Experimental Section

General. The IR spectra were taken on a Perkin-Elmer 257 spectrophotometer. Mass spectra were obtained on a AEI MS-902 by Mr. A. Kiewiet. ^{1}H NMR spectra were recorded using a Varian A-60 D or Hitachi-Perkin-Elmer R24B spectrometer with Me_4Si as internal standard. ^{13}C NMR spectra were recorded using a Varian XL-100 spectrometer operating at 25.2 MHz. All reactions were carried out under a dry nitrogen atmosphere. Irradiations were performed with a Hanau Q-81 high-pressure mercury arc.

Irradiation of Enone 3 and Iron Pentacarbonyl. Enone **3** (310 mg, 1.9 mmol) and iron pentacarbonyl (390 mg, 2.0 mmol) in 100 mL of THF were irradiated for 2 days. Solvent, excess iron pentacarbonyl, and enone were removed in vacuo (room temperature, 0.001 mmHg pressure) and the residue was extracted with *n*-pentane. After recrystallization from *n*-pentane at −40 °C, lactone **6** was obtained in 28% yield (100 mg, 0.5 mmol). Compound **6** was characterized by comparison with an authentic sample.[3] During the irradiation, samples were taken from the solution, the solvent was evaporated, and the residue was analyzed by IR and ^{1}H NMR, showing absorptions due to complex **5**. When the irradiation was performed for 3 days a mixture of lactone **6**, phenol **7**, and starting material was obtained. Extraction of this mixture with aqueous KOH solution and acidification with HCl gave phenol **7** as a white solid, which was purified by recrystallization from *n*-pentane at −40 °C. Phenol **7** was characterized by spectral data and melting point (125–127 °C, lit.[18] 129 °C).

Enone–Iron Tetracarbonyl Complex 5. Enone **3** (630 mg, 3.9 mmol) was treated with 1.46 g (4.0 mmol) of diron nonacarbonyl in 50 mL of THF at room temperature during 2 h. Solvent and starting material were removed in vacuo. The residue was extracted with *n*-pentane, leaving after removal of the solvent in vacuo iron complex **5** in 51% yield (based on ^{1}H NMR) as a yellow oil. Attempts to crystallize **5** from *n*-pentane at −50 °C were unsuccessful. Compound **5** could not be completely freed from small amounts of enone **3** (to an extent of about 10%): MS *m/e* 330 (M^+), 302 (found 302.020; calcd 302.024[19]), 274, 246, 218, 162 (successive loss of CO groups and Fe); IR absorptions at 2090, 2020, and 1975 [$Fe(CO)_4$] and 1710 (C=O) cm^{-1}; ^{1}H NMR (C_6D_6, 35 °C) δ 2.86 (d, J = 1.8 Hz, 1 H), 2.43 (d, J = 1.8 Hz, 1 H), 1.27 (s, 3 H), 1.05 (s, 3 H), 1.01 (s, 3 H), 0.67 (s, 3 H); ^{13}C NMR (C_6D_6, 10 °C) δ 212.8[19] (s, C=O), 210.1[19] (s, FeC≡O), 85.8 (s), 50.7 (s), 42.9 (s), 40.7 (s), 31.5 (t, J = 156 Hz), 31.2 (s), 8.0:4.8:3.3:3.0 (q, $J \simeq$ 125 Hz).

Irradiation of Complex 5. Complex **5** (200 mg, 0.63 mmol) was irradiated in THF solution for 4 h, during which evolution of gas took place and insoluble material deposited on the lamp. After removal of the solvent the residue was recrystallized from *n*-pentane at −40 °C, giving lactone **6** in 45% yield (53 mg, 0.28 mmol).

Registry No.—**3**, 56745-77-8; **5**, 64314-99-4; **6**, 60998-59-6; iron pentacarbonyl, 13463-40-6; diiron noncarbonyl, 15321-51-4.

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(19) The intensity of the parent peak was too low to be used for an exact mass determination. Therefore, the exact mass of the (M^+ − CO) fragment was taken. In the ^{13}C NMR spectrum the CO absorptions have an intensity of about 4:1, which allows the assignment given.

Acid-Catalyzed Isomerization of 2-Protoadamantenone to 8,9-Dehydro-2-adamantanone

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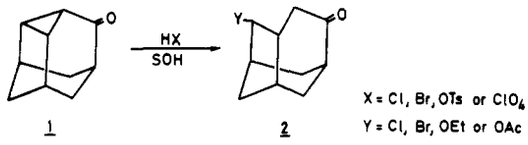
Rearrangements of the dehydroadamantyl and the protoadamantenyl cations are quite complex.[1–7] The course of these rearrangements depends highly on the reaction conditions. While the 8,9-dehydro-2-adamantyl cation undergoes rapid degenerate equilibrium under stable ion conditions,[7] 8,9-dehydro-2-adamantanol isomerizes in the presence of perchloric acid to 2-*exo*-protoadamantenol.[1,2] Under similar conditions, 8,9-dehydro-2-adamantanone (**1**) rearranges



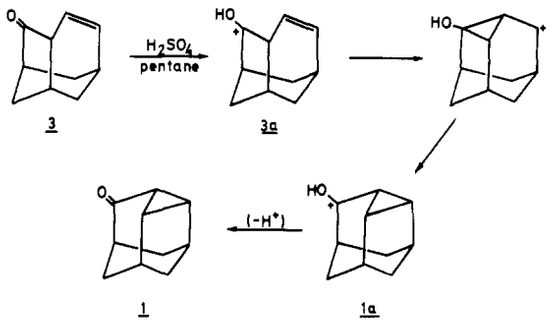
1 **2**

smoothly to 2-exo-substituted 5-protoadamantanones (**2**).[3] This rearrangement probably proceeds via the enol form of the 5-protoadamantanon-2-yl cation.

We report now an example of the reverse rearrangement: the acid-catalyzed isomerization of 2-protoadamantenone (**3**) to 8,9-dehydro-2-adamantanone (**1**). Treatment of **3** with 96% sulfuric acid in the presence of pentane at 22 °C afforded **1** in 30–40% yield. The product was stable under the reaction conditions used and was identified by IR,[1,6] ^{1}H NMR,[1,6] and ^{13}C NMR spectroscopy, mass spectrometry, and GLC comparison with an authentic sample which was prepared by the previously reported[1] procedure. The mechanism of this isomerization probably involves the initial protonation of the carbonyl group in **3** to give homoallyl cation **3a**, which then rearranges by the homoallyl–cyclopropylcarbinyl rearrangement to cation **1a** and ketone **1** (Scheme I).

This reaction provides the only example of the "solvolytic" π-route isomerization of 2-protoadamantenone (**3**) to 8,9-dehydro-2-adamantanone (**1**) and could be synthetically useful as an alternative to the photoisomerization[1] of **3** to **1**. Ketone **1** is a convenient starting material for the preparation of not only 2-substituted 8,9-dehydroadamantanes[1,6] but also

Scheme I



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a variety of 2,5-disubstituted protoadamantanes,[3] 2-substituted protoadamantenes,[2] and 2-substituted isotwistanes.[3]

Experimental Section

The ^{13}C NMR spectra were taken on a JEOL FX-100 spectrometer, the ^1H NMR spectra on a Varian A-60A spectrometer, the IR spectra on a Perkin-Elmer 257 spectrophotometer, and the mass spectra on a Varian CH-7 mass spectrometer. The GLC analyses were carried out on a Varian Aerograph 1800 gas chromatograph.

2-Protoadamantenone (3). Following the reported procedure,[8] a 1:1 mixture of 2-protoadamantenone (**3**) and 10-protoadamantenone (**4**) was obtained by thermal cyclization of 7-allyloxycycloheptatriene. The ketones were not satisfactorily separated either by column chromatography or preparative GLC. We found, however, that ketone **4** formed the ethylene ketal much faster than **3**.

A solution of the sublimed crude mixture of ketones **3** and **4** (1.5 g) was stirred in ethylene glycol (10 mL) in the presence of TsOH (2.1 g) at 80–85 °C for 2 h and then poured into a mixture of KOH (0.7 g) and crushed ice. The resulting mixture was extracted with ether (3 × 25 mL), and the combined extracts were washed with water and dried. Evaporation of ether gave 1.3 g of a crude oily product which contained two GLC-detectable components (10% Carbowax 20M, 150 °C): ketone **3** and the ethylene ketal of **4** (less than 5% of unreacted **4** was present). Pure ketone **3** (0.3 g) was obtained by column chromatography on silica gel using 1:49 ether–benzene as eluent. The physical and spectral properties of **3** agree with those previously reported for this compound.[8]

8,9-Dehydro-2-adamantanone (1). A typical experiment is described. Ketone **3** (75 mg, 0.5 mmol) was stirred with 0.5 mL of 96% sulfuric acid and 2 mL of pentane at 22 °C for 3 h. Ether (10 mL) and crushed ice were added, and the layers were separated. The aqueous layer was extracted with ether (2 × 5 mL), and the combined ether extracts were washed with saturated aqueous $NaHCO_3$ and dried. Evaporation of the solvent yielded crystalline crude product which contained 15% of unreacted **3** and 85% of 8,9-dehydro-2-adamantanone (**1**) (by GLC; 10% Carbowax 20M, 150 °C). Pure ketone **1** (≥98% by GLC; 26 mg, 35% based on **3**) was easily obtained by column chromatography on Al_2O_3 (neutral, activity II) using ether as an eluent. Its melting point (205–206 °C), IR, ^1H NMR, and the mass spectral data were in complete agreement with those previously reported[1,6] for this compound; the ^{13}C NMR spectrum [δ_{Me_4Si} ($CDCl_3$) 32.2, 34.2, 37.7, 39.6, 44.0, 51.4, and 214.4 ppm] of **1** was identical to that of an authentic sample prepared by the reported[1] photoisomerization of **3**.

Ketone **1** was also obtained in 10–20% yield directly from the crude (sublimed) product mixture of the thermal cyclization of 7-allyloxycycloheptatriene by the procedure described above.

A sample of pure **1** was subjected to the same reaction conditions as **3**. Essentially no rearranged products were detected by GLC.[9]

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Registry No.—**1**, 10497-56-0; **3**, 28673-75-8; **4**, 28673-76-9; **4** ethylene ketal, 64345-72-8; 7-allyoxycycloheptatriene, 28673-74-7.

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Protecting Groups. 6. Interaction of 2-Picoline 1-Oxides with Acylating and Phosphorylating Agents. A Case of Product Distribution Control[1]

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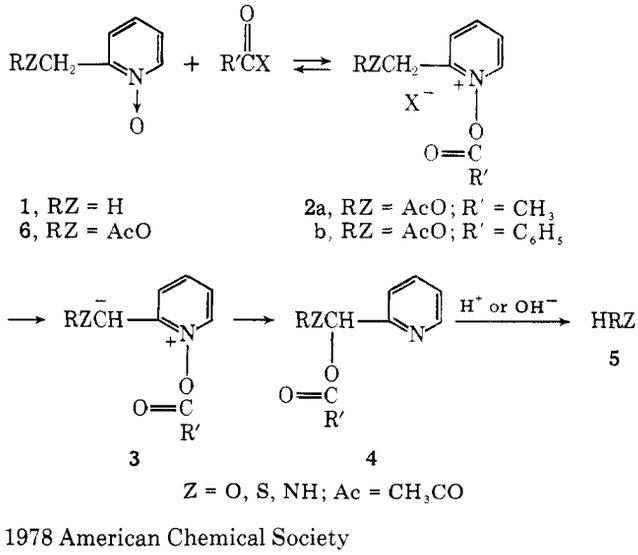
Previous reports from our laboratory show that the 2-picolyl 1-oxide group is potentially a useful protecting group in organic chemistry in general[2] and in oligonucleotide syntheses in particular.[1,3] The picolyl 1-oxide group can be removed from an ether, thioether, or amine (**1**, Scheme I) or from an ester **6** by treatment with an acid anhydride. The reaction may proceed by the following mechanism: O-acylation to the *N*-acyloxypyridinium salt **2** and subsequent proton abstraction from the α-methylene group of **2** by the conjugate base to afford **3**, followed by intramolecular electron transfer to complete the rearrangement from **3** to **4**.[4b]

In order to determine the scope and limitations of this protecting group, we undertook systematic studies on the interaction between picolyl 1-oxide acetate (**6**) and various acylating agents (Table I).[4] An acylating agent (3 equiv) was added portionwise to a solution of **6** in deuterated chloroform. Little spectral change of **6** occurred upon addition of acetic anhydride (**8**) or benzoyl fluoride (**13**). The spectrum of **6**, however, rapidly changed upon addition of acyl halide (except **13**), indicating the formation of the *N*-acyloxypicolinium salt **2**. A large paramagnetic shift of the H-6 signal of **6** was observed. The α-methylene signal of **2** also appeared in a lower field than that of **6** (Table I). The degree of this low-field shift of H-6 in **2** was found to be dependent upon the nature of the counterion. The largest shift was observed when the picolinium ion was associated with a hard base (Cl^-) and the smallest shift was observed when a soft base (I^-) was the counterion. The shape of the H-6 signal suggested that the strongest virtual coupling occurred with chloride and little virtual coupling was observed with iodide counterion. When bromide was the conjugate base, the long-range virtual coupling was medium.

Addition of acetyl iodide (**11**) to a preformed *N*-acetoxypicolinium chloride (**2a**, X = Cl) resulted in the formation of *N*-acetoxypicolinium iodide (**2a**, X = I) as observed by ^1H NMR spectroscopy. The bromide counterion of **2a** (X = Br) was also replaced by iodide by treatment of **2a** (X = Br) with **11**. The reverse (exchange of iodide by chloride or bromide)

Scheme I



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