(0.5 mL), acetic acid (0.3 g, 5 mmol), and 5% platinum on charcoal (0.05 g) until 2 equiv of hydrogen had been consumed (approximately 5 h). The catalyst was then removed by filtration, and the filtrate was diluted with about 15 mL of water. The product first separated as an oil, which on stirring solidified. The crude nitrone was collected, rinsed with 50% ethanol, and dried to give 1.85 g (6.6 mmol, 73%) of a bright yellow powder: mp 121–124 °C; NMR ($CDCl_3$, 90 MHz) δ 1.22 (t, 6 H, J = 7 Hz), 2.39 (s, 3 H), 3.42 (q, 4 H, J = 7 Hz), 6.65 (d, 2 H, J = 9 Hz), 7.16 (d, 2 H, J = 8 Hz), 7.61 (d, 2 H, J = 8 Hz), 7.69 (s, 1 H), 8.25 (d, 2 H, J = 9 Hz); UV (EtOH) λ_{max} 388 nm (ϵ 44 100), exact mass calcd for $C_{18}H_{22}N_2O$ 282.1732, found 282.1744.

α-(4-(Diethylamino)phenyl)-*N*-(4-cyanophenyl)nitrone (1e): mp 206–207 °C; NMR ($CDCl_3$, 90 MHz) δ 1.23 (t, 6 H, J = 7 Hz), 3.46 (q, 4 H, J = 7 Hz), 6.68 (d, 2 H, J = 9 Hz), 7.67 (d, 2 H, J = 9 Hz), 7.83 (s, 1 H), 7.93 (d, 2 H, J = 9 Hz), 8.32 (d, 2 H, J = 9 Hz); UV (EtOH) λ_{max} 427 nm (ϵ 39 300); exact mass calcd for $C_{18}H_{19}N_3O$ 293.1528, found 293.1536.

α-Phenyl-*N*-(4-carbethoxyphenyl)nitrone (1f): mp 143–145 °C (lit.[8] mp 141–142 °C); NMR ($CDCl_3$, 90 MHz) δ 1.48 (t, 3 H, J = 7 Hz), 4.44 (q, 2 H, J = 7 Hz), 7.4 (m, 3 H), 7.86 (d, 2 H, J = 8 Hz), 7.99 (s, 1 H), 8.18 (d, 2 H, J = 8 Hz), 8.4 (m, 2 H); UV (EtOH) λ_{max} 324 nm (ϵ 20 000); exact mass calcd for $C_{16}H_{15}NO_3$ 269.1052, found 269.1054.

α-(4-Cyanophenyl)-*N*-(4-carbethoxyphenyl)nitrone (1g): mp 185–187 °C; NMR ($CDCl_3$, 90 MHz) δ 1.46 (t, 3 H, J = 7 Hz), 4.42 (q, 2 H, J = 7 Hz), 7.72 (d, 2 H, J = 9 Hz), 7.83 (d, 2 H, J = 9 Hz), 8.03 (s, 1 H), 8.17 d, 2 H, J = 9 Hz), 8.48 (d, 2 H, J = 9 Hz); UV (EtOH) λ_{max} 336 nm (ϵ 29 100); exact mass calcd for $C_{17}H_{14}N_2O_3$ 294.1004, found 294.1005.

α-(4-Methoxyphenyl)-*N*-(4-carbethoxyphenyl)nitrone (1h): mp 152–154 °C; NMR ($CDCl_3$, 90 MHz) δ 1.41 (t, 3 H, J = 7 Hz), 3.89 (s, 3 H), 4.39 (q, 2 H, J = 7 Hz), 6.95 (d, 2 H, J = 9 Hz), 7.81 (d, 2 H, J = 8 Hz), 7.88 (s, 1 H), 8.11 (d, 2 H, J = 8 Hz), 8.38 (d, 2 H, J = 9 Hz); UV (EtOH) λ_{max} 346 nm (ϵ 26 000); exact mass calcd for $C_{17}H_{17}NO_4$ 299.1158, found 299.1163.

α-Phenyl-*N*-(4-cyanophenyl)nitrone (1i): mp 161–162 °C (lit.[20] mp 144–148 °C); NMR ($CDCl_3$, 90 MHz) δ 7.4 (m, 3 H), 7.71 (d, 2 H), 7.88 (d, 2 H), 7.89 (s, 1 H), 8.3 (m, 2 H); UV (EtOH) λ_{max} 328 nm (ϵ 21 200); exact mass calcd for $C_{14}H_{10}N_2O$ 222.0793, found 222.0797.

α-(4-Methoxyphenyl)-*N*-phenylnitrone (1j): mp 119–120 °C (lit.[21] mp 118 °C); NMR ($CDCl_3$, 90 MHz) 3.87 (s, 3 H), 6.94 (d, 2 H, J = 9 Hz), 7.3–7.5 (m, 3 H), 7.6–7.8 (m, 2 H), 7.80 (s, 1 H), 8.36 (d, 2 H, J = 9 Hz); UV (EtOH) λ_{max} 329 nm (ϵ 23 300); exact mass calcd for $C_{14}H_{13}NO_2$ 227.0946, found 227.0937.

α-(4-Methylphenyl)-*N*-phenylnitrone (1k): mp 91–93 °C (lit.[22] mp 85–87 °C); NMR ($CDCl_3$, 90 MHz) δ 2.37 (s, 3 H), 7.12 (d, 2 H, J = 9 Hz), 7.2–7.4 (m, 3 H), 7.6–7.7 (m, 2 H), 7.79 (s, 1 H), 8.19 (d, 2 H, J = 9 Hz); UV (EtOH) λ_{max} 318 nm (ϵ 24 000); exact mass calcd for $C_{14}H_{13}NO$ 211.0997, found 211.0992.

α-(4-(Dimethylamino)phenyl)-*N*-(3-nitrophenyl)nitrone (2): mp 179–181 °C (lit.[17] mp 172 °C; NMR ($CDCl_3$, 90 MHz) δ 3.12 (s, 3 H), 6.69 (d, 2 H, J = 8 Hz), 7.5–8.7 (m, 4 H), 7.83 (s, 1 H), 8.31 (d, 2 H, J = 8 Hz); UV (EtOH) λ_{max} 400 nm (ϵ 40 200); exact mass calcd for $C_{15}H_{15}N_3O_3$ 285.1113, found 285.1130.

α-Styryl-*N*-(4-carbethoxyphenyl)nitrone (3): mp 149–150 °C; NMR ($CDCl_3$, 90 MHz) δ 1.43 (t, 3 H, J = 7 Hz), 4.40 (q, 2 H, J = 7 Hz), 7–8 (m, 7 H), 7.80 (d, 2 H, J = 8 Hz), 7.87 (s, 1 H), 8.12 (d, 2 H, J = 8 Hz); UV (EtOH) λ_{max} 392 nm (ϵ 45 500); exact mass calcd for $C_{18}H_{17}NO_3$ 295.1208, found 295.1221.

α-[2-(2-Furyl)ethenyl]-*N*-(4-carbethoxyphenyl)nitrone (4): mp 164–166 °C; NMR ($CDCl_3$, 90 MHz) δ 1.43 (t, 3 H, J = 7 Hz), 4.39 (q, 2 H, J = 7 Hz), 6.4–6.5 (m, 1 H), 6.57 (d, 1 H, J = 3 Hz), 7.0–7.6 (m, 3 H), 7.79 (d, 2 H, J = 9 Hz), 7.81 (d, 2 H, J = 8 Hz), 8.12 (d, 2 H, J = 9 Hz); UV (EtOH) λ_{max} 388 nm (ϵ 34 900); exact mass calcd for $C_{16}H_{15}NO_4$ 285.1001, found 285.1002.

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A Novel Synthesis of Spironolactone. An Application of the Hydroformylation Reaction

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Spironolactone (1), an aldosterone antagonist introduced in the late 1950s is a high-volume diuretic and belongs to a growing class of steroidal spirolactones.[1] Our interest in this class of lactones has lead us to develop a new approach to spironolactone from the readily available acetylene adduct **2**. We thought that hydroformylation[2] of ethisterone **2** would lead to the lactol **3**, which would give lactone **8** upon oxidation. Initial attempts at hydroformylating ethisterone were successful but with the caveat that the 4,5 olefin was also reduced. However, we felt that if the alkene could be deconjugated by ketal formation the now isolated alkene would be less susceptible to reduction and the reaction would proceed in the desired sense. Indeed, when the derived ketal **5** was hydroformylated, a clean reaction ensued, giving lactol **6** as the primary product in 90% yield without over-reduction. The reaction can be carried out with as little as 0.01% catalyst in the form of $Rh_2(OAc)_4$, but reaction times at our standard 15 bar operating pressure tend to extend beyond 48 h. The best results were achieved with 0.1 mol % $Rh_2(OAc)_4$, 0.5 mol % triphenylphosphine in ethyl acetate at 80 °C, and 15 bar pressure of a 1:1 mixture of carbon monoxide/hydrogen. Triphenylphosphine was necessary to achieve clean conversions since its omission lead to much lower yields.

Oxidation of lactol **6** to the lactone **7** proceeded quantitatively with $Ru(Ph_3P)_3Cl_2$ and anhydrous *N*-methylmorpholine *N*-oxide.[3] If anhydrous NMO is not used the reaction fails to go to completion. Other oxidants such as PDC[4] and PCC[5] are also successful. Hydrolysis of the ketal proceeds smoothly, giving enone **8** in 97% overall yield. In general the intermediate ketal was not isolated but hydrolized to afford enone **8** directly. Introduction of the 5,6-alkene is the most troublesome step in the sequence. The best method is through chloranil oxidation,[6] which gives a 70–80% yield of product. Other methods give lower yields or are multiple-step processes that result in an overall lower yield.

Introduction of the thioacetate could be accomplished by traditional acid catalysis,[7] but this inevitably resulted in a thermodynamic mixture of α and β isomers **1** and **10** (ratios vary from 6:1 to 8:1). After exploring a number of unsuccessful approaches to achieving better diastereoselectity in the addition we found that 30 mol % TMSOTf catalizes the reaction to give a >50:1 ratio of α and β isomers.[8] However, when the catalyst concentration is

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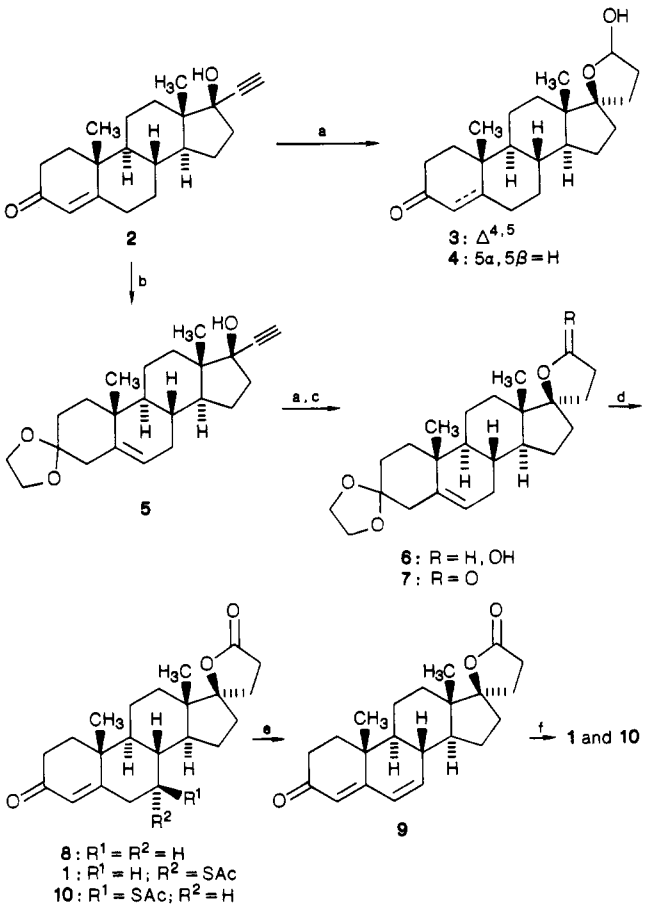
Scheme I[a]



[a] (a) H_2, CO, $Rh_2(OAc)_4$, Ph_3P, 12 bar; (b) MeOH, $HOCH_2CH_2OH$, TsOH, TMOF, 50 °C; (c) PDC, CH_2Cl_2, 38 °C; (d) H_3O^+; (e) chloranil, tBuOH, Δ; (f) AcSH, TMSOTf, THF.

reduced to 3% a 6:1 ratio of **1** and **10** is obtained. Solvents other than THF also resulted in lower selectivity. For example, methylene chloride gives a 1:1 ratio and acetonitrile gives only R_f = 0 material.

In conclusion this work demonstrates the utility of converting a propargylic alcohol to a lactol by the hydroformylation reaction. The hydroformylation of acetylenes has generally not been considered very useful because of the inability to obtain an unsaturated aldehyde from the reaction.[9] Acetylenes have the advantage that they are easily prepared by a number of methods.

Experimental Section

17α-Ethynyl-17β-hydroxy-5-androsten-3-one Ethylene Ketal (5). A 1 L three-necked round-bottomed flask was charged with 120 mL (2.16 mol, 134.0 g) of ethylene glycol, 37.4 g of ethisterone (0.12 mol), 240 mL of methanol, 24.4 mL of trimethyl orthoformate (0.22 mol), and 2.3 g of *p*-toluenesulfonic acid. The mixture was stirred mechanically at 50 °C until complete by TLC. After 3 h, the mixture was cooled to 5 °C and treated with 6.6 g of sodium acetate in 200 mL of water (temperature was maintained below 5 °C throughout the quench). When addition was complete the mixture was stirred cold for 1 h and then filtered. The white solids obtained were placed under high vacuum until no further weight loss to afford 41.9 g (98% yield) of ketal **5**. Mp: 245–251 °C. ^1H NMR ($CDCl_3/CD_3OD$): 0.87 (s, 3 H), 1.03 (s, 3 H), 2.57 (s, 1 H), 3.97 (s, 4 H), 5.23 (m, 1 H) ppm. TLC R_f (1:1 ethyl acetate/heptane) **2** = 0.4, **5** = 0.52. IR ($CHCl_3$): 3585 (s), 3410 (b), 3295 (s), 2938, 1375, 1360, 1090, 1020, 940 cm^{-1}.

5′-Hydroxyspiro[pregnane-17,2′-tetrahydrofuran]-5-en-3-one (6). A suspension of 3-(ethylene ketal) **5** (53.4 g, 0.15 mol) in 530 mL of ethyl acetate was placed in an autoclave and charged with 2.0 g of triphenylphosphine (7.6 mmol) and 76 mg (0.15 mmol) of rhodium acetate dimer. The autoclave was sealed and heated to 80 °C at 12 bar (168 psi) under an atmosphere of 1:1 carbon monoxide/hydrogen. After 20 h at constant pressure, the initially heterogeneous mixture becomes a light yellow homogeneous solution. The reaction mixture was cooled to room temperature. The precipitated product was isolated by filtration in 83% yield. Concentration of mother liquors and a second filtration afforded an additional 7% of lactol **6**. Anal. Calcd for $C_{24}H_{36}O_4$: C, 74.19; H, 9.34. Found: C, 74.42; H, 9.47. Mp. 203–208 °C. ^1H NMR ($CDCl_3$): 5.4 (m, 1 H), 3.95 (s, 4 H), 3.05 (m, 1 H), 1.08 (s, 3 H), 0.9 (s, 3 H) ppm. IR 3400, 2940, 1450, 1375, 1230, 1090, 1000 cm^{-1}. (*6*): R_f (1:1 ethyl acetate:heptane) 0.37.

Spiro[pregnane-17,2′-tetrahydrofuran]-4-ene-3,5′-dione (8). A 1-L three-necked round-bottomed flask equipped with mechanical stirrer, reflux condenser, thermometer, and nitrogen inlet was charged with 50.0 g of lactol **6** (0.13 mol), 260 mL of methylene chloride, and 53.3 g of pyridinium dichromate (0.14 mol, 1.07 equiv). The mixture was heated to 38 °C until TLC indicated the reaction complete (5 h). The mixture was cooled and treated with 20 g of Celite and filtered through a thin pad of Celite. The resulting brown solution was concentrated to remove methylene chloride. The viscous brown oil of lactone **7** was taken up in ethyl acetate/methyl *tert*-butyl ether, filtered, washed with saturated sodium bicarbonate, dried over magnesium sulfate, and concentrated to give 49.8 g of a light brown viscous oil. The oil was taken up in THF and was treated with 150 mL of 6 N HCl. The hydrolysis was complete in 30 min. Chloroform extraction followed by concentration gave 42.8 g of lactone **8** (97% yield). This lactone may be crystallized from EtOAc/hept but in general was pure enough to be used without crystallization. Lactone **7**. ^1H NMR ($CDCl_3$): 5.3 (m, 1 H), 3.93 (s, 4 H), 2.47 (s, 2 H), 1.04 (s, 3 H), 0.95 (s, 3 H) ppm. IR ($CHCl_3$): 2940, 1755, 1370, 1225, 1095 cm^{-1}. R_f (30% ethyl acetate/heptane) = 0.38. Mp: 148–150 °C.[10] Lactone **8**. Anal. Calcd for $C_{22}H_{30}O_3$: C, 77.16; H, 8.83. Found: C, 77.37; H, 9.00. ^1H NMR ($CDCl_3$): 1.0 (s, 3 H), 1.23 (s, 3 H), 5.7 (s, 1 H) ppm. IR ($CHCl_3$): 3500 (b), 2930, 2840, 1755, 1650, 1610, 1450, 1270, 1010, 910 cm^{-1}. R_f (30% ethyl acetate/heptane) = 0.28. Mp: 159–160 °C.

$RuCl_2(PPh_3)_3$ Oxidation. A DMF solution of 388 mg of lactol **6** was treated with 2 equiv of NMO and then 10 mol % $RuCl_2(Ph_3P)_3$. TLC analysis after 10 min showed the reaction to be complete. The solution was diluted with ethyl acetate, poured into aqueous sodium bicarbonate, and extracted (3×) with ethyl acetate. The combined organic extracts were dried over magnesium sulfate and concentrated to provide a quantitative yield of lactone **7**. If the solution is treated with aqueous HCl prior to ethyl acetate dilution the 3-(ethylene ketal) is hydrolyzed, and lactone **8** is obtained in 97% yield.

Spiro[pregnane-17,2′-tetrahydrofuran]-4,6-diene-3,5′-dione. Lactone **8** (42.8 g, 125.0 mmol) was dissolved in 350 mL of *tert*-butyl alcohol and treated with 1.2 equiv (37.0 g, 150.0 mmol) of *p*-chloranil. The mixture was heated to reflux until the reaction mixture went from a yellow suspension of chloranil to a brown homogeneous solution, at which point the reaction was complete as determined by NMR. The reaction mixture was concentrated in vacuo, taken up in chloroform, and washed four times with 100 mL of water, four times with 10% NaOH solution, and then with water until the emulsion is broken. The organic layer is a light brown color, and when concentrated provides 35.3 g of light brown solids with a purity of 85% by HPLC analysis (70% yield corrected for purity). This material can be upgraded by crystallization from $MeOH/H_2O$ with a 67% recovery and a mp of 162–164 °C but in general was used as is for the next step. Anal. Calcd for $C_{22}H_{28}O_3$: C, 77.61; H, 8.29. Found: C, 77.76; H, 8.54. ^1H NMR ($CDCl_3$): 1.03 (s, 3 H), 1.13 (s, 3 H), 5.67 (s, 1 H), 6.12 (s, 2 H) ppm. IR ($CHCl_3$): 2930, 2860, 1760, 1645, 1610, 1455, 1380, 1260, 1170, 1010, 874 cm^{-1}. R_f (1:1 ethyl acetate/heptane) = 0.19.

7α-(Acetylthio)-17β-hydroxy-3-oxopregn-4-ene-21-carboxylic Acid Lactone (1). Dienone (**9**) from above (28.0 g,

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82.0 mmol), was dissolved in 150 mL of THF and added to a 1-L three-necked round-bottom flask containing 150 mL of THF, 17.5 mL (18.7 g 246.0 mmol) of thiolacetic acid, and 4.7 mL of TMSOTf (5.5 g, 24.6 mmol). An exothermic reaction resulted (temperature rise from 23 °C to 38 °C). The mixture was stirred for 1 h at room temperature, and then diluted with 50 mL of ethyl acetate. The reaction was quenched by careful addition of saturated sodium bicarbonate solution until effervescing stopped. The mixture was transferred to a separatory funnel, extracted with ethyl acetate, dried over magnesium sulfate, and concentrated to give 38.0 g of light brown solids. HPLC analysis showed that the product obtained was 77% pure with an α/β ratio of 70:1 85% yield corrected for purity. The crude product was crystallized from methanol to afford 23.2 g (64%) of 98% pure spironolactone 1. Mp: 155–159 °C. ^{1}H NMR ($CDCl_3$): 1.03 (s, 3 H), 1.57 (s, 3 H), 2.33 (s, 3 H), 4.0 (m, 1 H), 5.7 (d, J = 1.6 Hz, 1 H). IR ($CHCl_3$): 2940, 2860, 1760, 1675, 1415, 1350, 1175, 1110, 950 cm^{-1}. R_f (10 $CHCl_3$/acetone) 1 = 0.56; 2 = 0.49; 8 = 0.42.

Registry No. 1, 52-01-7; 5, 50407-76-6; 6, 121936-43-4; 7, 75219-50-0; 8, 976-70-5; 9, 976-71-6; 10, 33784-05-3; $HOCH_2CH_2OH$, 107-21-1; ACSH, 507-09-5; ethisterone, 434-03-7.

Heterogeneous Permanganate Oxidations: An Improved Procedure for the Direct Conversion of Olefins to α-Diketones/α-Hydroxy Ketones

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A large number of solid-supported permanganate reagents have been developed in recent years for the oxidation of organic substrates under heterogeneous conditions.[1] Potassium permanganate supported on molecular sieves[2] or silica gel[3] has been used to oxidize alcohols to carbonyl compounds and for the cleavage of carbon–carbon double bonds.[4] Zinc permanganate supported on silica gel has been applied for the conversion of acetylenes to α-diketones and cyclic olefins to ketols.[5] Permanganate supported on copper sulfate pentahydrate has been used for the oxidation of alcohols to the corresponding carbonyl compounds,[6] diols to lactones,[7] and sulfides to sulfones.[8] The proposed mechanism[9] for the conversion of alcohols to carbonyl compounds using potassium permanganate and copper sulfate pentahydrate showed that olefins retard the reaction by forming a π-complex with the permanganate ion and thus remain unaffected under the reaction conditions.

Herein, we report that a slight modification of the heterogeneous permanganate oxidations with $KMnO_4$/$CuSO_4 \cdot 5H_2O$ can be used effectively for the direct conversion of olefins to α-diketones and α-hydroxy ketones under very mild conditions. It turns out that when olefins are treated with a well-ground mixture of $KMnO_4$/$CuSO_4 \cdot 5H_2O$ in dichloromethane containing catalytic amounts of *tert*-butyl alcohol/water at room temperature, α-diketones or α-hydroxy ketones are obtained in good yields. The results obtained by this modified procedure are summarized in Table I.

There are a number of interesting features of this methodology worth pointing out. The most common method widely used for the conversion of olefins to α-diketones is that of Sharpless[10a] using a $KMnO_4$–acetic anhydride system that involves a tedious workup procedure and fails to produce significant amounts of α-diketones from small-ring olefins. *cis*-Cyclooctene, the smallest cyclic olefin to be successfully oxidized, gave only a 23% yield of diketone. On the other hand, the present methodology gave the α-hydroxy ketones **2** (30%), **4** (59%), and **6a** (50%) from the corresponding olefins. In the case of cyclooctene when the same reaction was done along with cupric acetate (solid, 1 mole equiv) for 4 h, the intermediate α-hydroxy ketone **6a** was converted to cyclooctane 1,2-dione **6b** (48%), and cyclododecene **7**[10b] under similar conditions gave **8** (58%). Oxidation of olefinic ketone **9** afforded the hydroxy ketone **10** in 79% yield. In the reaction of **11** a mixture of epoxide **12a** and hydroxy ketone **12b** (1:1) was obtained (80%), and cholesteryl acetate **15** gave the β-epoxide **16** as the only product (92%). *trans*-Stilbene (**17**) and acylic olefins **19** and **21** underwent oxidative cleavage under the reaction conditions. However, diphenylacetylene **23** yielded benzil in high yield (97%). The amount of *tert*-butyl alcohol and water added in this reaction is very crucial for the success of this reaction. In the absence of either water or *tert*-butyl alcohol the reaction does not take place. This reaction would be particularly useful for cyclic (small, medium, and large) olefins and acylic trisubstituted olefins.

In studying the kinetics of substitution of benzyl halides with cyanide ion catalyzed by 18-crown-6, Liotta[11] observed a dramatic increase in rate with the addition of minute quantities of water. Ω-phase catalysis, a nonclassical phase-transfer system, has been invoked to explain the role of water in these reactions. It is very likely that in our oxidation the water/*tert*-butyl alcohol forms a third phase, i.e., Ω phase, by surrounding the inorganic solids, and it is in or on or by means of this interface that the reaction takes place.[12] It is noteworthy that, in general, the oxidation of alkenes with potassium permanganate under aqueous conditions yields insignificant amount of epoxides.[13] However, in the present study the epoxides **12a** and **16** were found to be formed either as a major product or sole product in the reaction of substrates **11** and **15**, respectively. It is possible that the epoxide formation increases with increasing lipophilicity of the substrates, and this would be in line with Ω-phase catalysis.[12] This observation is interesting and needs to be explored further.

Compared to all the existing procedures for olefin oxidation, this method appears to be more general, the reaction conditions are milder, and the yields of the product

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