Purification of **5** by GLC (5 ft × 0.25 in. FFAP column, 150°) provided a clear oil: $\delta_{TMS}(CDCl_3)$ 1.1–2.5 (br m, 12 H), 2.64 (br m, 1 H, CHCHO), and 9.89 (s, 1 H, CHO); $\nu(CHCl_3)$ 3030, 2930, 2855, 2800, 2700, 1720, 1675, 1455, 1440, 1330, 1205, 1185, 1120, 1065, 1005, 945, 910, and 880 cm^{-1}.

8,9-Dehydro-2-adamantanecarboxylic Acid (6). To a solution of **5** (90 mg, 0.6 mmol) in acetone (20 ml) was added 700 µl of a freshly prepared solution of Jones reagent (2.8 g of chromic anhydride, 4.5 ml of sulfuric acid, and 12 ml of water). The reaction mixture was stirred at 0–5° for 3 hr, then quenched with water (40 ml) and extracted with ether (5 × 30 ml). The combined ether extracts were in turn extracted with 1 *N* sodium hydroxide (5 × 30 ml). The basic extracts were acidified to pH 2, saturated with sodium chloride, and extracted with ether (5 × 50 ml). The combined ether extracts were washed with water (2 × 20 ml) and dried over anhydrous magnesium sulfate. Evaporation of the ether gave **6** in ca. 60% yield by ^{1}H NMR analysis. Purification of **6** by GLC (5 ft × 0.25 in. FFAP column, 210°) afforded a waxy solid: $\delta_{TMS}(CDCl_3)$ 0.9–2.7 (br m, 12 H), 2.87 (br m, 1 H, CHCOOH), and 8.95 (br s, 1 H, COOH); $\nu(CHCl_3)$ 3500–2500 (br), 2940, 2860, 1705, 1410, 1235, 1165, 1110, 1105, 1060, 1035, 1020, 1005, and 865 cm^{-1}.

Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.93; H, 7.89.

2-Amino-8,9-dehydroadamantane (7). A solution of **1** (194 mg, 1.31 mmol), ammonium acetate (7.7 g, 0.1 mol), and sodium cyanohydridoborate (165 mg, 2.62 mmol) in 30 ml of freshly distilled methanol was stirred for 48 hr at 25° with 3 Å molecular sieves.[15] The residue was filtered and washed with methanol. Concentrated hydrochloric acid was added to the filtrate until pH <2, and the methanol was then evaporated at reduced pressure. The resulting residue was dissolved in water (20 ml) and extracted with ether (5 × 30 ml). The aqueous solution was then brought to pH >10 by the addition of solid potassium hydroxide, saturated with sodium chloride, and extracted with ether (5 × 30 ml). The combined ether extracts were washed with 5% aqueous sodium hydroxide (2 × 100 ml) and dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure provided an oil which by ^1H NMR analysis contained **7** in ca. 40% yield. Sublimation (25° at 0.5 mm) gave **7** as a white solid at −78° which became a clear oil at 25°: $\delta_{TMS}(CDCl_3)$ 1.0–2.5 (br m, 14 H) and 3.18 [br s, 1 H, $CH(NH_2)$]; $\nu(CHCl_3)$ 3450–3100 (br), 3040, 2940, 2860, 1575, 1460, 1335, 1080, 1055, 1040, 1010, 885, and 855 cm^{-1}.

The 3,5-dinitrobenzamide derivative of **7** was prepared by adding 115 mg (0.5 mmol) of 3,5-dinitrobenzoyl chloride to a solution of **7** (30 mg, 0.2 mmol) in 2.5 ml of pyridine. The mixture was refluxed for 1 hr and then quenched with water (40 ml). The aqueous solution was extracted with ether (5 × 25 ml). The combined ether extracts were dried over anhydrous magnesium sulfate and the solvent was exhaustively evaporated at reduced pressure. Two recrystallizations of the residue from chloroform–heptane gave an off-white solid: mp 203–204°; $\delta_{TMS}(CDCl_3)$ 1.1–2.5 (br m, 12 H), 4.60 [br d of t, J = 7 and 2.5 Hz, 1 H, CH(NHBz)], 6.80 (br d, J = 7 Hz, 1 H, NHBz), and 8.9–9.15 (br m, 3 H, aromatic protons).

Anal. calcd for $C_{17}H_{17}N_3O_5$: C, 59.47; H, 4.99; N, 12.24. Found: C, 59.41; H, 5.16; N, 12.39.

2-Methylene-8,9-dehydroadamantane (8). The mineral oil was removed from a sodium hydride mineral oil dispersion (478 mg, 20 mmol as sodium hydride) by washing with several portions of *n*-pentane. Dimethyl sulfoxide (DMSO) (4 ml) was introduced, and the mixture was heated with stirring under nitrogen at 90° until hydrogen evolution ceased (ca. 45 min).[16] The solution was cooled and methyltriphenylphosphonium bromide (3.9 g, 10.9 mmol) in DMSO (20 ml) was added. After stirring for ca. 10 min, **1** (303 mg, 2.0 mmol) was added and the stirred solution was heated at 55–60° for 10 hr. The solution was cooled and poured into 150 ml of water, and the aqueous portion was extracted with pentane (4 × 100 ml). The combined pentane extracts were washed with water (2 × 50 ml) and saturated sodium chloride solution (2 × 50 ml), and dried over anhydrous magnesium sulfate. Evaporation of the pentane provided a yellow oil which contained **8** in ca. 25% yield by ^1H NMR analysis. Column chromatography of the crude product on silica gel with pentane as eluent, followed by purification by GLC (5 ft × 0.25 in. FFAP column, 115°), gave **8** as a clear oil: $\delta_{TMS}(CDCl_3)$ 1.4–2.6 (br m, 12 H) and 4.67 (apparent s, 2 H, olefinic protons); ν (CCl_4) 3070, 3030, 2935, 2860, 1650, 1460, 1440, 1330, 1070, 1030, 895, and 865 cm^{-1}.

Anal. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.50; H, 9.49.

2-Methyl-8,9-dehydro-2-adamantanol (9). A solution of methyllithium (3.5 mmol) in ether was added at 0° to a solution of **1** (101 mg, 0.67 mmol) in 20 ml of anhydrous ether (freshly distilled from lithium aluminum hydride). Stirring was maintained for 1 hr at 0°, at which point 30 ml of water was carefully added. The reaction mixture was extracted with ether (3 × 30 ml) and the combined extracts were dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure provided a clear oil which contained **9** in quantitative yield by ^1H NMR analysis. Purification of **9** by sublimation (50° at 1 mm) or crystallization from pentane afforded a white solid: mp 72–80°; $\delta_{TMS}(CDCl_3)$ 1.41 (s, 3 H, CH_3) and 1.1–2.4 (br m, 12 H); ν (CCl_4) 3610, 3440 (br), 3035, 3000, 2940, 2865, 1440, 1370, 1330, 1115, 1045, 1030, 980, 920 and 890 cm^{-1}.

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.63; H, 9.57.

5-Methyl-2-*exo*-protoadamantenol (11). A solution of **9** (865 mg, 5.27 mmol) in 15 ml of 80% aqueous acetone which was 0.005 *M* in perchloric acid was stirred at ca. 70° for 16 hr. The solution was then saturated with sodium chloride and extracted with ether (4 × 50 ml) and the combined ether extracts were dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure gave an oil which by ^1H NMR analysis contained **11** in ca. 70% yield. GLC analysis (10 ft × 0.25 in. FFAP column, 190°) showed a single component to be present which was purified by GLC (identical conditions) to give **11** as a clear oil: $\delta_{TMS}(CDCl_3)$ 1.1–2.7 (br m, 13 H) which includes 1.68 (d, J = 1.5 Hz, 3 H, CH_3), 3.68 [br s, 1 H, CH(OH)], and 5.63 [br d, J = 5 Hz, 1 H, $(CH_3)C{=}CH$]; ν (CCl_4) 3630, 3350 (br), 3015, 2915, 1460, 1430, 1095, 1060, 1050, 1030, 1015, 1000, 970, 945, 920, 895, and 870 cm^{-1}.

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.18; H, 9.92.

5-Methyl-2-protoadamantenone (12). To a stirred solution of **11** (582 mg, 3.55 mmol) in 15 ml of acetone at 0° was added 2.2 ml of a freshly prepared solution of Jones reagent. The reaction mixture was stirred at 0° for 1 hr and then at room temperature for 2 hr, at which point the mixture was diluted with 5 ml of water and stirred for an additional 0.5 hr. The solution was saturated with sodium chloride and neutralized with a saturated solution of sodium bicarbonate. The resulting solution was extracted with ether (4 × 50 ml), the combined ether extracts were dried over anhydrous magnesium sulfate, and the solvent was evaporated at reduced pressure. ^1H NMR analysis of the residue indicated that **12** was obtained in ca. 90% yield. GLC analysis (5 ft × 0.25 in. FFAP column, 165°) showed a single component to be present and purification of **12** by GLC (identical conditions) gave a clear oil: $\delta_{TMS}(CDCl_3)$ 1.1–3.0 (br m, 13 H) which includes 1.77 (d, J = 1.5 Hz, 3 H, CH_3), and 5.62 [br d, J = 7 Hz, 1 H, $(CH_3)C{=}CH$]; ν (CCl_4) 3020, 2960, 2880, 1430, 1190, 1135, 1085, 1060, 1040, 895, and 860 cm^{-1}.

Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.56; H, 8.53.

3-Methyl-2-protoadamantenone (13). A solution of 158 mg of **12** in 25 ml of ether was irradiated through a Pyrex filter with a Hanovia L 450-W high-pressure mercury lamp. The reaction was monitored by GLC (5 ft × 0.25 in. FFAP column, 175°) at hourly increments for a total of 12 hr of irradiation. As the reaction proceeded, the starting material gradually decreased in concentration and concurrently a photoproduct appeared at a shorter retention time and increased in concentration until a photostationary state was reached after 10 hr of irradiation. Evaporation of the solvent at reduced pressure provided an oil, and ^1H NMR analysis of the residue showed that the reaction had proceeded with ca. 50% conversion of **12** to give **13** in nearly quantitative yield. Purification of **13** by GLC (above conditions) afforded a white solid: mp 117–119°; $\delta_{TMS}(CDCl_3)$ 1.27 (s, 3 H, CH_3), 1.4–2.7 (br m, 9 H), 5.57 [d, J = 8.8 Hz, 1 H, $(CH_3)CCH{=}CH$], and 6.42 [dd, J = 8.8 and 8.5 Hz, 1 H, $(CH_3)CCH{=}CH$]; ν (CCl_4) 3050, 2950, 2880, 1745, 1260, 1210, 1160, 1090, 1070, 1035, 970, and 875 cm^{-1}.

Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.38; H, 8.68.

The photoequilibrium of **12** and **13** was confirmed by irradiation (above conditions) of a solution of 10 mg of **13** in 1 ml of ether. Monitoring the reaction by GLC (above conditions) indicated that upon irradiation the concentration of **13** diminished and a photoproduct with a retention time identical with that of **12** appeared. The reaction reached a photostationary state after 4 hr irradiation, at which point the GLC trace of the photomixture was virtually identical with the GLC trace obtained after photoequilibrium was established beginning with pure **12**.

8-Methyl-8,9-dehydro-2-adamantanone (14). A solution of 141 mg of **12** in 30 ml of acetone was irradiated through a Pyrex filter with a Hanovia L 450-W high-pressure mercury lamp. Monitoring the photolysis by GLC (5 ft × 0.25 in. FFAP column, 175°) showed that after 3 hr irradiation the concentration of **12** had significantly decreased and a photoproduct with a longer retention time than **12** had appeared. A photoproduct with a shorter retention time than **12** was also detected and, following isolation by GLC, this compound proved to be **13**. After irradiation for 25 hr, GLC analysis indicated the presence of only the photoproduct of longest retention time. Evaporation of the solvent at reduced pressure followed by column chromatography of the residue on silica gel with benzene as eluent gave 93 mg (66% yield) of **14**. Final purification of **14** by GLC (above conditions) provided a clear oil: $\delta_{TMS}(CDCl_3)$ 1.33 (s, 3 H, CH_3) and 1.5–2.6 (br m, 11 H); ν (CCl_4) 3030, 2945, 2865, 1710, 1450, 1340, 1250, 1150, 1120, 1095, 1085, 1030, 985, 885, and 860 cm^{-1}.

Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.17; H, 8.70.

2-Methyl-2,4-dehydroadamantane (15). A solution of **14** (85 mg, 0.53 mmol), 400 mg of 95% hydrazine, and 500 mg of potassium hydroxide in 5 ml of diethylene glycol was stirred in an oil bath at 110°.[23] The temperature was raised over 0.5 hr to 180° and the reaction mixture was maintained at reflux (180°) for 3 hr. The reaction mixture was then cooled to room temperature and the contents of both the condenser and the pot were rinsed with cyclohexane (50 ml) and then water (30 ml). The combined aqueous rinses were saturated with sodium chloride and extracted with cyclohexane (2 × 25 ml). The combined cyclohexane rinses and extracts were dried over anhydrous magnesium sulfate and the solvent was evaporated at reduced pressure. GLC analysis (10 ft × 0.25 in. FFAP column, 100°) of the residue indicated a single hydrocarbon product, which was purified by GLC (above conditions) to give **15** as a clear oil: $\delta_{\mathrm{TMS}}(\mathrm{CDCl_3})$ 1.16 (s, 3 H, CH_3) and 0.8–2.3 (br m, 13 H); ν (CCl_4) 3020, 2990, 2875, 2850, 1455, 1340, 1160, 1140, 1105, 1055, 990, 965, and 945 cm^{-1}; MS *m/e* (rel intensity) 148 (100), 133 (60), 107 (36), 106 (71), 105 (50), 93 (52), 92 (52), 91 (73), and 79 (80).

Anal. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 88.96; H, 10.99.

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Registry No.—**1**, 10497-56-0; **2**, 28673-75-8; **4a**, 54003-44-0; **4b**, 54003-45-1; **5**, 54003-46-2; **6**, 54003-47-3; **7**, 54019-69-1; **7** 3,5-dinitrobenzamide derivative, 54003-48-4; **8**, 54003-49-5; **9**, 53075-01-7; **11**, 53075-02-8; **12**, 53075-00-6; **13**, 53075-04-0; **14**, 53075-03-9; **15**, 54003-50-8.

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(22) P. S. Engel and M. A. Schexnayder have previously reported [*J. Am. Chem. Soc.*, **94**, 9252 (1972)] an "unprecedented triplet 1,3-acyl shift" in the photochemistry of a β,γ-unsaturated ketone. It is not clear if a similar isomerization is occurring in the present study or if the formation of **13** from **12** with triplet sensitization simply results from some "leakage" to the excited singlet of **12** under the photolysis conditions employed.

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A Palladium-Catalyzed Conjugated Diene Synthesis from Vinylic Halides and Olefinic Compounds

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Conjugated dienes are obtained when vinylic bromides or iodides are treated with olefinic compounds in the presence of a trialkylamine and a catalytic amount of $Pd[P(C_6H_5)_3]_2(OAc)_2$ at 100–150°. In some instances, with the less substituted reactants, the initially formed dienes undergo subsequent Diels–Alder reactions. The new conjugated diene synthesis shows appreciable stereospecificity when (*Z*)- or (*E*)-vinylic halides are treated.

The palladium-catalyzed reaction of vinylic halides with olefinic compounds in the presence of a trialkylamine to form conjugated dienes has been noted previously,[1,2] but the scope of the reaction has not been investigated. We report herein an investigation of the reaction with a variety of vinylic halides and olefinic compounds.

Results and Discussion

Eight vinylic halides with different structural features were treated with various olefinic compounds to demonstrate several applications of the reaction. The results are summarized in Table I.

The reaction is believed to occur in three steps.[2] The "catalyst" is first reduced by the olefinic compound to a palladium(0) phosphine complex, which then reacts with the vinylic halide by oxidative addition. The vinylic palladium complex formed next adds to the olefin and the adduct eliminates an hydridopalladium group, forming the conjugated diene. The hydrido complex then loses hydrogen halide to the tertiary amine present, re-forming the palladium(0) phosphine complex, and the cycle is complete.

The reaction may be complicated by the conjugated diene product undergoing subsequent reactions such as double-bond isomerization or Diels–Alder reactions with starting material. The reaction of the 1-halo-1-hexenes with ethylene, for example, produces mainly the rearranged diene, 2,4-octadiene, rather than the expected 1,3-octa-