Synthesis of 4,5,9,10-Tetradehydroadamantan-2-one

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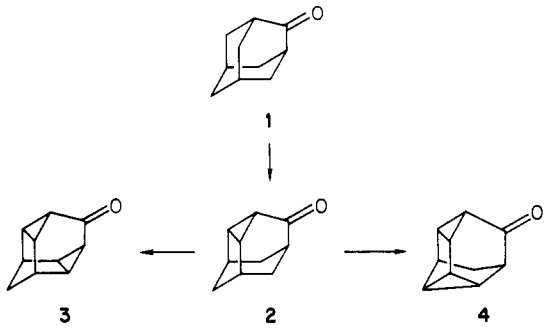
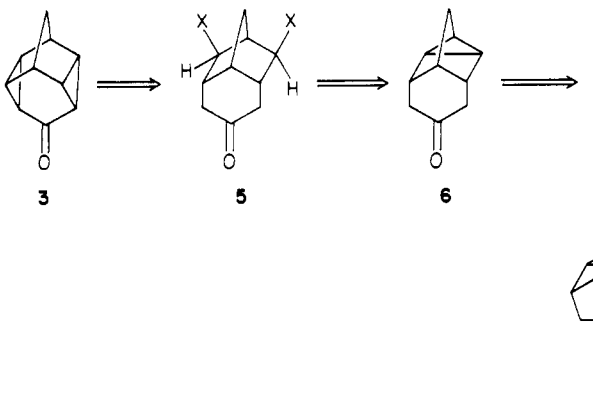
The first synthesis of the strained dicyclopropyl ketone, 4,5,9,10-tetradehydroadamantan-2-one, is described. This compound has been prepared in 10 steps from norbornadiene.

If only nonbridgehead positions are connected by σ bonds, then the carbon skeleton of adamantanone (**1**) allows for one didehydroadamantanone (**2**) and two tetradehydroadamantanones (**3** and **4**) that contain conjugated cyclopropyl ketone moieties. Since the chemistry of conjugated cyclopropyl ketones and their derivatives is extensive,[1] ketones **2–4** offer access to a variety of polycyclic compounds. Although 8,9-didehydroadamantan-2-one (**2**) has been known for some time,[2] neither **3** nor **4** has been prepared. We now wish to report the synthesis of 4,5,9,10-tetradehydroadamantan-2-one (**3**).



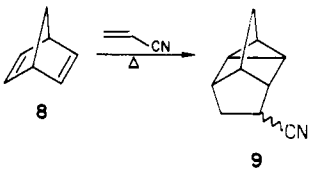
Results and Discussion

Initially, it was anticipated that ketone **3** might be obtained by the elimination of 2 equiv of HX from **5** which,



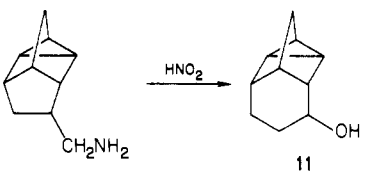
in turn, might be prepared by the addition of X_2 to the unknown ketone **6**. In principle, **6** should be available by homologation of deltacyclan-8-one (**7**).

Two related methods have been reported for the synthesis of **7**.[3,4] Recently, Watt and his co-workers have developed a general one-pot procedure to convert secondary nitriles to ketones by oxidative decyanation.[5] In this approach, a secondary nitrile is initially treated with lithium diisopropylamide and the anion is trapped with molecular oxygen. Subsequent reduction of the resulting α-hydroperoxy nitrile with stannous chloride in aqueous hydrochloric acid provides a cyanohydrin which is then hydrolyzed with aqueous base to the corresponding ketone. Addition of acrylonitrile to norbornadiene (**8**) at 120 °C in the presence of bis(triphenylphosphine)dicarbonylnickel affords 8-cyanodeltacyclane (**9**) in 83% yield.[6] Treatment



of **9** according to the Watt procedure provided **7** in 71% yield. This appears to be the method of choice for the synthesis of deltacyclan-8-one.

The homologation of **7** to **6** formally requires the insertion of a methylene between the carbonyl carbon and the more substituted adjacent carbon in **7**. A conventional method for the homologation of ketones is the Evans modification[7] of the Tiffeneau–Demjanov procedure.[8] In this approach, a ketone is converted in two steps to the corresponding β-aminomethyl alcohol, which is then treated with nitrous acid. However, the reported homologations of several bicyclic and polycyclic ketones by this method show a significant preference for insertion of the new skeletal carbon between the carbonyl carbon and the less substituted adjacent carbon.[9] Particularly distressing in this regard was the observation by Hall that ring expansion of **10** upon reaction with nitrous acid gives **11** in greater than 90% purity.[10]



(1) For a review see: Tunemoto, D.; Kondo, K. *Yuki Gosei Kagaku Kyokaishi* **1977**, *35*, 1070–1086.

(2) (a) Baldwin, J. E.; Foglesong, W. D. *J. Am. Chem. Soc.* **1968**, *90*, 4303–4310. (b) Murray, R. K., Jr.; Morgan, T. K., Jr.; Babiak, K. A. *J. Org. Chem.* **1975**, *40*, 1079–1083. (c) Karlovic, G.; Majerski, Z. *Ibid.* **1978**, *43*, 746–747.

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(8) For a review see: Smith, P. A. S.; Baer, D. R. *Org. React.* **1960**, *11*, 157–188.

(9) (a) Sasaki, T.; Eguchi, S.; Toru, T.; Itoh, E. K. *J. Am. Chem. Soc.* **1972**, *94*, 1357–1360. (b) McKinney, M. A.; Patel, P. P. *J. Org. Chem.* **1973**, *38*, 4059–4064. (c) Miyashita, M.; Yoshikoshi, A. *J. Am. Chem. Soc.* **1974**, *96*, 1917–1925. (d) Breitholle, E. G.; Fallis, A. G. *J. Org. Chem.* **1978**, *43*, 1964–1968.

(10) Hall, H. K., Jr. *J. Org. Chem.* **1960**, *25*, 42–44.

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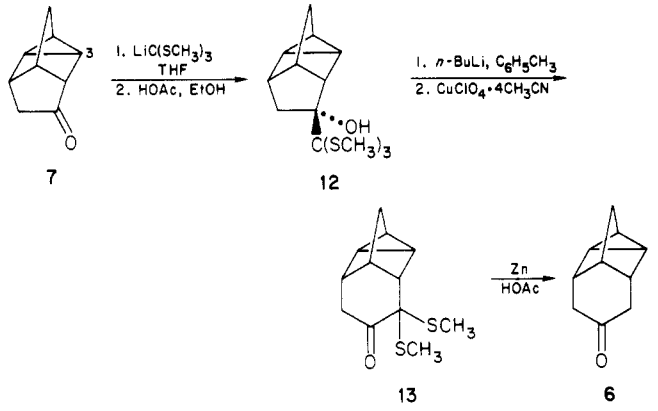
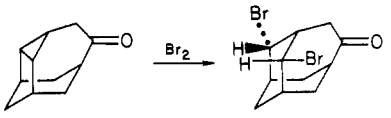
In striking contrast to these results, Knapp and his coworkers have recently reported a method for the regiospecific homologation of 2-norbornanone which proceeds by exclusive migration of the more substituted carbon.[11] Application of this procedure to deltacyclan-8-one provided a straightforward route to ketone **6**. Treatment of **7** with



7 12 13 6

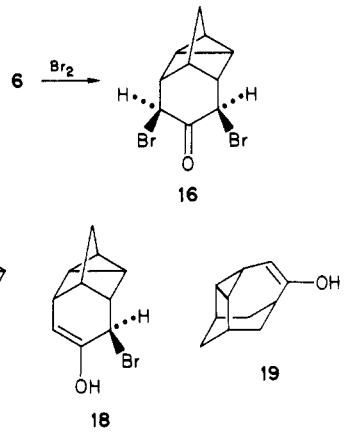
tris(methylthio)methyllithium in tetrahydrofuran gave **12** in 75% yield. The stereochemistry assigned to the substituents in **12** follows from an examination of a molecular model of **7** which shows that attack at the endo face of the carbonyl carbon in **7** should be significantly impeded by the hydrogen at C-3. By contrast, there is no apparent steric hindrance to attack at the exo face of the carbonyl. A toluene solution of **12** was converted initially to its lithium salt with *n*-butyllithium at −78 °C, then treated with 2.2 equiv of tetrakis(acetonitrile)copper(I) perchlorate at this temperature, and finally warmed at 75 °C for two hours. This procedure provided 8,8-bis(methylthio)tetracyclo[4.4.0.$0^{2,4}$.$0^{3,7}$]decan-9-one (**13**) in 71% yield. Reduction of **13** with zinc in acetic acid gave the target ketone **6** in 77% yield.

As noted earlier, we had planned that addition of a halogen to ketone **6** would provide **5**. Although literature reports on the electrophilic reactions of halogens with cyclopropanes are extensive, nearly all of these studies have been carried out with hydrocarbons that are devoid of other functionality.[12] However, we were encouraged by the observation that greater than 90% of the material isolated from the reaction of bromine with 2,11-didehydrohomoadamantan-5-one (**14**) is **15**.[13] Treatment



14 15

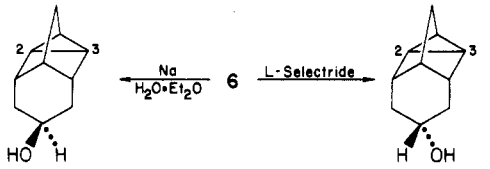
of ketone **6** with bromine in carbon tetrachloride gave a single product which contained two bromines. However, analysis of the ^{1}H and ^{13}C NMR spectra of this material clearly indicated that it was **16**. This dibromo ketone is obviously the result of stepwise bromination of enols **17** and **18**. Apparently, the increase in strain energy necessary to form enol **19** from **14** is sufficient so that electrophilic



16 17 18 19

addition of bromine to the cyclopropyl group in **14** becomes the favored pathway for this particular cyclopropyl ketone.

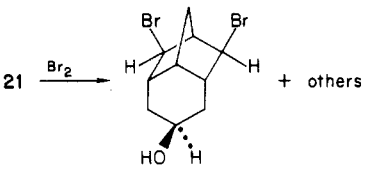
It was hoped that this complication in the synthesis could be circumvented by adding a halogen across the cyclopropane moiety in an alcohol derived from ketone **6**. Endo alcohol **20** was obtained in 79% yield by treatment of **6** with the bulky reducing reagent L-Selectride. This was the expected stereochemical result since examination of a molecular model of **6** shows that nucleophilic attack at the endo face of the carbonyl carbon in **6** should be significantly impeded by the hydrogens at C-2 and C-3. Exo alcohol **21** was prepared in 69% yield by reduction



21 20

of **6** with sodium in moist ether. The stereochemical outcome of this reaction follows the generalization that the more stable alcohol is frequently (but not always) the major product in the dissolving-metal reduction of ketones.[14] In order to firmly establish the stereochemistry of the hydroxyl substituents in **20** and **21**, the lanthanide-induced chemical shifts of the ^{13}C NMR resonances of **20** and **21** were determined in the presence of Eu(thd)$_3$. Consistent with the structure assignments, the change in chemical shift of the resonance due to C-2 and C-3 in **20** in the presence of the shift reagent was found to be considerably greater than that due to the corresponding signal in **21**.

The product resulting from the reaction of bromine with endo alcohol **20** did not contain a hydroxyl substituent and so it was not investigated in further detail. Analysis by ^{13}C NMR spectroscopy of the crude reaction residue resulting from the treatment of exo alcohol **21** with a solution



22

of bromine in carbon tetrachloride at room temperature indicated the presence of at least three components. However, fractional crystallization of this material from

(11) Knapp, S.; Trope, A. F.; Theodore, M. S.; Hirata, N.; Barchi, J. J. *J. Org. Chem.* **1984**, *49*, 608–614.

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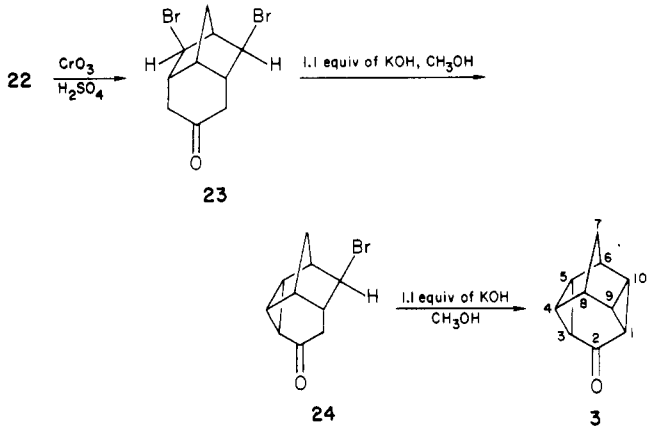
chloroform–hexane (ca. 1:1) provided pure **22** in 27% yield. The carbon skeleton of **22** was firmly established by its reduction with lithium and *tert*-butyl alcohol in tetrahydrofuran to regenerate **21**.

Jones oxidation of **22** proceeded smoothly to provide **23** in 89% yield. This dibromo ketone was converted to **3** in



a stepwise procedure. Reaction of **23** with 1.1 equiv of potassium hydroxide in methanol afforded **24**. Further treatment of this material with another 1.1 equiv of base gave **3** in 21% overall yield from **23**.

The structure of 4,5,9,10-tetradehydroadamantan-2-one follows from its spectroscopic characteristics. The carbonyl absorption of this dicyclopropyl ketone appears at 1686 cm^{-1} in the infrared. This value is to be compared with the carbonyl absorptions of ketones **1**[15] and **2**[2] which occur at 1727 and 1702 cm^{-1}, respectively. The ^{13}C NMR spectrum of **3** contains only five resonances. Of particular interest is the chemical shift of the methylene carbon at C-7 which occurs far downfield at δ 69.6. Recently, it has been recognized that incorporation of a bicyclo[3.1.0]-hexane moiety into a rigid cage system produces a large downfield shift in C-3 of that unit if C-3 is anti to the cyclopropyl group.[16] For example, the signals for C-6 in **1**[17] and **2**[18] occur at δ 36.3 and 51.3, respectively. Moreover, such effects appear to be additive for a given skeletal framework.[16] Consequently, the expected chemical shift for C-7 in **3** is δ 66.3.

In summary, 4,5,9,10-tetradehydroadamantan-2-one has been prepared in 10 steps from commercially available norbornadiene.

Experimental Section

Melting points were obtained in sealed capillary tubes in a Mel-Temp melting point apparatus and are uncorrected. Infrared spectra were recorded on Perkin-Elmer 180 or Unicam SP1100 spectrophotometers. Proton magnetic resonance spectra were obtained with a Bruker AM 250-MHz spectrometer. Apparent splittings are reported in all cases. Carbon magnetic resonance spectra were recorded with the Bruker instrument at 62.9 MHz. Both the ^1H and ^{13}C NMR spectra were obtained with $CDCl_3$ as the solvent and are referenced to an internal standard of tetramethylsilane. Electron impact mass spectra were obtained with a DuPont 21-492B mass spectrometer at an ionization potential of 70 eV. Elemental analyses were performed by Micro-Analysis, Inc., Wilmington, DE.

Deltacyclan-8-one (7). A solution of lithium diisopropylamide in tetrahydrofuran was prepared by the dropwise addition of *n*-butyllithium (2.83 mL of a 1.36 M solution in hexane, 3.85 mmol) to a stirred solution of diisopropylamine (394 mg, 3.90 mmol) in anhydrous tetrahydrofuran (6 mL) which was maintained at −78 °C under nitrogen. The reaction mixture was stirred at −78 °C for 15 min, and then at 0 °C for 15 min, before it was recooled to −78 °C. A solution of 8-cyanodeltacyclane[6] (500 mg, 3.80 mmol) in anhydrous tetrahydrofuran (3 mL) was then added dropwise over 10 min to this reaction mixture. The resulting solution was stirred at −78 °C for 1 h. The solution was then maintained at −78 °C, and oxygen was bubbled through it for 30 min. At this point the reaction was quenched by the addition of 2 M aqueous hydrochloric acid that was 1 M in stannous chloride (7 mL), and the resulting mixture was stirred at 0 °C for 30 min. The reaction mixture was then diluted with ether (25 mL) and washed successively with water (25 mL), 1.0 M aqueous sodium hydroxide (50 mL), water (25 mL), and brine (25 mL) and finally dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure provided a yellow oil which was Kugelrohr distilled (55–56 °C at 1.0 mm) to give 363 mg (71% yield) of **7** as a colorless oil. The spectral characteristics of this material were identical with those previously reported for **7**.[3,4]

8-*endo*-Hydroxy-8-*exo*-[tris(methylthio)methyl]-deltacyclane (12). *n*-Butyllithium (7.9 mL of a 1.42 M solution in hexane, 11.2 mmol) was added dropwise to a stirred solution of tris(methylthio)methane[19] (1.72 g, 11.2 mmol) in anhydrous tetrahydrofuran (50 mL) which was maintained at −78 °C under nitrogen. The resulting solution was stirred at −78 °C for 30 min, and then a solution of **7** (1.0 g, 7.46 mmol) in anhydrous tetrahydrofuran (10 mL) was added dropwise over 15 min. This solution was stirred at −78 °C for 1.5 h. The reaction was quenched at −78 °C with an equivalent of acetic acid dissolved in ethanol (5.0 mL) and allowed to warm to room temperature. The reaction mixture was diluted with methylene chloride (50 mL), washed with saturated aqueous ammonium chloride (50 mL), and then dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure gave a yellow oil. The excess tris(methylthio)methane that was present was removed by Kugelrohr distillation (65–70 °C, 0.4 mm). The residual oil was then column chromatographed on silica gel with petroleum ether/ether (9:1) as eluent to give 1.61 g (75% yield) of **12**: ^{13}C NMR δ 91.0 (s), 79.3 (s), 51.8 (d), 42.9 (d), 42.1 (d), 41.6 (t), 32.4 (t), 15.5 (q), 14.3 (d), 13.8 (d), 12.5 (d).

8,8-Bis(methylthio)tetracyclo[4.4.0.0^{2,4}.0^{3,7}]decan-9-one (13). *n*-Butyllithium (9.96 mL of a 1.42 M solution in hexane, 14.2 mmol) was added slowly via syringe to a stirred solution of **12** (4.06 g, 14.1 mmol) in dry toluene (150 mL) which was maintained at −78 °C under nitrogen. The resulting solution was stirred at −78 °C for 0.5 h and then tetrakis(acetonitrile)copper(I) perchlorate[20] (10.18 g, 31.13 mmol) was added. (**Cautionary note**: Care must be exercised in the synthesis, drying, and handling of solvated metal perchlorates, which may prove to be explosive.[21]) The cooling bath was removed and the reaction mixture was stirred at room temperature for 1.5 h. The reaction mixture was then warmed to 78 °C and stirred for an additional 2.0 h. At this point, the reaction was quenched by the addition of aqueous ammonium chloride/ammonium hydroxide (pH ca. 8.0) and cooled to room temperature. The reaction mixture was then filtered under reduced pressure, and the filter cake was washed with ether (3 × 20 mL). The combined ether washings were added to the filtrate and the layers were separated. The organic phase was washed with water (50 mL) and dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure afforded an oil which was Kugelrohr distilled to give 2.40 g (71% yield) of **13** as a yellow oil: ^1H NMR δ 3.23 (dd, J = 16.2 and 3.4 Hz, 1 H), 2.41–2.31 (m, 2 H), 2.19 (br s, 1 H), 2.10 (br s, 1 H), 1.98 (s, 3 H), 1.91 (s, 3 H), 1.60 (t, J = 4.8 Hz, 1 H), 1.53 (br s, 2 H), 1.25 (t, J = 5.2 Hz, 1 H), 1.16 (t, J = 5.1 Hz, 1 H); ^{13}C NMR δ 202.1 (C-9), 70.0 (C-8), 49.4 (t), 40.8 (d), 38.7 (t), 34.9 (d), 34.2

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(17) Duddeck, H. *Org. Mag. Res.* **1975**, *7*, 151–153.
(18) **2**: ^{13}C NMR δ 213.5 (C-2), 51.3 (C-6), 43.9 (C-3), 39.2 (C-5 and C-7), 37.6 (C-4 and C-10), 34.1 (C-1), 32.2 (C-8 and C-9).
(19) Eliel, E. L.; Hartmann, A. A.; Abatjoglou, A. G. *J. Am. Chem. Soc.* **1974**, *96*, 1807–1816.
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(21) (a) Raymond, K. N. *Chem. Eng. News* **1983**, *61*, No. 49, 4. (b) Bretherick, L. *Ibid.* **1983**, *61*, No. 50, 2.

(d), 14.9 (q), 14.5 (q), 13.4 (d), 12.4 (d), 9.6 (d); IR ν (CCl_4) 2990, 2920, 2870, 1705, 1415, 1360, 1345 cm^{-1}. The sample for mass spectrometry was purified by GLC (10 ft × 0.25 in. QF-1 column, 200 °C). Exact mass calcd for $C_{12}H_{16}OS_2$: 240.064. Found: 240.064.

Tetracyclo[4.4.0.0^{2,4}.0^{3,7}]decan-9-one (6). A solution of **13** (4.28 g, 18.3 mmol) in acetic acid (20 mL) was added to a stirred suspension of zinc dust (10.0 g, 153 mmol) in acetic acid (125 mL), and the reaction mixture was then refluxed for 16 h. Upon cooling, the reaction mixture was filtered, and the filter cake was washed with ether (100 mL). The filtrate and ether washings were combined and washed with 1.0 N aqueous sodium hydroxide (5 × 100 mL) and water (3 × 100 mL). The aqueous solution was back extracted with ether (3 × 50 mL), and the combined ether extracts were added to the organic material. This material was then washed with 1.0 N aqueous sodium hydroxide (5 × 50 mL) and dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure provided on oil which was Kugelrohr distilled to give 2.09 g (77% yield) of **6** as a colorless oil: ^{1}H NMR δ 2.51 (dd, J = 16.2 and 3.4 Hz, 2 H, exo hydrogens at C-8 and C-10), 2.39 (dd, J = 15.8 and 2.4 Hz, 2 H, endo hydrogens at C-8 and C-10), 2.07 (br s, 2 H, hydrogens at C-1 and C-7), 1.97 (br s, 1 H, hydrogen at C-6), 1.46 (br s, hydrogens at C-5), 1.2–1.1 (m, 3 H, cyclopropyl hydrogens); ^{13}C NMR δ 211.4 (C-9), 42.7 (C-8 and C-10), 40.8 (C-1 and C-7), 36.7 (C-6), 33.8 (C-5), 15.0 (C-2 and C-3), 13.3 (C-4); IR ν (CCl_4) 3070, 2950, 2870, 1720, 1415, 1360 cm^{-1}. Exact mass calcd for $C_{10}H_{12}O$: 148.089. Found: 148.089.

Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 80.86; H, 8.21.

8-*exo*,10-*exo*-Dibromotetracyclo[4.4.0.0^{2,4}.0^{3,7}]decan-9-one (16). Bromine (0.6 mL) was added to a stirred solution of **6** (105 mg, 0.709 mmol) in carbon tetrachloride (30 mL). The solution was stirred at room temperature for 24 h and then quenched with water (50 mL). At this point solid sodium bisulfite was added to the reaction mixture until the excess bromine that was present was destroyed. The resulting layers were separated and the organic phase was washed with water (25 mL) and then dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure gave a yellow oil which was sublimed to give 163 mg (75% yield) of **16**: ^{1}H NMR δ 4.28 (d, J = 2.4 Hz, 2 H, CHBr), 2.73 (br s, 1 H), 2.41 (br s, 2 H), 1.66–1.51 (m, 1 H), 1.59 (br s, 2 H), 1.26 (d, J = 5.2 Hz, 2 H); ^{13}C NMR δ 200.0 (C-9), 48.6 (C-8 and C-10), 44.3 (C-1 and C-7), 33.2 (C-5), 30.7 (C-6), 16.4 (C-4), 15.2 (C-2 and C-3); IR ν (CCl_4) 2945, 2870, 1725, 1365, 1340, 1245, 1240, 1180 cm^{-1}.

Tetracyclo[4.4.0.0^{2,4}.0^{3,7}]decan-9-*endo*-ol (20). A solution of L-Selectride (2.034 mL, 2.034 mmol) in anhydrous tetrahydrofuran was added to a stirred solution of **6** (100 mg, 0.678 mmol) in anhydrous tetrahydrofuran (5 mL) at −78 °C under nitrogen. The resulting solution was maintained at −78 °C for 4.0 h at which point it was quenched by the slow addition of 3 M aqueous sodium hydroxide (2.5 mL), followed by the slow addition of 30% hydrogen peroxide (2.5 mL). The resulting material was saturated with potassium carbonate and the layers were separated. The resulting organic phase was dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure gave a clear oil which was Kugelrohr distilled to give 80 mg (79% yield) of **20** as a colorless oil: ^{1}H NMR δ 3.81 (br s, 1 H, CHOH), 2.57 (d, J = 9 Hz, 1 H), 1.98–1.84 (m, 4 H), 1.81 (br s, 2 H), 1.50 (s, 1 H), 1.32 (s, 2 H), 1.29–1.22 (m, 1 H), 1.18 (d, J = 5.2 Hz, 2 H). The ^{13}C NMR spectrum of **20** was obtained in $CDCl_3$ after the cumulative addition of 0.0, 0.2, 0.4, and 0.6 molar equivalents of tris(2,2,6,6-tetramethyl-3,5-heptanedionato)europium. Following is a summary of the chemical shifts of the ^{13}C NMR resonances of **20**. Indicated in parentheses is the induced downfield shift in ppm for each signal for a 0.6:1 molar ratio of the shift reagent to substrate and the particular atom to which each chemical shift is assigned. ^{13}C NMR δ 65.9 (C-9), 38.5 (8.7, C-1 and C-7), 37.6 (6.0, C-6), 34.0 (11.7, C-8 and C-10), 33.8 (3.65, C-5), 16.4 (4.5, C-4), 14.8 (8.6, C-2 and C-3). IR ν (CCl_4) 3620, 3480, 3070, 2980, 2940, 2870, 1405, 1190, 1120, 1080, 1060 cm^{-1}. Exact mass calcd for $C_{10}H_{14}O$: 150.105. Found: 150.105.

Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 79.87; H, 9.27.

Tetracyclo[4.4.0.0^{2,4}.0^{3,7}]decan-9-*exo*-ol (21). Three drops of water were added to a mechanically stirred mixture of "sodium sand" (200 mg, 8.70 mmol; prepared by heating sodium metal in xylene until it was molten and then vigorously stirring the mixture with a mechanical stirrer while cooling it to room temperature), **6** (200 mg, 1.35 mmol), and anhydrous ether (15 mL) at room temperature. The reaction mixture was stirred for 16 h. At this point, additional water (2 mL) was slowly added to quench the reaction, and the reaction mixture was extracted with ether (3 × 20 mL). The combined ether extracts were washed with water (2 × 20 mL) and then dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure afforded a yellow oil which was Kugelrohr distilled to give 140 mg (69% yield) of **21** as a colorless oil: ^{1}H NMR δ 4.15 (heptet, J = 5.5 Hz, 1 H, CHOH), 3.32 (br s, 1 H, OH), 2.08–1.95 (m, 2 H), 1.79 (br s, 2 H), 1.53–1.10 (m, 5 H), 1.08–1.02 (m, 1 H), 0.87 (d, J = 5.3 Hz, 2 H). The ^{13}C NMR spectrum of **21** was obtained in $CDCl_3$ after the cumulative addition of 0.0, 0.2, 0.4, and 0.6 molar equivalents of tris(2,2,6,6-tetramethyl-3,5-heptanedionato)europium. Following is a summary of the chemical shifts of the ^{13}C NMR resonances of **21**. Indicated in parentheses is the induced downfield shift in ppm for each signal for a 0.6:1 molar ratio of the shift reagent to substrate and the particular atom to which each chemical shift is assigned. ^{13}C NMR: δ 64.7 (C-9), 40.1 (5.3, C-1 and C-7), 37.1 (2.5, C-5), 35.7 (12.8, C-8 and C-10), 32.7 (2.5, C-5), 13.1 (4.63, C-2 and C-3), 13.1 (2.7, C-4). IR ν (CCl_4) 3640, 3390, 3070, 2930, 2870, 1295, 1055 cm^{-1}. Exact mass calcd for $C_{10}H_{14}O$: 150.104. Found: 150.104.

Anal. Calcd for $C_{10}H_{14}O$: C, 79.86; H, 9.39. Found: C, 79.76; H, 9.41.

2-*exo*,10-*exo*-Dibromotricyclo[5.2.1.0^{3,8}]decan-5-*exo*-ol (22). A solution of bromine (0.925 mL, 3.27 mmol) in carbon tetrachloride (spectral grade which was passed through a column of basic alumina and stored over 4-Å molecular sieves) was added to a stirred solution of **21** (490 mg, 3.27 mmol) in carbon tetrachloride (10 mL) at room temperature. The resulting solution was stirred at room temperature for 15 min and then water (20 mL) was added. At this point solid sodium bisulfite was added to the reaction mixture until the excess bromine that was present was destroyed. The layers were separated and the organic phase was dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure provided an oil. Crystallization of this material from chloroform/hexane afforded 278 mg (27% yield) of **22**: mp 150–152 °C; 3.78–3.60 (m, 3 H), 2.73 (s, 1 H), 2.61 (br s, 2 H), 2.28–2.0 (m, 5 H), 1.37–1.22 (m, 3 H); ^{13}C NMR δ 62.8 (C-5), 56.6 (C-1), 51.4 (C-2 and C-10), 48.5 (C-3 and C-7), 42.5 (C-8), 35.1 (C-9), 34.5 (C-4 and C-6).

Dehalogenation of 22. Lithium metal (250 mg, 35.2 mmol) was added to a solution of **22** (60 mg, 0.194 mmol) in anhydrous *tert*-butyl alcohol (4 mL) and anhydrous tetrahydrofuran (20 mL), and the mixture was stirred at room temperature for 16 h. At this point, water (10 mL) was added and stirring was continued for an additional 30 min. The resulting solution was extracted with ether (3 × 25 mL), and the combined ether extracts were dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure gave an oil which was Kugelrohr distilled to give 24.8 mg (85% yield) of **21** containing approximately 15% (by ^{13}C NMR analysis) of another component which may be tricyclo[5.2.1.0^{3,8}]decan-5-*exo*-ol.

2-*exo*,10-*exo*-Dibromotricyclo[5.2.1.0^{3,8}]decan-5-one (23). Freshly prepared Jones reagent (2.8 g of chromium trioxide, 4.5 mL of sulfuric acid, and 12 mL of water) was added to a stirred solution of **22** (170 mg, 0.552 mmol) in acetone (10 mL) that was maintained at 0 °C. The reaction mixture was stirred at 0 °C for 1 h and at room temperature for 30 min. At this point, water (5 mL) was added and the mixture was stirred for an additional 30 min. The reaction mixture was then neutralized with saturated aqueous sodium bicarbonate, saturated with sodium chloride, and extracted with ether (4 × 20 mL). The combined organic extracts were dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure provided 200 mg of a solid which was sublimed (60–65 °C, 0.3 mm) to give 150 mg (89% yield) of **23** as a white solid: mp 94.5–96 °C; ^{1}H NMR δ 3.36 (br s, 2 H, CHBr), 2.84 (br s, 2 H), 2.70 (br s, 1 H), 2.60–2.33 (m, 5 H), 2.15 (br s, 2 H); ^{13}C NMR δ 208.4 (C-5), 55.6 (C-1), 51.1 (C-2 and C-10 *or* C-3 and C-7), 50.7 (C-3 and C-7 *or* C-2 and C-10), 41.9 (C-8),

41.8 (C-4 and C-6), 35.5 (C-9); IR ν (CCl_4) 2965, 1713, 1465, 1420, 1360, 1305, 1260 cm^{-1}. Exact mass calcd for $C_{10}H_{12}OBr_2$: 305.926. Found: 305.928.

Anal. Calcd for $C_{10}H_{12}OBr_2$: C, 39.00; H, 3.93. Found: C, 38.62; H, 4.00.

10-*exo*-Bromotetracyclo[5.3.0.0^{4,6}.0^{5,9}]decan-3-one (24). A solution of potassium hydroxide (15.2 mg, 0.271 mmol) in methanol (1.5 mL) was added to a stirred solution of **23** (76.0 mg, 0.247 mmol) in methanol (5 mL), and the resulting solution was refluxed for 1 h. After cooling to room temperature, water (100 mL) was added and the reaction mixture was extracted with ether (3 × 25 mL). The combined ether extracts were washed with water (2 × 25 mL) and dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure afforded a yellow oil which was Kugelrohr distilled to give 28.3 mg (50% yield) of **24**. Analysis of this material by ^{13}C NMR showed that **24** and **3** were present in a ratio of ca. 4:1. The ^{13}C NMR resonances of **24** occur at δ 208.2 (C-3), 55.1 (d), 53.1 (t), 48.4 (d), 44.4 (d), 42.2 (d), 39.2 (d), 38.2 (t), 34.5 (d), 27.7 (d).

4,5,9,10-Tetradehydroadamantan-2-one (3). A solution of potassium hydroxide (10.0 mg, 0.178 mmol) in methanol (1.0 mL) was added to a solution of a 4:1 mixture of **24** and **3**, respectively, (27.0 mg, 0.119 mmol) in methanol (10 mL) and the resulting solution was refluxed for 1 h. After cooling, water (100 mL) was added and the reaction mixture was extracted with ether (3 × 25 mL). The combined ether extracts were washed with water (2 × 25 mL) and dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure gave an oil which was column chromatographed on silica gel with methylene chloride–hexane–ether (45:45:10) as eluent to provide 7.2 mg of **3**: mp 92–93 °C; ^1H NMR δ 2.60–2.52 (br s, 2 H), 2.46 (s, 2 H), 2.44–2.36 (m, 4 H), 1.88 (t, J = 7 Hz, 2 H); ^{13}C NMR δ 208.0 (C-2), 69.6 (C-7), 40.6 (C-4, C-5, C-9, and C-10), 35.5 (C-1 and C-3), 34.5 (C-6 and C-8); IR ν (CCl_4) 3040, 2980, 2865, 1686, 1395, 1320, 1110, 1060 cm^{-1}. Exact mass calcd for $C_{10}H_{10}O$: 146.073. Found: 146.073.

Anal. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.89. Found: C, 82.05; H, 6.92.

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Registry No. **3**, 98652-85-8; **6**, 98652-79-0; **7**, 16282-07-8; **8**, 121-46-0; **9**, 16282-06-7; **12**, 98652-77-8; **13**, 98652-78-9; **16**, 98652-80-3; **20**, 98652-81-4; **21**, 98717-51-2; **22**, 98652-82-5; **23**, 98652-83-6; **24**, 98652-84-7; tris(methylthio)methane, 5418-86-0; tetrakis(acetonitrile)copper(I) perchlorate, 14057-91-1.

Novel Photochemical Reactions of 3(2*H*)-Furanones†

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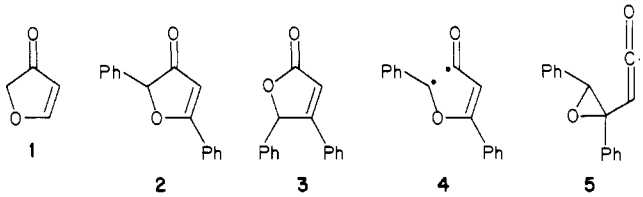
Irradiation ($\lambda \geq 280$ nm) of furanones **6–9** leads to rearrangement to enol lactones **14–17**, while the di-*tert*-butyl-substituted derivative **10** undergoes decarbonylation to form **21**. Both types of reaction are readily quenched by 2,3-dimethyl-1,3-butadiene, and a common mechanism is suggested, involving rearrangement of the furanone to an acylcyclopropanone (as **18**), followed by either reverse [1,3] shift to furnish enol lactone or alternatively decarbonylation to yield **21**. A convenient route to 3(2*H*)-furanones is provided by mercuric acetate oxidation of readily available allenic ketones.

The synthesis and reactions of simple derivatives of 3(2*H*)-furanone (**1**) have attracted considerable attention in recent years,[1-4] primarily in connection with development of routes to antitumor agents[5] that contain this ring as a central structural unit. In contrast, the intramolecular photochemistry of 3(2*H*)-furanones has received no consideration, apart from one brief study a decade ago.[6] In this earlier work Padwa[7] found that 2,5-diphenyl-3(2*H*)-furanone (**2**) rearranged on irradiation through Vycor (λ > approximately 210 nm) to form lactone **3**. The structure of **3** was confirmed by independent synthesis, and a pathway involving α-cleavage to **4**, closure to **5**, and then rearrangement to **3** was suggested to account for the observed reaction.[7] Since these proposed steps have close analogies in the photochemistry of both cyclopentenones[8] and 2-alkoxypyrrolin-5-ones,[9] rearrangement of **2** to **3** appeared reasonable, and this result may well have discouraged further photochemical exploration in this series. We now report that none of the five alkyl-substituted 3(2*H*)-furanones **6–10** behaves like **2** on irradiation; **6–9** undergo a novel isomerization, while **10** suffers two unexpected fragmentation reactions. Details are reported



† Dedicated to Professor Harold H. Warren on the occasion of his retirement.

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