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THE REACTION OF ALDEHYDE ENOL SILYL ETHERS WITH LEAD(IV) ACETATE

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Abstract—The treatment of aldehyde enol silyl ethers 1 with lead(IV) acetate (LTA) using methylene chloride as solvent gives rise to the production of α-acetoxy aldehydes 2 and glycolic ester derivatives 3 or enals 5. Structural variations in 1 are used to explain the divergent trends. When 1 is treated with LTA/KOAc/AcOH, high yields of the corresponding α-acetoxy aldehydes 2 are obtained with the formation of 3 and 5 being subverted.

The continuing interest in the use of α-oxygenated carbonyl compounds in organic synthesis[1] has led us to explore the oxidation reactions of enol silyl ethers. Thus, treatment of these nucleophilic alkenes with *m*-chloroperbenzoic acid,[2] lead(IV) carboxylates,[3] or silver carboxylates in conjunction with iodine[4] affords the high yield synthesis of a variety of α-oxygenated carbonyl systems. In one of our studies we were able to show that α-acetoxy enones are produced when the appropriate enol silyl ethers are treated sequentially with *m*-chloroperbenzoic acid and then with a mixture containing triethylammonium fluoride/triethylamine/acetic anhydride.[5] A modification of this procedure had previously been reported to give moderate yields of α-acetoxy aldehydes (39–46%, 4 cases) when applied to the corresponding aldehyde enol silyl ethers 1.[6] With hopes of developing a general, high yield method for the α-oxygenation of aldehydes, we have studied the reaction of aldehyde enol silyl ethers 1 with lead(IV) acetate (LTA) in order to obtain α-acetoxy aldehydes 2. The results of this study are presented in the following account.

1 2

RESULTS

The enol silyl ethers 1, readily prepared by the method of House,[7] were allowed to react with excess LTA in methylene chloride as solvent. Workup and purification of mixtures revealed two major trends (Table 1). First, with 1 (R^1 = H, R^2 = alkyl), mixtures of 2 along with the "over-oxidized" glycolic esters 3 were obtained in reasonable overall yield. In one instance (oxidation of **1d** in benzene), both over-oxidation and rearrangement occurred to afford 4 in low yield (16%). The identity of 4 was confirmed by an independent synthesis.[8] The second trend was found with 1 (R^1 and R^2 = alkyl). In these cases, oxidation led to the exclusive production of the enals 5. Scheme 1 summarizes our initial experimental results for the LTA oxidation of 1.

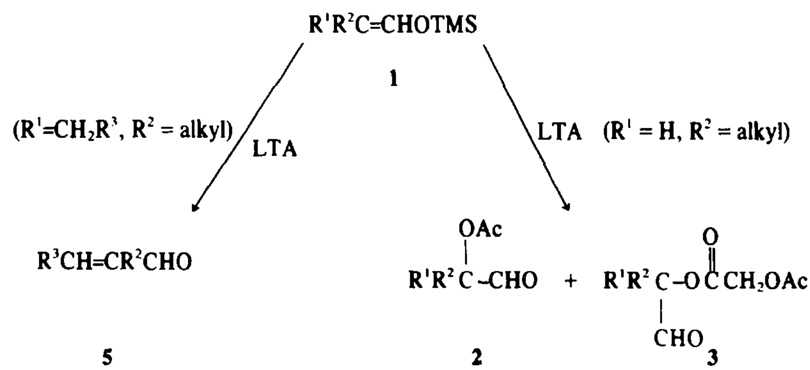
Although **1d** underwent oxidation with benzene as solvent, only unchanged 1 (NMR) was isolated when **1a** and **1h** were treated with LTA in benzene. The LTA

$(Ph)_2C{=}CHOTMS$

1h

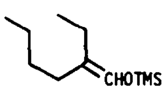
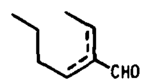
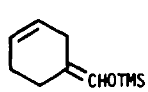
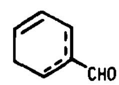
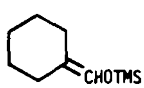
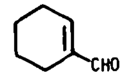
reaction of **1b** run in THF resulted in the isolation of **2b** and **3b** in yields of 24% and 44%, respectively. These values represent a substantial increase in the amount of over-oxidized product obtained relative to the **2b**:**3b** ratio of 40:21 observed when methylene chloride was the solvent used.

The formation of the glycolic esters 3 finds literature precedent in the LTA oxidation of cyclopentadiene wherein 6 was isolated as one of the major oxidation products.[9] Both this reaction and the formation of 2, 3 and 5 can be accommodated by the mechanism outlined in Scheme 2. Initial interaction of 1 with LTA gives rise to carbocation 7, and then to 8, analogous to the reaction

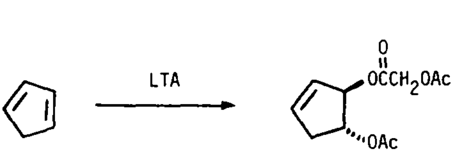


Scheme 1.

Table 1. LTA oxidation of aldehyde enol silyl ethers to give 2 and 3 or enal, 5

Enol Silyl Ether, 1[a]	Product(s) (% yield)[b]	
$PhCH_2CH{=}CHOTMS$ **1a**	$PhCH_2CH(OAc)\text{-}CHO$ **2a** (59)	$PhCH_2CH(CHO)\text{-}OC(O)CH_2OAc$ **3a** (22)
$n\text{-}C_5H_{11}CH{=}CHOTMS$ **1b**	$n\text{-}C_5H_{11}CH(OAc)\text{-}CHO$ **2b** (40)	$n\text{-}C_5H_{11}CH(CHO)\text{-}OC(O)CH_2OAc$ **3b** (21)
$(CH_3)_2CHCH{=}CHOTMS$ **1c**	$(CH_3)_2CHCH(OAc)\text{-}CHO$ **2c** (24)	$(CH_3)_2CHCH(CHO)\text{-}OC(O)CH_2OAc$ **3c** (35)
$PhCH{=}CHOTMS$ **1d**	$PhCOCH_2\text{-}OC(O)CH_2OAc$ **4** (16)[c]	
 **1e**	 **5a** (62)	
 **1f**	 **5b** (90)	
 **1g**	 **5c** (76)	

a. (E)/(Z)-mixture with the exception of **1g**; see experimental. b. Yield of isolated product. c. Oxidation in benzene, all others in CH_2Cl_2.



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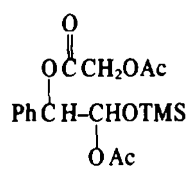
of simple alkenes with LTA.[10] Decomposition of **8** affords carbocation **9** which can lose a proton to produce **10**, the precursor to enal **5**. This mode of behavior is favored in systems where the cation center in **9** is tertiary. In these cases cyclization of **9** to give the dioxolenium ion **11** is disfavored due either to eclipsing interactions which would be encountered upon the formation of **11** (i.e. **1e**) or to the necessity of spiro-ring formation as with **1f** and **1g**. In those instances where the cation center in **9** is not tertiary (**1a–1c**), neighboring group participation by acetate gives **11**. The cation **11** can then either be intercepted by acetate ion to give **12** and then **2**, or loss of a proton can afford the ketene acetal **13**. Oxidation of **13** by LTA via **14** gives **15** and then the glycolic esters **3**. In general, this scheme parallels that presented in the literature for the LTA oxidation of cyclopentadiene.[11] The appearance of **4** from the oxidation of **1d** can be envisioned as occurring via rearrangement of **16** during hydrolytic workup.[12]



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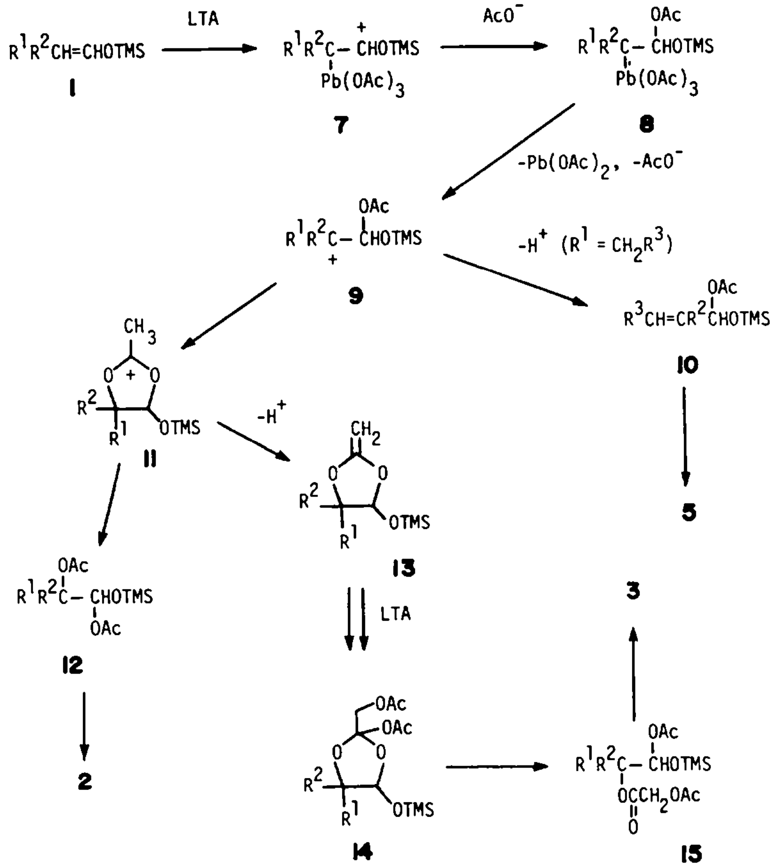
The failure of **1** to react with LTA in benzene is probably due to the relatively non-polar nature of the reaction medium using this solvent. THF, on the other hand, could enhance the formation of **13** due to the basic nature of this solvent. With these facts in mind, it was felt that if the formation of **13** could be subverted then the amount of **2** formed might well increase dramatically. A brief study of the stability of **1b** in a heterogeneous mixture containing THF/KOAc and in a homogeneous solution made up of THF/HOAc revealed that **1b** undergoes no decomposition after 1 hr under either set of



Scheme 2.

conditions (NMR).[8] With these results in hand, **1b**, **1c**, **1f** and **1g** were treated with LTA/KOAc using HOAc as solvent. In each case, a high yield of **2** was obtained (Table 2) since **11** (or **9**) is channeled to **12** at the expense of **13**. Unfortunately, **1a**, **1d**, and **1e** gave no reaction using this set of conditions. The reason for the lack of reactivity towards these substrates is not clear, but the results, at least in our hands, seem to be reproducible.

In summary, aldehyde enol silyl ethers **1** react with LTA/methylene chloride to give **2** and **3** or **5** depending upon the structure of **1**. On the other hand, **1** react with LTA/KOAc/HOAc to afford high yields of pure **2** without production of the unwanted by-products. Thus, the latter conditions provide a useful route for the synthesis of α-acetoxy aldehydes.

EXPERIMENTAL

General. m.ps were determined with a Thomas–Hoover m.p. apparatus and are uncorrected. PMR spectra were recorded at 60 MHz on a Varian Anaspect EM 360 spectrometer using TMS as internal standard. IR spectra were obtained on a Perkin-Elmer 621 grating IR spectrometer and low resolution MS were obtained with a Hitachi Perkin-Elmer RMU 6E instrument at 15 eV and are recorded as *m/z* with relative abundance in parentheses. Elemental microanalyses were determined with a Perkin-Elmer 240 elemental analyzer. Preparative and analytical GLC runs were carried out on an Aerograph Model A90 gas chromatograph using a 5% SE-30 on Anakrom ABS 110–120, 9′ × 0.25″ column. Triethylammonium fluoride was prepared by the method of Hünig,[13] and anhyd $MgSO_4$ served as drying agent. CH_2Cl_2 was dried by storage over $CaCl_2$. LTA (90%, Alfa-Ventron) was freed of residual HOAc by rotoevaporation with benzene immediately prior to use. HOAc refers to glacial acetic acid.

Preparation of enol silyl ethers **1**. These were prepared by procedure "A" outlined by House *et al.* in ref 7.

(E)/(Z)-3-*Phenyl*-1-*trimethylsiloxypropene*, **1a**. 80%; b.p. 99.5–104° (5.8 mm) lit.[14] b.p. 98–102° (5.2 mm); IR (neat) 1655 cm^{-1} lit.[14] 1655 cm^{-1}.

(E)/(Z)-1-*Trimethylsiloxyheptene*, **1b**. 95%; b.p. 112–123° (70 mm) lit.[15] b.p. 85° (15 mm).

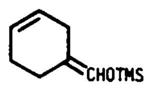
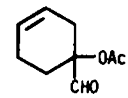
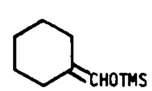
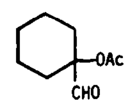
(E)/(Z) - 3 - *Methyl* - 1 - *trimethylsiloxy* - 1 - *butene*, **1c**. 84%; b.p. 72–85° (75 mm); IR (neat) 1655 cm^{-1}; NMR (CCl_4, (E)-**1c**, 55%) δ 0.14 (s, 9H), 0.90 (d, 3H, J = 7 Hz), 1.56—*ca* 2.3 (m, 1H), 4.62–5.00 (d of d, 1H, J = 8, 12 Hz), 5.97–6.18 (d of d, 1H, J = 1, 12 Hz), NMR (CCl_4, (Z)-**1c**, 45%) δ 0.14 (s, 9H), 0.94 (d, 3H, J = 7 Hz), *ca.* 2.3–3.07 (m, 1H), 4.08–4.39 (d of d, 1H, J = 5, 9 Hz), 5.84–5.97 (d of d, 1H, J = 1, 5 Hz); MS *m/z* 158 (M$^+$, 22), 143 (100), 86 (32), 75 (94), 73 (57), metastables 129.4, 39.3, 37.3. (Found: C, 60.66; H, 11.63. Calc. for $C_8H_{18}OSi$: C, 60.67; H, 11.46%.)

(E)/(Z)-β-*Trimethylsiloxystyrene*, **1d**. 64%; b.p. 109–111° (11.5 mm); IR (neat) 1640 cm^{-1}; NMR (CCl_4, (E)-**1d**, 47%) δ 0.23 (s, 9H), 5.92 (d, 1H, J = 12 Hz), 6.88 (d, 1H, J = 12 Hz), 6.9–7.6 (m, 5H), NMR (CCl_4, (Z)-**1d**, 53%) δ 0.26 (s, 9H), 5.23 (d, 1H, J = 5 Hz), 6.32 (d, 1H, J = 5 Hz), 6.9–7.6 (m, 5H); MS *m/z* 192 (M$^+$, 100), 177 (27), 73 (45), metastables 163.2, 146.5. (Found: C, 68.45; H, 8.35. Calc. for $C_{11}H_{16}OSi$: C, 68.69; H, 8.39%.)

(E)/(Z) - 2 - *Ethyl* - 1 - *trimethylsiloxy* - 1 - *hexene*, **1e**. 60%; b.p. 67–74° (4 mm); IR (neat) 1665 cm^{-1}; NMR (CCl_4) δ 0.15 (s, 9H), 0.72—*ca.* 1.1 (m, 6H), *ca.* 1.1–1.51 (m, 4H), 1.67–2.26 (m, 4H), 5.86–6.05 (overlapping singlets, 1H, (E)/(Z)); MS *m/z* 200 (M$^+$, 54), 157 (100), 72 (74), 57 (26), metastable 123.9. (Found: C, 65.85; H, 11.91. Calc. for $C_{11}H_{24}OSi$: C, 65.94; H, 12.18%.)

(E)/(Z) - *Trimethylsiloxymethylene* - 3 - *cyclohexene*, **1f**. 85%; b.p. 73–74° (1.3 mm); IR (neat) 1680, 1650 cm^{-1}; NMR (CCl_4) δ 0.17 (s, 9H), 2.0–2.8 (m, 6H), 5.63 (s, 2H), 5.9–6.08 (overlapping singlets, 1H, (*E*)/(*Z*)); MS *m/z* 182 (M$^+$, 100), 92 (36), 73 (19), metastables 153.5, 47.0. (Found: C, 65.98; H, 9.68. Calc. for $C_{10}H_{18}OSi$; C, 65.87; H, 9.95%.)

Table 2. LTA oxidation of aldehyde enol silyl ethers in the presence of KOAc/HOAc

Enol Silyl Ether, 1[a]	Product (% yield)[b]
n-C_5H_{11}CH=CHOTMS 1b	n-C_5H_{11}CH(OAc)-CHO 2b (78)
$(CH_3)_2$CHCH=CHOTMS 1c	$(CH_3)_2$CHCH(OAc)-CHO 2c (72)
 1f	 2f (73)
 1g	 2g (45)

a. (E)/(Z)-mixture with the exception of 1g; see experimental. b. Yield of isolated product.

Trimethylsiloxymethylenecyclohexane, **1g**. 58%; b.p. 48–52° (110 mm); IR (neat) 1680 cm^{-1}; NMR (CCl_4) δ 0.12 (s, 9H), 0.90–2.20 (m, 10H), 5.85 (s, 1H); MS m/z 184 (M^+, 100), 94 (24). (Found: C, 65.41; H, 10.68. Calc. for $C_{10}H_{20}OSi$: C, 65.16; H, 10.94%.)

α-Phenyl-β-trimethylsiloxystyrene, **1h**. 86%; b.p. 151–153° (0.6 mm); IR (neat) 1625 cm^{-1}; NMR (CCl_4) δ 0.35 (s, 9H), 6.73 (s, 1H), 7.2–7.4 (m, 10H); MS m/z 268 (M^+, 100), 75 (22), 73 (20). (Found: C, 76.07; H, 7.34. Calc. for $C_{17}H_{20}OSi$: C, 76.07; H, 7.51%.)

LTA oxidation of aldehyde enol silyl ethers, **1**, *in methylene chloride*

General procedure. To a precooled (ice/MeOH) soln of 2.2 molar equivalents of LTA in CH_2Cl_2 was added, with stirring, 1 molar equiv of neat **1**. With the addition completed, the cooling bath was removed and the mixture was stirred at room temp for 30 min. The mixture was then filtered and the filtrate treated with 1 molar equiv of triethylammonium fluoride (TEAF). After 30 min of stirring, the CH_2Cl_2 soln was treated sequentially with 50 mL 5% HClaq, 2 × 50 mL portions 5% $NaHCO_3$aq, and 50 mL water. The organic portion was dried and filtered and solvent removed *in vacuo* to afford crude **2** and **3** or **5**. Purification of the crude product(s) was then accomplished using vacuum distillation.

LTA oxidation of **1a**. Oxidation of 24 mmol of **1a** resulted in the production of 59% **2a** and 22% **3a**.

2-Acetoxy-3-phenylpropanal, **2a**. 59%; b.p. 93–105° (0.08 mm) lit.[6] b.p. 110° (0.1 mm).

2-(O-Acetyl)glycoloxy-3-phenylpropanal, **3a**. 22%; b.p. 125–135° (0.08 mm); IR (neat) 1750 cm^{-1}; NMR (CCl_4) δ 2.06 (s, 3H), 2.80–3.18 (m, 2H), 4.54 (s, 2H), 5.02–5.33 (m, 1H), 7.20 (s, 5H), 9.48 (s, 1H); MS m/z 250 (M^+, 1), 132 (100), 131 (23), 101 (22), metastable 130.0. (Found: C, 62.66; H, 5.92. Calc. for $C_{13}H_{14}O_5$: C, 62.39; H, 5.64%.)

LTA oxidation of **1b**. Oxidation of 16 mmol of **1b** resulted in the production of 40% **2b** and 21% **3b**.

2-Acetoxyheptanal, **2b**. 40%; b.p. 117–120° (4 mm) lit.[16] b.p. 101–102°; IR (neat) 1750 cm^{-1} lit.[16] IR 1755 cm^{-1}.

2-(O-Acetyl)glycoloxyheptanal, **3b**. 21%; b.p. 114–116° (0.03 mm); IR (neat) 1745 cm^{-1}; NMR (CCl_4) δ 0.06–2.10 (m, 11H), 2.02 (s, 3H), 4.52 (s, 2H), 4.78–5.07 (m, 1H), 9.40 (s, 1H); MS m/z 201 (M-29, <1), 101 (32), 43 (100), metastables 52.3, 47.6. (Found: C, 57.33; H, 7.86. Calc. for $C_{11}H_{18}O_5$: C, 57.35; H, 7.88%.)

LTA oxidation of **1b** *in THF.* Oxidation of 9 mmol of **1b**, as above, using THF as solvent resulted in the production of 24% **2b** and 44% **3b** identical to the two compounds isolated from the LTA oxidation of **1b** using CH_2Cl_2 as solvent.

LTA oxidation of **1c**. Oxidation of 16 mmol of **1c** resulted in the production of 24% **2c** and 35% **3c**.

2-Acetoxy-2-methylbutanal, **2c**. 24%; b.p. 70–75° (1.5 mm); IR (neat) 1740 cm^{-1}; NMR (CCl_4) δ 0.94 (d, 3H, J = 7 Hz), 1.00 (d, 3H, J = 7 Hz), 1.73–2.36 (m, 1H), 2.09 (s, 3H), 4.71 (d, 1H, J = 4 Hz), 9.42 (s, 1H); MS m/z 115 (M-29, 41), 84 (23), 43 (100). (Found: C, 58.18; H, 8.34. Calc. for $C_7H_{12}O_3$: C, 58.35; H, 8.39%.)

2-(O-Acetyl)glycoloxy-3-methylbutanal, **3c**. 35%; b.p. 126–128° (1.0 mm), IR (neat) 1755 cm^{-1}; NMR (CCl_4) δ 0.95 (d, 3H, J = 7 Hz), 1.01 (d, 3H, J = 7 Hz), 1.81–2.43 (m, 1H), 2.10 (s, 3H), 4.74 (s, 2H), 4.83 (d, 1H, J = 4 Hz), 9.40 (s, 1H), MS m/z 173 (M-29, 4), 101 (100), 84 (32), 73 (25), 71 (36), 43 (37). (Found: C, 53.49; H, 6.95. Calc. for $C_9H_{14}O_5$: C, 53.47; H, 6.93%.)

LTA oxidation of **1d** *in benzene.* A stirred soln of 3.65 g (7.8 mmol) LTA in 30 mL dry benzene was cooled to *ca.* 10° (ice bath) and treated with 1.52 g (7.9 mm) neat **1d**. With the addition complete, the mixture was stirred at room temp for an additional hour. The mixture was then filtered through celite and the filtrate washed with 20 mL 0.75 N HCl and then with 20 mL water. The solvent was removed *in vacuo* and 15 mL DMF, 0.50 g (86 mmol) KF, and 1 mL water were added to the residue. After 20 hr stirring at room temp, the mixture was diluted with 150 mL ether and the organic layer was extracted with 4 × 30 mL water. The ethereal soln was then dried, filtered, anl solvent removed *in vacuo* to afford an oil. Crystallization from ether gave 0.30 g (16%) pure **4**, m.p. 74–75°; IR (nujol mull) 1760, 1700 cm^{-1}; NMR ($CDCl_3$) δ 2.17 (s, 3H), 4.80 (s, 2H), 5.40 (s, 2H), 7.4–8.0 (m, 5H); MS m/z 236 (M^+, < 1), 105 (100), 77 (26), 43 (29). (Found: C, 61.05; H, 5.13. Calc. for $C_{12}H_{12}O_5$: C, 61.01; H, 5.12%.) No attempt was made to optimize yields of **4** using two molar equiv of LTA.

Acetylglycolic acid.[17] A 125 mL round bottom flask fitted with a dropping funnel and reflux condenser was charged with 10 g (131 mmol) glycolic acid. Acetyl chloride (20 g, 255 mmol) was then added slowly. When the evolution of HCl had ceased, the reflux condenser was removed and heat was applied to remove excess acetyl chloride (fume hood). The crude product thus obtained was crystallized from benzene to yield 14.2 g (92%) acetylglycolic acid, m.p. 66–68° lit.[17] m.p. 61–63.

O-Acetylphenacylglycolate, **4**. To 1.0 g (8.5 mmol) acetylglycolic acid in 5 mL water was added 10% KOHaq. When the pH of the mixture was *ca.* 7.0, a soln of 1.6 g (8.4 mmol) phenacyl bromide in 12 mL 95% EtOH was added and the resulting mixture was refluxed for 1 hr. Cooling (ice bath), filtration, and recrystallization of the solid residue gave 0.85 g (42%) of pure **4**, m.p. 74–75°. This material exhibited spectral properties (IR, NMR, MS) identical to those of **4** produced from the LTA oxidation of **1d** in benzene (see above). Further, no depression of m.p. was observed upon admixture of **4** prepared by the two independent methods (m.m.p. 74–75°).

LTA oxidation of **1e**. Oxidation of 31 mmol **1e** resulted in the production of 62% of a 76:24 mixture (NMR) of **5a** (2-butyl-2-butenal and 2-ethyl-2-hexenal), b.p. 94–102° (9.0 mm); IR (neat) 1730, 1690, 1640 cm^{-1}; NMR (neat/TMS) δ 0.48–2.43 (m, 12H; 1.82, d, J = 7 Hz), 6.15–6.68 (m, 1H; 6.30, t, J = 8 Hz, minor; 6.48, q, J = 7 Hz, major), 9.23 (s, 1H); MS *m/z* 126 (M^+, 100), 111 (60), 97 (63), 85 (20), 84 (28), 83 (28), 77 (26), 69 (20), 57 (22), 55 (36), metastables 97.8, 75.7. Attempts to resolve mixture **5a** by glc failed.

LTA oxidation of **1f**. Oxidation of 2 mmol of **1f** resulted in the production of 90% of a 70:30 mixture (NMR) of **5b** (1-formyl-1, 3-cyclohexadiene and 1-formyl-1, 4-cyclohexadiene), b.p. 78–80° (6.0 mm) lit.[18] b.p. 74–76° (20 mm); IR (neat) 1670 cm^{-1} lit.[18] IR (CCl_4) 1675 cm^{-1}; NMR (CCl_4) δ 2.36 (s, 4H, major), 2.72–3.13 (m, 4H, minor), 5.62–5.89 (m, 2H, minor), 6.18–6.33 (m, 2H, major), 6.65–6.82 (m, 1H, major and minor overlapping), 9.43 (s, 1H, minor), 9.48 (s, 1H, major). Peaks assigned as "major" are in accord with those reported for 1-formyl-1, 3-cyclohexadiene in ref 18; MS *m/z* 108 (M^+, 100), 107 (42), 79 (82), 77 (23), metastables 75.0, 59.1, 57.8. Attempts to resolve mixture **5b** by glc failed.

LTA oxidation of **1g**. Oxidation of 22 mmol of **1g** resulted in the production of 76% **5c**, b.p. 78–80° (12 mm) lit.[19] b.p. 70° (13 mm); n_D^{20} 1.4912 lit.[19] n_D^{20} 1.4924; IR (neat) 1685, 1643 cm^{-1}; NMR (CCl_4) δ 1.25–1.9 (m, 4H), 1.9–2.52 (m, 4H), 6.57–6.82 (m, 1H), 9.30 (s, 1H); MS *m/z* 110 (M^+, 100), 95 (29), 81 (83), metastables 90.2, 77.0, 59.7, 54.7.

Attempted LTA oxidation of **1h** *in benzene*. Attempted LTA oxidation of **1h** in refluxing benzene gave < 10% oxidation by NMR analysis.

Acetolysis of enol silyl ether **1b** *by* KOAc/THF

NMR experiment. A mixture of 36 mg of **1b**, 0.25 mL THF, and 20.0 mg anhyd KOAc was sealed in an NMR tube and the region between 10 and 5 ppm was scanned by NMR. After 1 hr, the vinyl proton of **1b** but *no* aldehyde proton was observed. After 17 hr, integration of aldehyde: vinyl proton peaks gave a ratio of 3:10.

Acetolysis of enol silyl ether **1b** *by* HOAc/THF

NMR experiment. A soln of 36 mg of **1b** in 0.1 mL HOAc and 0.25 mL THF was sealed in an NMR tube and the peak positions mentioned in the previous experiment were monitored by NMR. After 1 hr, no acetolysis was noted. After 19 hr, the ratio of aldehyde to vinyl protons was observed to be 8:19. With glacial AcOH as solvent no acetolysis was noted after 3 hr.

LTA oxidation of aldehyde enol silyl ethers, **1**, *in* HOAc/KOAc

General procedure. A mixture of 20 mmol LTA and 100 mmol KOAc in 30 mL HOAc was treated with 20 mmol of neat **1**. After stirring at the appropriate temp, the mixture was diluted with 30 mL water and extracted with 3 × 200 mL pentane. The combined pentane extracts were washed with 2 × 50 mL portions of 5% Na_2CO_3aq, dried, filtered, and solvent removed *in vacuo* to afford crude **2**, which was purified by vacuum distillation.

LTA oxidation of **1b**. Oxidation of 20 mmol of **1b** for 1 hr at room temp gave a 78% yield pure **2b**, b.p. 110–115° (4.0 mm), identical to **2b** prepared as described above.

LTA oxidation of **1c**. Oxidation of 20 mmol **1c** for 1 hr at room temp gave a 72% yield of pure **2c**, b.p. 70–72° (1.1 mm), identical to **2c** prepared as described above.

LTA oxidation of **1f**. Oxidation of 43 mmol of **1f** for 1 hr at room temp gave a 73% yield of **2f**, b.p. 78–79° (0.04 mm) lit.[6] b.p. 90° (0.1 mm). Glc analysis of the crude mixture showed the major impurities to be the enals **5b**.

LTA oxidation of **1g**. Oxidation of 10 mmol of **1g** for 18 hr at room temp gave a 45% yield of **2g**, b.p. 70–72° (0.7 mm) lit.[20] b.p. 80° (2.5 mm). Glc analysis of the crude mixture showed the mjaor impurity to be formylcyclohexane.

Attempted LTA oxidation of **1a**, **1d**, *and* **1e**. Under the conditions noted above (LTA/KOAc/HOAc) these oxidations gave only recovered starting material. With **1a**, no oxidation was noted even after 1 hr at reflux. With **1e**, increasing the reaction temp to 50°C for 1 hr led to the recovery of 2-ethylhexanal.

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