ligands, which does not seem unlikely in view of the well-known ability of Ce(IV) to complex alcohols and alkoxides.[11,12] The two reaction products would thus be formed by one-step, competing ligand-transfer reactions, with no benzyl cations involved as intermediates. The observed effect of added chloride ions could be explained as due to an increase of the ratio of chloro ligands to methoxy ligands, thus leading to a reduced ratio of methoxylation to chlorination.

Experimental Section

Most techniques and apparatus were as previously reported.[1] MeOH (Erba RS, water content 0.05%) and EtOH (Erba RSE, 99.9% pure) were used as received. The aromatic substrates (reagent grade chemicals) were purified by standard methods. CPC was prepared in good yield according to a literature method.[11]

General Oxidation Procedure. A solution of CPC (6.4 g, 12 mmol) in either MeOH or EtOH (150 mL) was flushed with nitrogen at room temperature (15 min), the proper methylbenzene (6 mmol) was added, and the resulting mixture was brought to boil by immersion in a preheated oil bath. After the red-orange color of Ce(IV) faded, the solution was rapidly cooled and poured into light petroleum that was thoroughly washed with water and dried (Na_2SO_4). The crude material obtained after removal of the solvent was eluted on acid-washed silica gel with $CHCl_3$/light petroleum 1:1. All isolated compounds were checked by GLC and found to be at least 99% pure.

Acknowledgments. The C.N.R. financial support is greatly acknowledged for the part of the work carried out at the University of Perugia. Thanks are also due to Professors E. Baciocchi and G. Illuminati for stimulating discussions.

Registry No.—**3**, 65915-93-7; CPC, 40888-83-3.

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Reaction of Singlet Oxygen with Enamino Lactones. Conversion of Lactones to α-Keto Lactones

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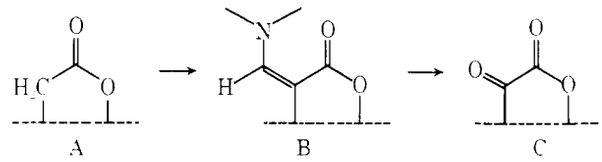
We have recently reported[1] a novel method for the conversion of ketones to α-diketones utilizing the facile cleavage of intermediate enamino ketones with singlet oxygen. The mildness and selectivity of this synthetic sequence prompted us to investigate its application to other carbonyl systems. We now report an extension of this procedure to the conversion of lactones to α-keto lactones.

Previous syntheses of α-keto lactones have generally been limited to the condensation of α-keto acids or esters with aldehydes followed by lactonization to α-keto-γ-butyrolactones.[2-5] These methods are often accompanied by side reactions such as dehydration of the intermediate γ-hydroxy-α-keto acids.[5] In our procedure, the α-keto lactones (both five- and six-membered cases) are formed *directly* from the parent lactones by a two-step process which, as outlined below, should have general applicability. The method involves conversion of the lactone A to the enamino lactone B by treatment with tris(dimethylamino)methane followed by oxidative cleavage of the enamine double bond with singlet oxygen to form the α-keto lactone C or its enol tautomer.



Our initial attempts to form the enamino intermediate B employed alkoxybis(dimethylamino)methane reagents along the lines of our earlier investigation on the oxidation of ketones to α-diketones.[1] Under these conditions, however, conversion to B was slow and often incomplete. We therefore used the more reactive DMF derivative, tris(dimethylamino)methane,[6] as recently reported by Martin and Moore[7] for the preparation of α-enamino butyrolactones.

Table I summarizes the systems studied, reaction conditions, and yields. All of the lactones (**1–6**) reacted readily with tris(dimethylamino)methane to yield the α-enamino derivatives (**7–12**). The second stage oxidative cleavage under conditions of dye-sensitized photooxygenation gave the desired α-keto lactones (**13–18**) in the yields shown. In all cases investigated, the α-keto lactones exist either exclusively or primarily in their enol forms.

Current interest in the preparation of α-methylene lactones[8] prompted us to explore the reaction of α-keto lactones **16** and **18** with phosphoranes under a large variety of reaction conditions[9] (temperature, solvent, reaction time, and method of ylide generation). Thus far, we have been unsuccessful in effecting a Wittig condensation with these systems. Under all conditions studied, the relatively acidic enol was rapidly and irreversibly deprotonated by the ylide to give, upon workup, only polymeric material, starting keto lactone, and traces of triphenylphosphine oxide.

We are currently studying further extensions of this synthetic sequence for the preparation of other α-keto carbonyl systems.

Experimental Section

Melting points were obtained in a Melt-Temp apparatus and are uncorrected. Infrared spectra were recorded in chloroform or neat using a Perkin-Elmer 700A spectrometer. NMR spectra were obtained with either a Perkin-Elmer R-32 90-MHz instrument or a Bruker 270-MHz instrument using tetramethylsilane as an internal standard. Mass spectra were recorded on a Hitachi RMU-6 spectrometer operated at 70 eV. Elemental analyses were performed by Dr. Robert Rittner, Olin Laboratories, New Haven, Conn.

Tris(dimethylamino)methane.[6] A mixture of 94.0 g (1.30 mol) of dimethylformamide and 57.0 g (0.53 mol) of dimethylcarbamyl chloride was heated at 120 °C under nitrogen for 24 h. The mixture was cooled to room temperature, and the resulting white crystals were filtered and washed several times with 100-mL portions of DMF and dried under vacuum for 48 h. A solution of 0.12 mol of lithium dimethylamide was prepared by adding 54 mL of a 2.2 M *n*-BuLi–hexane solution to a −78 °C solution of excess dimethylamine in 500 mL of THF followed by warming to 0 °C for 30 min. The solution was again cooled to −78 °C, and 13.5 g (0.10 mol) of the DMF–dimethylcarbamyl chloride adduct was added through Gooch tubing. The resulting slurry was stirred at room temperature for 18 h. Removal of solvent by distillation followed by vacuum distillation gave 7.4 g (51%) of the desired tris(dimethylamino)methane: bp 48 °C (12 mm) [lit.[6] bp 40–43 °C (12 mm)]; IR (neat) 3000–2700, 1475, 1450, 1345 cm^{-1}; NMR ($CDCl_3$) δ 3.05 (s, 1 H), 2.31 (s, 18 H); MS *m/e* 102, 44, 43.

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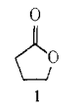
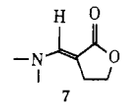
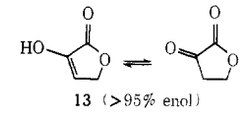
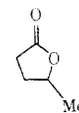
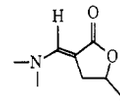
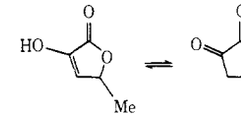
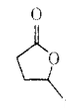
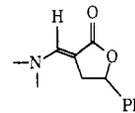
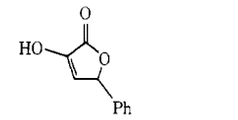
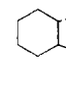
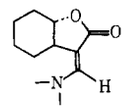
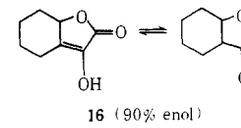
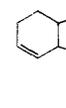
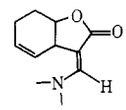
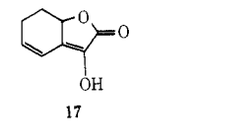
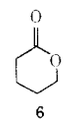
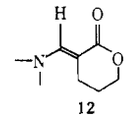
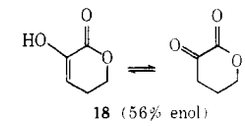
Table I. Conversion of Lactones to α-Keto Lactones

Lactone		Enamino lactone		Keto lactone[c]
 1	a, 48 h, 90%	 7	b, 86%	 13 (>95% enol)
 2	a, 48 h, 90%	 8	b, 86%	 14 (>95% enol)
 3	a, 24 h, 87%	 9	b, 65%	 15
 4	a, 72 h, 86%	 10	b, 86%	 16 (90% enol)
 5	a, 60 h, 87%	 11	b, 72%	 17
 6	a, 30 h, 86%	 12	b, 72%	 18 (56% enol)

[a] Reaction of the lactone with 1.5 equiv of tris(dimethylamino)methane at 70 °C. [b] Photooxygenation of the enamino lactone in methylene chloride at −78 °C using 5 mg of bis(acenapthalene)thiophene and a Sylvania DWY 650-W lamp operated at 70 V followed by column chromatography on silica gel. [c] A mixture of keto and enol forms. The ratio of tautomers was determined by 90- and 270-MHz NMR spectroscopy in $CDCl_3$ at 25 °C.

α-(Dimethylaminomethylene)-γ-butyrolactone (7). A mixture of 0.35 g (4.0 mmol) of γ-butyrolactone and 0.79 g (5.4 mmol) of tris(dimethylamino)methane was heated under nitrogen with stirring at 70 °C for 48 h. The crude product was dried under vacuum for 2 h and crystallized from ether to give 0.53 g (90%) of **7**: mp 97–99 °C; IR ($CHCl_3$) 1710, 1620–1640 cm^{-1}; NMR ($CDCl_3$) δ 7.15 (t, 1 H), 4.25 (t, 2 H), 3.06 (m, 2 H), 3.04 (s, 6 H).

Anal. Calcd for $C_7H_{11}NO_2$: C, 59.56; H, 7.85; N, 9.92. Found: C, 59.69; H, 7.85; N, 10.10.

α-(Dimethylaminomethylene)-γ-valerolactone (8). A mixture of 0.67 g (6.7 mmol) of γ-valerolactone (**2**) and 1.40 g (9.75 mmol) of tris(dimethylamino)methane was heated under nitrogen with stirring at 70 °C for 48 h. The crude product was dried under vacuum and crystallized from ether to give 0.94 g (90%) of **8**: mp 54–55 °C; IR ($CHCl_3$) 1710, 1620, 1340, 1300 cm^{-1}; NMR ($CDCl_3$) δ 7.10 (t, 1 H), 4.52 (m, 1 H), 3.02 (s, 6 H), 3.0 (dd, 2 H), 1.30 (d, 3 H).

Anal. Calcd for $C_8H_{13}NO_2$: C, 61.91; H, 8.44; N, 9.03. Found: C, 61.70; H, 8.32; N, 9.20.

α-(Dimethylaminomethylene)-γ-phenyl-γ-butyrolactone (9). A mixture of 0.48 g (3.0 mmol) of γ-phenyl-γ-butyrolactone (**3**) and 0.65 g (4.5 mmol) of tris(dimethylamino)methane was heated at 70 °C under nitrogen with stirring for 24 h. The crude yellow solid was dried under vacuum and recrystallized from ether/ethyl acetate (4:1) to give 0.57 g (87%) of **9**: mp 145–147 °C: IR ($CHCl_3$) 1715, 1625, 1320 cm^{-1}; NMR ($CDCl_3$) δ 7.33 (s, 5 H), 7.17 (t, 1 H), 5.35 (dd, 1 H), 3.60 (dd, 1 H), 2.98 (s, 6 H), 2.90 (dd, 1 H).

Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45. Found: C, 71.86; H, 6.85; N, 6.51.

***trans*-2-(Dimethylaminomethylene)-2-(2-hydroxycyclohexyl)acetic Acid Lactone (10).** A mixture of 1.60 g (11.4 mmol) of lactone **4** and 1.84 g (12.7 mmol) of tris(dimethylamino)methane was heated under nitrogen with stirring at 70 °C. After 48 h the crude product was crystallized from ether/pentane (4:1) to give 1.90 g (86%) of enamino lactone **10**: mp 76–78 °C; IR ($CHCl_3$) 1715, 1620, 1440, 1290 cm^{-1}; NMR ($CDCl_3$) δ 7.15 (d, 1 H), 3.50 (bm, 1 H), 3.00 (s, 6 H), 3.0–0.70 (bm, 9 H).

Anal. Calcd for $C_{11}H_{17}NO_2$: C, 67.66; H, 8.78; N, 7.17. Found: C, 67.60; H, 8.69; N, 7.20.

***cis*-2-(Dimethylaminomethylene)-2-(2-hydroxycyclohex-5-enyl)acetic Acid Lactone (11).** A mixture of 0.60 g (4.34 mmol) of lactone **5** and 0.93 g (6.44 mmol) of tris(dimethylamino)methane was heated under nitrogen with stirring at 70 °C for 60 h. The crude product was crystallized from ether/acetone (20:1) to give 0.73 g (87%) of enamino lactone **11**: mp 100–102 °C; IR ($CHCl_3$) 1710, 1620, 1280, 1190 cm^{-1}; NMR ($CDCl_3$) δ 7.14 (s, 1 H), 5.80 (m, 1 H), 5.50 (m, 1 H), 4.62 (m, 1 H), 3.69 (m, 1 H), 3.04 (s, 6 H), 2.5–1.5 (m, 4 H).

Anal. Calcd for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25. Found: C, 65.65; H, 7.44; N, 7.00.

α-(Dimethylaminomethylene)-δ-valerolactone (12). A mixture of 0.40 g (4.0 mmol) of lactone **6** and 0.87 g (6.0 mmol) of tris(dimethylamino)methane was heated at 70 °C under nitrogen with stirring for 30 h. The crude product was crystallized from ether/pentane (5:1) to give 0.53 g (86%) of enamino lactone **12**: mp 59–60 °C; IR ($CHCl_3$) 1675, 1575, 1440, 1390 cm^{-1}; NMR ($CDCl_3$) δ 7.52 (s, 1 H), 4.20 (t, 2 H), 3.10 (s, 6 H), 2.67 (p, 2 H), 1.85 (t, 2 H).

Anal. Calcd for $C_8H_{13}NO_2$: C, 61.91; H, 8.44; N, 9.03. Found: C, 61.87; H, 8.28; N, 9.05.

General Photooxygenation Procedure. A solution of 3–5 mmol of enamino lactone and 5 mg of bis(acenaphthalene)thiophene (BANT) in 150 mL of dry methylene chloride was photooxygenated at −78 °C using a constant circulating oxygen supply and a Sylvania DWY 650-W lamp operated externally through Pyrex at 70 V. The uptake of oxygen was rapid and ceased after 30 min and 1.2 equiv of oxygen. The irradation was stopped, and the reaction mixture was allowed to warm slowly to room temperature. The mixture was concentrated and column chromatographed on silica gel using 2% acetone in methylene chloride to give the corresponding α-keto lactone.

α-Keto-γ-butyrolactone (13): 86%; IR ($CHCl_3$) 3600–2900, 1760 cm^{-1}; NMR ($CDCl_3$) δ 6.95 (s, 1 H), 4.75 (s, 1 H), 2.95 (m, 2 H); DNP derivative, mp 219–220 °C (lit.[5] mp 218 °C).

Anal. Calcd for $C_{10}H_8N_4O_6$: C, 42.87; H, 2.88; N, 20.00. Found: C, 42.68; H, 2.90; N, 19.83.

α-Keto-γ-valerolactone (14): 68%; mp 71–73 °C (lit.[5] mp 70–73 °C); IR ($CHCl_3$) 3500, 3300, 1760, 1400, 1320 cm^{-1}; NMR ($CDCl_3$) δ 6.65 (bs, 1 H), 6.27 (d, 1 H), 5.08 (m, 1 H), 3.0 (m), 2.25 (m), 1.42 (d, 3 H); MS *m/e* 114 (M^+), 69, 57, 44.

Anal. Calcd for $C_5H_6O_3$: C, 52.63; H, 5.30. Found: C, 52.19; H, 4.98.

α-Keto-γ-phenyl-γ-butyrolactone (15): 66%; IR ($CHCl_3$) 3500, 3350, 1765, 1500 cm^{-1}; NMR ($CDCl_3$) δ 7.30 (bs, 5 H), 6.29 (d, 1 H), 5.82 (d, 1 H); DNP derivative, mp 115–117 °C.

Anal. Calcd for $C_{16}H_{12}N_4O_6$: C, 53.94; H, 3.39; N, 15.72. Found: C, 54.28; H, 3.60; N, 15.96.

α-Keto Lactone 16: 86%; mp 98–101 °C (lit.[3] mp 99–110 °C); IR ($CHCl_3$) 3500, 3300, 1750 cm^{-1}; NMR ($CDCl_3$) δ 6.55 (bs, 1 H), 4.58 (m, 1 H), 3.00 (m, 2 H), 2.6–1.0 (m, 6 H); MS *m/e* 154 (M^+), 110, 97, 80, 79.

α-Keto Lactone 17: 72%; mp 93–96 °C: IR ($CHCl_3$) 3500, 3300, 1750, 1690, 1600 cm^{-1}; NMR ($CDCl_3$) δ 6.55 (d, 1 H), 6.08 (m, 1 H), 5.87 (dd, 1 H), 2.71–1.4 (m, 4 H).

Anal. Calcd for $C_8H_8O_3$: C, 63.15; H, 5.30. Found: C, 62.80; H, 5.04.

α-Keto-δ-valerolactone (18): 72%; IR ($CHCl_3$) 3450, 1765–1700 cm^{-1}; NMR ($CDCl_3$) δ 5.95 (t, 1 H), 5.75 (bs, 1 H), 4.60 (t, 2 H), 4.45 (t, 2 H), 2.87 (t, 2 H), 2.50 (m, 2 H); MS *m/e* 114 (M^+), 69, 57, 56, 41.

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Registry No.—**1**, 96-48-0; **2**, 108-29-2; **3**, 1008-76-0; **4**, 27345-71-7; **5**, 34896-02-1; **6**, 542-28-9; **7**, 34009-40-0; **8**, 62527-57-5; **9**, 66516-03-8; **10**, 66516-02-7; **11**, 66516-01-6; **12**, 66516-00-5; **13**, 25409-36-3; **13** DNP, 3777-94-4; **14**, 21053-73-6; **15**, 19252-20-1; **15** DNP, 66515-98-8; **16**, 66515-99-9; **17**, 66516-05-0; **18**, 66516-04-9; tris(dimethylamino)-methane, 5762-56-1; dimethylformamide, 68-12-2; dimethylcarbamyl chloride, 79-44-7.

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An Efficient Route to Intermediates for the Synthesis of 11-Deoxyprostaglandins

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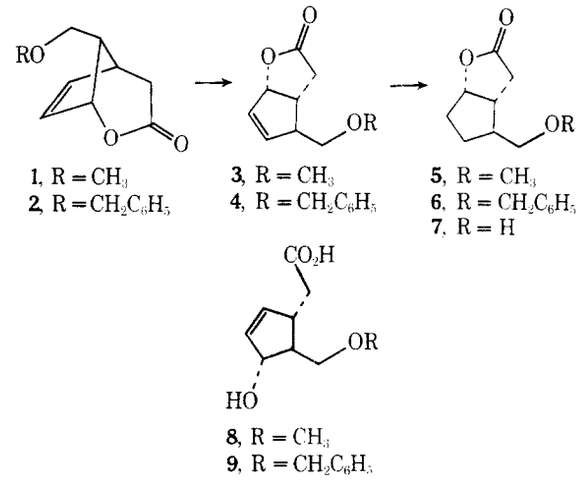
The benzyloxy bicyclic lactone **2** is an important starting material for the preparation of the unsaturated lactone **4**, an intermediate for the synthesis of A prostaglandins[1] and the lactone alcohol **7**. The latter is a key intermediate for the synthesis of pharmacologically interesting 11-deoxyprostaglandins.[2] Since the existing route from the bicyclic lactone **2** to **4** and thence to **7** involves several steps,[3–5] we have developed a simple one-step transformation of **2** to **4** involving a cationic rearrangement cyclization sequence. Compound **4** can be transformed into **7** in two additional steps, thus providing a convenient approach to 11-deoxyprostaglandins. A corresponding sequence from **1**, the methyl ether analogue of **2**, to **7** has also been developed.



1, R = CH_3
2, R = $CH_2C_6H_5$
3, R = CH_3
4, R = $CH_2C_6H_5$
5, R = CH_3
6, R = $CH_2C_6H_5$
7, R = H
8, R = CH_3
9, R = $CH_2C_6H_5$

Treatment of the lactone methyl ether **1** or the benzyl ether **2** with concentrated sulfuric acid in an aprotic solvent at room temperature for 12 h smoothly afforded in ca. 90% yield the rearranged lactones **3** and **4**. The rearrangement was effected in similar yields with *p*-toluenesulfonic acid or boron trifluoride etherate as catalysts. Alternatively, the optically active lactones **3** and **4** were obtained directly from the resolved intermediates **8** and **9** by treatment with concentrated H_2SO_4 as described above. Catalytic hydrogenation of **3** over 5% Rh/alumina gave the saturated ether **5**, which was demethylated using BBr_3 to furnish the desired alcohol **7** in 77% overall yield. However, catalytic hydrogenation and debenzylation of the benzyl ether **4** to provide **7** in 90% overall yield were best effected sequentially over 5% Rh/alumina[4] (to give **6**) followed by 5% Pd/C in ethyl acetate. Contrary to an earlier report, there was no evidence of hydrogenolysis of the allylic hydroxyl group in **4**.[3,6]

The three-step sequence of **2** to **7** or alternatively **9** to **7** (if optically active material is desired) constitutes the preferred route for intermediates for the preparation of 11-deoxyprostaglandins.

Experimental Section[7]

Preparation of Methyl Ether Lactone 3. A solution of 5.26 g (15 mmol) of the lactone **1** in 30 mL of Et_2O was treated with 0.3 mL of concentrated H_2SO_4, and the mixture was stirred under a nitrogen atmosphere overnight at room temperature. The reaction mixture was neutralized (pH 8) with saturated sodium bicarbonate solution, the Et_2O layer was separated, and the aqueous layer was further extracted with EtOAc (3 × 15 mL). The combined organic extracts were dried (Na_2SO_4) and evaporated to a crude oil weighing 2.4 g (95% yield). The product was purified by chromatography on silica gel (Baker) using CH_2Cl_2 followed by CH_2Cl_2/EtOAc (9:1) as eluent to furnish **3**: 2.2 g (87% yield); mp 50–51 °C; IR ($CHCl_3$) 1779 cm^{-1}; NMR ($CDCl_3$) δ 2.0–3.1 (4 H, m), 3.25 (3 H, s, $-OCH_3$), 3.2–3.4 (2 H, m, $-CH_2O$), 5.45 (1 H, m, –CHOCO), and 5.94 (2 H, m, olefinic); TLC R_f 0.5 (EtOAc).

Reduction of the Methyl Ether Lactone 3 to 5. A solution of 1.8 g (10.7 mmol) of unsaturated lactone methyl ether **3** in 20 mL of THF and 0.2 g of 5% rhodium on alumina was hydrogenated at 25 °C and atmospheric pressure until absorption ceased (15 min). The reaction mixture was filtered through Celite and evaporated to yield an oil weighing 1.8 g (100% yield). The oil was chromatographed on silica gel (Baker) eluting with CH_2Cl_2 followed by CH_2Cl_2/EtOAc (4:1) to afford **5** as a colorless oil: 1.76 g (96.0% yield); IR 1779 cm^{-1}; NMR ($CDCl_3$) δ 1.2–3.0 (8 H, m), 3.35 (2 H, d, J = 6 Hz, $-CH_2O-$), 3.38 (3 H, s, $-OCH_3$), and 5.00 (1 H, br, –CHOCO); TLC R_f 0.25 (3:1 C_6H_6/EtOAc).

Preparation of Benzyl Ether Lactone 4. Following the procedure described for the preparation of **3**, the lactone **2** or the corresponding hydroxy acid (+)-**9** was converted to **4** (91% yield), a pale yellow oil, identical in all respects with a sample prepared by the method of Corey and Snider.[4] Optically active material had $[\alpha]^{27}_D$ +214° (*c* 1.0, $CHCl_3$).

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