dried over potassium carbonate.

B. When relatively high boiling products were expected (i.e., III and IV), the products were extracted with pentane. This was done by pouring the acetolysis products into an equal volume of cold water, extracting the organic layer with pentane, and washing with water, 5% sodium bicarbonate, and once again with water. The pentane solution was dried over potassium carbonate and then concentrated on a rotary evaporator.

From either procedure, acetate percentages were calculated from infrared spectra, nuclear magnetic resonance spectra, and microhydrogenation data. Olefins were identified by NMR analysis and by subjecting the hydrogenated acetolysis products to vapor-phase chromatographic studies.

Acetolysis of 2,2,5,5-Tetramethylcyclopentyl Tosylate (II). The tosylate (2.14 g, 0.072 mol) was added to a solution of 0.783 g (0.095 mol) of sodium acetate in 40 mL anhydrous acetic acid. The procedure for volatile acetolysis products was followed as in general procedure A. There was 0.85 g (95% if all olefin) of product isolated.

The infrared spectrum showed no evidence of acetate. Only one peak appeared in the GLC on a Carbowax on Firebrick column (110 °C). The product absorbed 96% of the calculated amount of H_2 for 1,2,5,5-tetramethylcyclopentene. The NMR (CCl_4) showed no evidence of vinyl protons.

Acetolysis of 2-Indanyl Tosylate (III). A solution of 3.81 g (13.2 mmol) of the tosylate and 1.50 g (18.3 mmol) of sodium acetate in 100 mL of anhydrous acetic acid was kept at 80 °C for 96 h. The acetolysis products were isolated according to general procedure B and this yielded 1.45 g of product (83% if all olefin).

The infrared showed strong acetate absorption at 1740 and 1245 cm^{-1}. In the NMR the region between 6.9 and 7.5 ppm was used as a standard (4 H) to calculate the percentage of indene, 1-indanyl acetate, and 2-indanyl acetate. The absorptions between 3.15–3.30, 2.81–2.85, and 2.75–2.81 ppm were assigned to indene, 1-indanyl acetate, and 2-indanyl acetate, respectively. The ratio of the two acetates was determined after expansion of the sweep width from 500 to 100 Hz. The product mixture contained 40% indene, 24% 1-indanyl acetate, and 36% 2-indanyl acetate. Each acetate was identified by the enrichment technique.

Acetolysis of 1,1,3,3-Tetramethyl-2-indanyl Tosylate (IV). The tosylate (0.645 g, 1.87 mmol) was added to a solution of 0.172 g (2.09 mmol) of sodium acetate in 60 mL of anhydrous acetate acid in a 100-mL round-bottom flask. The end of the flask was sealed with an oxygen flame. The flask was then placed in an oil bath at 135 °C for 72 h. The flask was then removed and allowed to cool. The top of the flask was broken and the contents were poured into a separatory funnel. The flask was washed several times with acetic acid. Ice cold water (50 mL) was then added. The solution was then treated according to general procedure B and this produced 0.310 g of product (96% if all olefin).

The NMR (CCl_4) spectrum of the acetolysis products showed sharp singlets (4 H) and (6 H) at 7.03 and 1.10 ppm, respectively. There were also singlets (3 H each) at 2.88 and 2.76 ppm. This spectrum agreed favorably with that of 1,2,3,3-tetramethylindene in the literature.[7]

The infrared spectrum showed a weak carbonyl absorption at 1740 cm^{-1}. The amount of acetate present was found to be 7% by weight. This value was obtained by preparing standard solutions of 1,1,3,3-tetramethyl-2-indanyl acetate in 1,2,3,3-tetramethylindene and then comparing the carbonyl absorption of the acetate in the acetolysis products to the carbonyl absorption of the standard solutions.

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Base-Catalyzed Autoxidation of Cyclic Ketones

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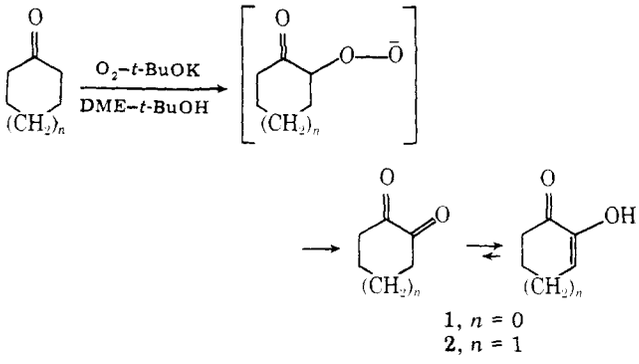
The base-catalyzed autoxidation of ketones yields carboxylic acids.[1] In the case of cyclic ketones, the corresponding dicarboxylic acids are obtained.[1,2] The reaction proceeds via α-ketohydroperoxide anion, followed by carbon–carbon bond cleavage, yielding aldehyde-carboxylic acid which rapidly undergoes further autoxidation to dicarboxylic acid. The intermediate α-ketohydroperoxide can be isolated in the autoxidation of α-substituted ketones. For example, 2-hydroperoxy-2-methylcyclohexanone was obtained from 2-methylcyclohexanone at −50 °C in dimethoxyethane–*tert*-butyl alcohol using potassium *tert*-butoxide as the base.[3] When the reaction was carried out at −8 °C, the major product was 6-ketoheptanoic acid.[3]

If the autoxidation of cyclic ketones is conducted at −20 °C under similar conditions, carbon–carbon bond cleavage is minimized and the intermediate α-ketohydroperoxide eliminates hydroxide ion with formation of α-diketones as the major products.[4] Thus, autoxidation of cyclopentanone in a mixture of dimethoxyethane and *tert*-butyl alcohol (3:2) in the presence of potassium *tert*-butoxide as the base yields 35.7% of cyclopentane-1,2-dione (1) and 18.9% glutaric acid. Autoxidation of cyclohexanone under similar conditions produces 60% of cyclohexane-1,2-dione (2), and 10% adipic acid was isolated from the reaction mixture.



1, n = 0
2, n = 1

Low temperature (−20 °C) autoxidation of cycloheptanone also produces the corresponding diketone. The latter undergoes base-catalyzed aldol condensation with the starting ketone to produce 1-hydroxy-1,1′-bicycloheptyl-2,2′-dione (3). The aldol 3 was formed exclusively when the reaction mixture was worked up without acidification. However, when the reaction mixture was acidified and worked up, along with aldol 3, its dehydration product 1,2,3,4,5,9,10,11-octahydrodicyclohepta[*b*,*d*]furan (4) was isolated as the minor product.

The structures of 3 and 4 were elucidated by NMR (^{13}C and

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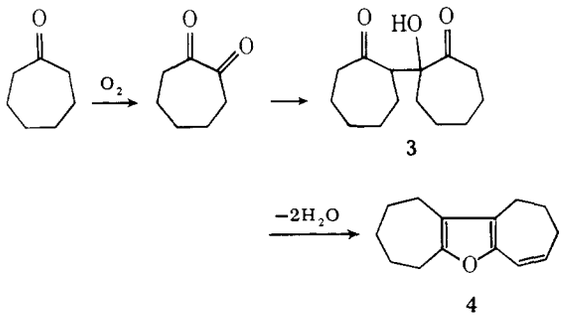
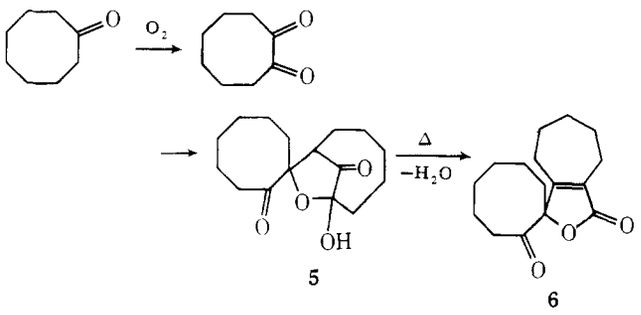


^{1}H) and IR spectroscopy. **3** exhibited two carbonyl carbon signals at δ 217.23 and 215.47 (cycloheptanone carbonyl carbon, δ 211.70[5]) in its ^{13}C NMR spectrum and an IR carbonyl absorption at 1700 cm^{-1}. The signal at δ 4.13 in the ^{1}H NMR spectrum which disappeared on shaking with D_2O and an IR absorption band at 3475 cm^{-1} were ascribed to the hydroxyl group. The lack of carbonyl absorption in the IR spectrum of **4**, two multiplets centered at δ 6.08 and 5.41 for the two vinyl protons in the ^{1}H NMR spectrum, and four ^{13}C NMR signals at δ 151.26, 146.17, 122.50, and 119.82 (furan carbons) and two signals at δ 125.96 and 123.67 (vinyl carbons) confirm the assigned structure. The assignment was further substantiated by the off-resonance decoupled ^{13}C NMR spectrum. The four signals assigned for furan carbons remained unchanged, whereas the two vinyl carbons were split into two doublets.

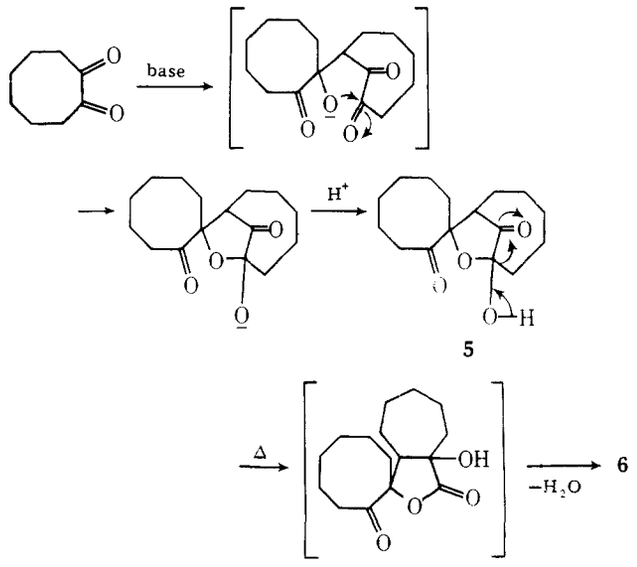
The diketone obtained in the autoxidation of cyclooctanone undergoes self-condensation in base to give 7′-hydroxyspiro[cyclooctane-1,9′-[8]oxabicyclo[5.2.1]decane]-2,10′-dione (**5**) in 56% yield. Heating of **5** above 180 °C causes dehydration with formation of 5,6,7,8-tetrahydrospiro[1*H*-cyclohepta[*c*]-furan-1,1′-cyclooctane]-2′,3(4*H*)-dione (**6**) in 61.1% yield.



The IR spectrum of **5** shows two carbonyl absorptions at 1700 and 1770 cm^{-1} which were assigned to the carbonyl in the eight- and five-membered rings, respectively.[6] In the ^{13}C spectrum **5** exhibited two carbonyl signals at δ 219.43 (furanone carbonyl carbon[8]) and 216.89 (cyclooctanone carbonyl carbon, δ 215.9[5]).

In the IR spectrum **6** showed two carbonyl absorption bands at 1702 and 1788 cm^{-1}. The former was assigned to the cyclooctanone carbonyl and the latter to the γ-lactone carbonyl (butyrolactone carbonyl, 1770 cm^{-1} [9]). In the ^{13}C NMR spectrum of **6** two carbonyl carbon signals appeared at δ 207.52 and 174.00. The former was assigned to the carbonyl carbon of the eight-membered ring and the latter to the δ-lactone carbon (butyrolactone, δ 178.0[5]). The three upfield carbon signals at δ 159.90, 117.04, and 67.43, which in the off-resonance decoupled spectrum did not show any splitting, were assigned to the two vinyl carbons and the spiro carbon, respectively.

Biacetyl undergoes self-condensation under basic conditions at low temperatures (2–5 °C) to yield 1-hydroxy-2,5-dimethyl-5-acetyldihydro-3(2*H*)-furanone.[7] Compound **5** forms in a similar manner from cyclooctane-1,2-dione. Upon heating, **5** undergoes retro-aldol reaction followed by dehydration to yield **6**.



The isolation of the diketones in the case of five- and six-membered rings can be explained by the fact that these compounds exist exclusively in their enol form.[10] In contrast, diketones of seven-membered and larger rings exist predominantly in the keto form, which explains further condensation in base.[12]

In conclusion, the low temperature autoxidation procedure offers an attractive route to diketones from the corresponding ketones, provided that the resulting diketones are enolizable.

Experimental Section

Infrared, ^{1}H NMR, and ^{13}C NMR spectra were obtained on Perkin-Elmer Model 297, Varian T-60, and Varian CFT-20 spectrometers, respectively. Tetramethylsilane was used as an internal standard. All melting points are uncorrected. GLC analysis was carried out on a Hewlett-Packard Model 7620A gas chromatograph using 6 ft 5% Carbowax 20M on 100/120 Supelcoport (for ketones) and 0.1% SP-1000 on 80/100 Carbopack C columns (for diketones 1 and 2) (supplied by Supelco Inc., Bellefonte, Pa.).

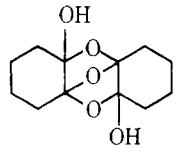
Materials. All ketones were obtained from Aldrich Chemical Co. Potassium *tert*-butoxide (99% dry powder) was from K and K Laboratories, Cleveland, Ohio. Dimethoxyethane (DME) was dried by distilling over CaH_2 and was used immediately.

Autoxidation Procedure. A typical procedure used with cyclohexanone was applied to all of the other ketones. In a four-neck flask equipped with a Vibromixer, low temperature thermometer, and gas inlet tube was dissolved potassium *tert*-butoxide (13.0 g, 0.11 mol) in 200 mL of DME and *tert*-butyl alcohol in a 3:2 ratio. The solution, under vigorous stirring, was cooled to −20 °C in a dry ice–acetone bath, and a rapid stream of oxygen was maintained. After 5 min, cyclohexanone (9.8 g, 0.1 mol) was introduced from a dropping funnel over a period of 15 min and bubbling of oxygen was maintained at −20 °C for a period of 45 min. The reaction mixture was then diluted with 100 mL of water and extracted with 200 mL of ethyl acetate. The aqueous layer was acidified with 15 mL of concentrated HCl followed by extraction with 500 mL of ethyl acetate. The ethyl acetate layer was washed with 5% sodium bicarbonate solution. From the initial ethyl acetate extract was isolated cyclohexanone (1.8 g, 81.6% conversion), and from the sodium bicarbonate extract was isolated adipic acid (1.3 g, 10.9% based on cyclohexanone converted; mp 145–147 °C; IR spectral comparison with an authentic sample). The ethyl acetate extract after sodium bicarbonate washing was dried ($MgSO_4$), and removal of the solvent gave cyclohexane-1,2-dione (**2**) (4.0 g, 43.7% based on cyclohexanone consumed). Vacuum distillation (bp 35–40 °C/0.1 mm) yielded a crystalline solid, mp 36–38 °C. This material was found to be identical with an authentic sample of **2**: ^{1}H NMR ($CDCl_3$) δ 1.5–2.7 (m, 6), 6.06 (t, 1, vinyl), 7.96 (s, hydroxyl); ^{13}C NMR ($CDCl_3$) δ 195.66, 147.37, 118.60, 36.68, 23.99, 23.35.

In another run, after the reaction CO_2 was bubbled into the reaction mixture until the pH was 8. It was diluted with 500 mL of ethyl acetate and filtered. The filtrate was concentrated in vacuo, and the residue was found to contain cyclohexanone (1.6 g, 84.3% conversion) and **2** (7.7 g, 82.1% yield based on cyclohexanone converted) by GLC. After

vacuum distilling at 0.1 mm, **2** (5.6 g, 60.0%) was obtained as a crystalline solid, mp 38–40 °C.

The autoxidation was carried out as before using sodium methoxide (10.8 g, 0.20 mol) in a mixture of 30 mL of hexamethylphosphoramide and 120 mL of DME. By the above workup, **2** and adipic acid were isolated in 41.6 and 24.7% yields, respectively. On standing, a small amount (0.4 g) of a white solid crystallized, mp 150–154 °C. It was recrystallized from acetonitrile. Anal. Calcd for $C_{12}H_{18}O_5$: C, 59.49; H, 7.49. Found: C, 59.43; H, 7.54. It was readily converted to **2** when heated in Me_2SO (performed in an NMR tube). Based on an earlier report, it was found to be the intramolecular hemiacetal of **2**.[13]



Autoxidation of Cyclopentanone. The autoxidation was carried out using cyclopentanone (8.4 g, 0.1 mol) and potassium *tert*-butoxide (13.0 g, 0.11 mol) as above. Cyclopentane-1,2-dione (**1**) and glutaric acid were obtained in 35.7 and 18.9% yields, respectively. The diketone **1** was purified by vacuum distillation: mp 56–58 °C; ^1H NMR ($CDCl_3$) δ 2.10–2.62 (m, 4), 6.50 (t, 1, vinyl), 6.75 (broad s, -OH); ^{13}C NMR ($CDCl_3$) δ 187.53, 153.62, 131.36, 32.58, 22.01.

Autoxidation of Cycloheptanone. Cycloheptanone (11.2 g, 0.1 mol) was autoxidized in 200 mL of a 3:2 mixture of DME–*tert*-butyl alcohol using potassium *tert*-butoxide (13.0 g, 0.11 mol). From the sodium bicarbonate extract a small amount of tarry material was isolated. From the ethyl acetate extract was isolated a light yellow liquid (10.0 g). It was vacuum distilled at 0.1 mm. Fraction 1 (4.0 g), collected between 26–55 °C, was found (by GLC) to be cycloheptanone. By GLC this fraction was found to contain traces of cycloheptane-1,2-dione. Fraction 2 (4.5 g) was collected at 144–148 °C and partly solidified. TLC (silica gel plates, *n*-hexane) showed that it contained two components. By column chromatography (150 g of Bio-Sil A, 100–200 mesh), **4** and **3** were separated with *n*-hexane (1.3 g) and with benzene (2.8 g), respectively. On standing, **3** solidified and was recrystallized from *n*-hexane to give a white solid: mp 69–70 °C; IR ($CHCl_3$) 3450 (OH), 1700 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87–2.20 (m, 5), 2.20–3.10 (m, 5), 4.13 (s, 1, -OH); ^{13}C NMR ($CDCl_3$) δ 217.23 and 215.47 (carbonyl carbons). Anal. Calcd for $C_{14}H_{22}O_3$: C, 70.55; H, 9.31. Found: C, 70.51; H, 9.22.

4 was vacuum distilled, bp 90–93 °C/0.3 mm, to give a pale yellow liquid that was a solid below 10 °C: ^1H NMR ($CDCl_3$) δ 1.17–2.81 (m, 8), 2.05–2.81 (m, 8), 5.41 (m, 1, vinyl), 6.03 (m, 1, vinyl); ^{13}C NMR ($CDCl_3$) δ 123.67 and 125.96 (2 vinyl carbons), 119.82, 122.50, 146.17, and 151.26 (4 furan carbons), 23.70, 24.11, 25.49, 26.66, 28.60, 28.93, 30.75, 30.94. Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.90; H, 9.04.

Further chromatography with chloroform gave a crystalline compound (~50 mg). It was recrystallized from *n*-hexane: mp 76–78 °C; IR ($CHCl_3$) 1720 and 1785 cm^{-1} (C=O). Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.73; H, 7.91. It was confirmed as a cycloheptanone analogue of **6**.

Exclusive Formation of 3. Cycloheptanone was autoxidized, and the reaction mixture was diluted with water and extracted with ethyl acetate. It was washed with sodium bicarbonate solution, dried ($MgSO_4$), and concentrated in vacuo to give a yellow liquid (10.0 g). The liquid was vacuum distilled, and cycloheptanone (with traces of 1,2-dione) was collected at 26–30 °C/0.1 mm (4.5 g) and **3** at 120–130 °C/0.1 mm (4.0 g) (42.8% conversion; yield of **3**, 39.0%).

Conversion of 3 to 4. The aldol **3** (5.0 g, 0.02 mol) was dissolved in 100 mL of ether, 4–5 drops of concentrated HCl was added, and the mixture was stirred at room temperature. The reaction mixture turned brown, and after 30 min it was washed with sodium bicarbonate solution, dried ($MgSO_4$), and concentrated to give **4**, which was vacuum distilled, bp 90–95 °C/0.3 mm (4.0 g, 94.2%).

Autoxidation of Cyclooctanone. Cyclooctanone (12.6 g, 0.1 mol) in 200 mL of DME–*tert*-butyl alcohol (3:2), using potassium *tert*-butoxide (13.5 g, 0.11 mol), was autoxidized at −20 °C for 1 h. Along with a small amount of suberic acid (0.2 g), mp 135–140 °C (identical with an authentic sample, IR and mixture melting point), a light brown liquid (10.0 g) was isolated. It was vacuum distilled, and cyclooctane was collected at 25–35 °C/0.1 mm (7.0 g, 48.1% conversion; by GLC it was found to contain a small amount of the corresponding 1,2-diketone) and **5** solidified in the distillation flask (3.5 g, 56.0%), mp 100–130 °C. It was recrystallized from methanol–water (1:1): mp 138–140 °C; IR ($CHCl_3$) 3580 and 3425 (OH), 1770 and 1700 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.73 (s, 1, OH, disappears with D_2O), 3.20 (t, 1); mass spectrum, (M^+) 280; ^{13}C NMR ($CDCl_3$) δ 219.43 and 216.89 (carbonyl carbons). Anal. Calcd for $C_{16}H_{24}O_4$: C, 68.54; H, 8.63. Found: C, 68.62; H, 8.74.

Thermal Conversion of 5 to 6. Crude **5** (3.5 g, 0.012 mol) was distilled at 180 °C in an oil bath at 0.1 mm pressure. **6** was collected as a syrupy liquid (2.0 g, 61.1%), which solidified on standing, mp 74–76 °C. It was recrystallized from *n*-hexane: mp 81–83 °C; IR ($CHCl_3$) 1788 and 1702 cm^{-1} (C=O); ^{13}C NMR ($CDCl_3$) δ 207.52 and 174.00 (carbonyl carbons), 150.90 and 117.04 (vinyl carbons), 67.43 (spiro carbon); mass spectrum, (M^+) 262. Anal. Calcd for $C_{16}H_{22}O_3$: C, 73.25; H, 8.45. Found: C, 73.47; H, 8.66.

Registry No.—**1**, 3008-40-0; **2**, 765-87-7; **2** intramolecular hemiacetal, 33832-15-4; **3**, 68258-05-9; **4**, 68258-06-0; **5**, 68258-07-1; **6**, 68258-08-2; 4,5,6,7-tetrahydrospiro[cycloheptane-1,1′(3′*H*)-isobenzofuran]-2,3′-dione, 68258-09-3; cyclohexanone, 108-94-1; cyclopentanone, 120-92-3; cycloheptanone, 502-42-1; cyclooctanone, 502-49-8.

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Mercuric Acetate Oxidation of 1-Vinylcycloalkenes: Diels–Alder Reactivity of Resultant Allylic Diene Acetates

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Diels–Alder chemistry recently has been the subject of accelerated interest among synthetic chemists. Coupling of the inherent power of the Diels–Alder cycloaddition of simple substrates with the use of structurally sophisticated dienes and dienophiles has been the major focus of this effort. Many of the variations of the dienic Diels–Alder partner have arisen from a formal direct replacement of one or more of the vinylic hydrogen atoms of readily available dienes by other substituents. We were interested in obtaining 1-vinylcyclohexene and 1-vinylcyclopentene which were oxidized at C_6 and C_5, respectively, that is, dienes in which a carbon atom allylic to the diene itself bears a heteroatomic substituent, for use as Diels–Alder dienes. This paper describes the direct oxidation of 1-vinylcyclohexene and 1-vinylcyclopentene and some Diels–Alder reactivity of the resultant diene acetates.

The allylic acetoxylation of 1-(1-cyclohexenyl)cyclohexene (**1**) by reaction with 2 equiv of mercuric acetate [$Hg(OAc)_2$]

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