agreed well with those reported.[4] The washed 10% sodium hydroxide solution was acidified with 10% hydrochloric acid to afford 7.56 g (70 mol %; 70% yield) of **5**.

(b) The *tert*-Butylation with 3. Similarly, to a mixture of 53.08 g (0.5 mol) of **1** and 16.4 g (0.1 mol) of **3** was added at 5 °C the $AlCl_3$–CH_3NO_2 catalyst (19.8 g/40 mL). The reaction mixture was stirred for 15 min and it was treated and worked up as described above to afford 6.5 g (40.1 mol %, 40.1% yield) of **4**, 3.42 g (16%) of the recovered **3**, and 8.38 g (77.6%) of **5**.

Registry No.—**1**, 106-42-3; **2**, 128-37-0; **3**, 2409-55-4; **4**, 42861-84-7; **5**, 106-44-5; $AlCl_3$, 7446-70-0; CH_3NO_2, 75-52-5.

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(6) This value was calculated as follows: amount of **4** (mol)/amount of **2** used (mol) × 100. Therefore, the usual yield of **4** was half of the mol % yield.
(7) In this case, the mol % yield is same as the usual yield.
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Novel Photochemically Induced Carbon Monoxide Insertion of an Enone–Iron Tetracarbonyl Complex to Yield a Lactone

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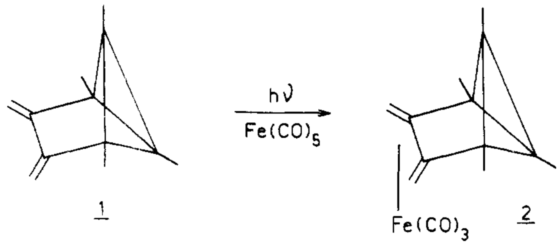
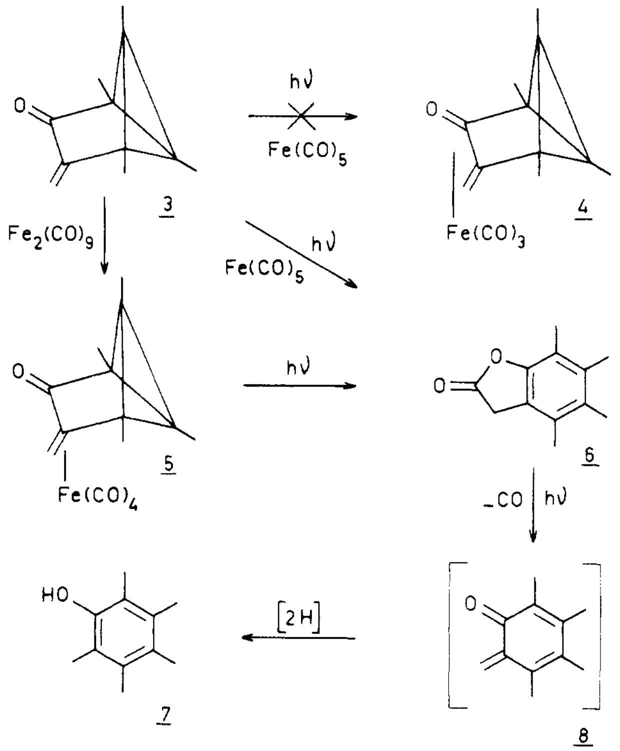
Recently, we reported the synthesis of the bicyclobutane-bridged diene–iron tricarbonyl complex **2** from the corresponding diene **1**[1] (Scheme I). Because both diene **1** and enone **3**[2] show an unexpected reactivity toward the $[Rh(CO)_2Cl]_2/CO$ catalyst system[3] and, moreover, because the extremely high reactivity (e.g., in Diels–Alder cycloadditions[4]) of diene **1** can be suppressed by complex formation to iron tricarbonyl, we undertook to prepare the related enone–iron tricarbonyl complex **4**. Unexpectedly, this proved to be impossible and a different reaction, viz., intramolecular CO insertion to yield a lactone, was observed. In view of the current interest in the preparation and properties of enone–iron tetra- and tricarbonyl complexes,[5-8] an account of the results obtained is given herewith.

Following the usual procedure for formation of enone–iron tricarbonyl complexes,[5] enone **3** and iron pentacarbonyl were irradiated in THF solution. However, no iron tricarbonyl complex **4** was isolated, but instead we obtained lactone **6** in 28% yield. IR and ^{1}H NMR measurements performed during the irradiation showed the presence of small amounts of iron tetracarbonyl complex **5**. Prolonged irradiation in the presence of excess iron pentacarbonyl did not increase the yield of **6**, but formation of substantial amounts of phenol **7**[9] was observed, probably via intermediacy of *o*-quinone methide **8**.[10] (See Scheme II.) Iron tetracarbonyl complex **5** was prepared independently as a yellow oil in 51% yield by treating **3** with diiron nonacarbonyl in THF. On warming at temperatures above 40 °C complex **5** decomposes back to enone **3**. Irradiation of **5** in THF or benzene solution gave lactone **6** in 45% yield but no **4**.[11]

Scheme I

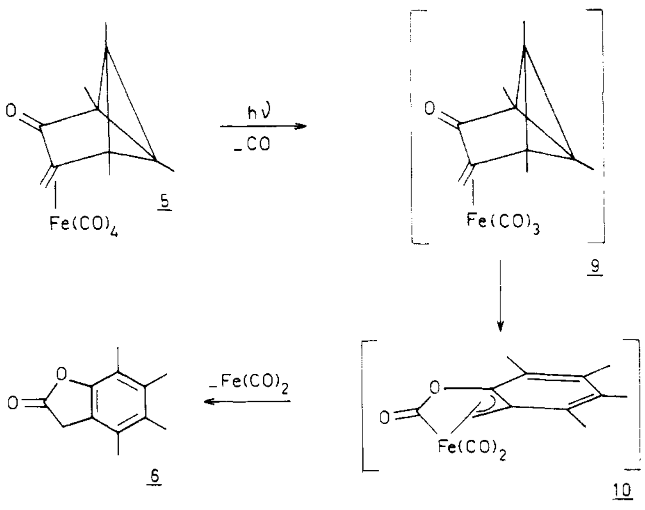


Scheme II



A satisfactory explanation for the unusual photochemically induced reaction of **5** → **6** in comparison with the normal conversion of enone–iron tetracarbonyl into iron tricarbonyl complexes must involve the special nature of the organic ligand. It is conceivable that on irradiation a coordinatively unsaturated complex **9** is formed, which—rather than to complex to the ketone moiety—gives the CO-inserted σ,π-complex **10**, followed by extrusion of the $Fe(CO)_2$ moiety to yield lactone **6** (Scheme III). Subtle differences between the chemical behavior of the iron tetracarbonyl complexes of diene **1** and **3** result in formation of diene complex **2**, on the one hand, and lactone **6**, on the other hand. This may be related to the difference in thermodynamic stability of enone–iron tricarbonyl and diene–iron tricarbonyl complexes.[17]

Scheme III



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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, $FeC{\equiv}O$), 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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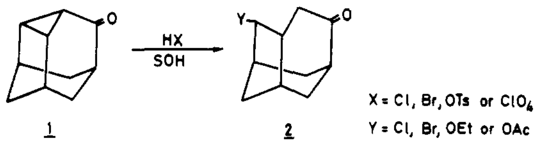
Rearrangements of the dehydroadamantyl and the protoadamantenyl cations are quite complex.[1–7] The course of these rearrangements depends highly on the reaction conditions. While the 8,9-dehydro-2-adamantyl cation undergoes rapid degenerate equilibrium under stable ion conditions,[7] 8,9-dehydro-2-adamantanol isomerizes in the presence of perchloric acid to 2-*exo*-protoadamantenol.[1,2] Under similar conditions, 8,9-dehydro-2-adamantanone (**1**) rearranges smoothly to 2-exo-substituted 5-protoadamantanones (**2**).[3] This rearrangement probably proceeds via the enol form of the 5-protoadamantanon-2-yl cation.



1 **2**

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