chromatography (20% SE-30 on Chromasorb W, AW-DMCS, 80 °C): NMR ($CDCl_3$, 270 MHz) δ 2.33 (br s, 3 H), 6.37 (br d, J = 2 Hz, 1 H), 7.28 (d, J = 2 Hz, 1 H). Small amounts of 2,4-dimethyl-3-iodofuran were also detected in previous reaction mixtures: ^1H NMR (270 MHz, $CDCl_3$) δ 1.92 (d, J = 1.1 Hz, 3 H), 2.31 (s, 3 H), 7.13 (q, J = 1.1 Hz, 1 H).

3-Iodo-2-methoxy-4-methyl-2,5-dihydrofuran (3). A solution of 0.484 mL (500 mg, 5.00 mmol) of 4-hydroxy-1-methoxy-2-butyne[5] was metalated (5.7 mL, 1.75 M t-BuLi, 10 mmol), methylated (0.620 mL, 1.42 g, 10 mmol of methyl iodide), and iodinated (1.52 g, 6.00 mmol of I_2) as in the previous procedure. The solution was poured into 10% $Na_2S_2O_3$–7% $NaHCO_3$/Et_2O–pentane. The organic layer was washed with brine, dried (Na_2SO_4), evaporated, and distilled [Kugelrohr; 85 °C (20 mm)] to give **3**: ^1H NMR (CCl_4, 100 MHz) δ 1.92 (br s, 3 H), 3.24 (s, 3 H), 4.48 (m, 2 H), 5.50 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 14.3, 53.0, 77.0, 85.9, 112.4, 146.1; ^{13}C NMR (benzene-d_6, 15 MHz) δ 13.8, 52.6, 76.7, 86.7, 112.6, 145.7; IR 3440 (br), 2920, 1658, 1437, 1378, 1193, 1123, 1048, 995, 826 cm^{-1}; MS, (M^+) 239.9647, calcd for $C_6H_9IO_2$ 239.9648. A small amount of 3-iodo-4-methylfuran (~10%) was visible in the ^1H NMR spectrum.

1-Methoxy-3-methyl-4-[(trimethylsilyl)oxy]-1,2-butadiene. To a solution of 0.29 mL of 2-butyne-1,4-diol monomethyl ether[5] (0.30 g, 3.0 mmol) in 6 mL of THF at −78 °C was added 4.2 mL of 1.5 M t-BuLi (6.3 mmol). After 1 h, 0.25 mL (0.57 g, 4.0 mmol) of methyl iodide was added, followed in 20 min by 0.51 mL (0.43 g, 4.0 mmol) of chlorotrimethylsilane. After 15 min, the reaction mixture was warmed to 0 °C, stirred 15 min, then treated with 0.15 mL of triethylamine, and partitioned between cold aqueous 7% $NaHCO_3$ and 1:1 Et_2O–pentane. The organic layer was washed with brine, dried (Na_2SO_4, then K_2CO_3), and evaporated. A few milligrams of 3-*tert*-butyl-4-hydroxy-5-methylphenyl sulfide was added, and the crude product was distilled [Kugelrohr; 80 °C (20 mm)] to give 0.51 g (91%) of 1-methoxy-3-methyl-5-[(trimethylsilyl)oxy]-1,2-butadiene as a clear oil: NMR (CCl_4, 100 MHz) δ 1.94 (d, J = 2 Hz, 3 H), 3.34 (s, 3 H), 4.08 (br s, 2 H), 6.52 (pentet, J = 2 Hz, 1 H); IR 2970, 1951, 1462, 1260, 1135, 1080, 885, 850, 764 cm^{-1}.

4-Methyl-3-furancarboxaldehyde. To a solution of 16.1 mL of 1.74 M t-BuLi (28 mmol) in 100 mL THF was added 1.50 mL (2.87 g, 13.8 mmol) of 3-iodo-4-methylfuran (1) over 5 min. After 30 min, 1.16 mL (1.10 g, 15.0 mmol) of N,N-dimethylformamide was added. The mixture was stirred 30 min at −78 °C and 30 min at 0 °C and then poured into Et_2O–pentane (1:1)—7% $NaHCO_3$ (50 mL each). The aqueous layer was extracted with 50 mL of Et_2O–pentane, and the combined organic layers were washed with brine and dried (Na_2SO_4). The solvent was removed by distillation and the residue purified by Kugelrohr distillation [67 °C (20 mm)] to give 1.10 g (72%) of 4-methyl-3-furancarboxaldehyde: NMR ($CDCl_3$, 100 MHz) δ 2.08 (s, 3 H), 7.08 (br s, 1 H), 7.82 (s, 1 H), 9.82 (s, 1 H); IR 3120, 2820, 2725, 1685, 1540, 1141, 1041, 863, 752 cm^{-1}; MS, (M^+) 110.0368, calcd for $C_6H_6O_2$ 110.0368.

Acknowledgment. We thank the National Science Foundation for generous support of this work.

Registry No. 1, 107658-18-4; 3, 107658-20-8; 5, 107658-19-5; $H_3COCH_2C{\equiv}CCH_2OH$, 18857-03-9; $H_3COCH{=}C{=}C(CH_3)CH_2OSi(CH_3)_3$, 107658-21-9.

A Mild Method for the Reductive Desulfurization of α-Phenylthio and α-Phenylsulfinyl Carbonyl Compounds

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Received November 18, 1986

In the last two decades α-phenylthio and α-phenylsulfinyl ketones and esters have become very popular synthetic intermediates. They have been found to serve effectively as reagents or intermediates for a wide variety of transformations in many different situations.[3] One of the attractive features of these groups is their ease of removal; several different reagents have been used for this purpose.[4]

During the course of our studies directed toward aphidicolin[5] total synthesis[6] as well as our efforts to explore diastereoselectivity and enantioselectivity in the kinetic Michael addition,[7] we encountered the necessity for reductive removal of phenylthio or phenylsulfinyl groups on many occasions. In several of these cases the existing methods gave unacceptably poor results due either to competing side reactions or to reactivity with other functional groups present in the compound of interest.

We have, therefore, developed a mild method for reductive desulfurization of α-phenylthio and α-phenylsulfinyl carbonyl compounds that we have found to be unusually effective, particularly in the presence of other functional groups. The method is based upon the original observations of Russell and Mikol, who found that (methylsulfinyl)acetophenones were reduced to the corresponding acetophenones in 83–88% yields by zinc in acetic acid.[4k,8] In many cases these conditions are too acidic to permit the survival of other acid-labile functional groups. We have overcome this problem by the use of activated zinc in a mixture of THF and saturated aqueous ammonium chloride solution at 25 °C. Results for the reduction of a series of representative α-phenylthio and α-phenylsulfinyl ketones and esters under these conditions are listed in Table I.

Several features of this reductive desulfurization are

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(9) All yields refer to isolated, spectrally (NMR) and chromatographically (TLC) homogeneous materials.

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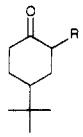
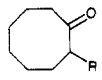
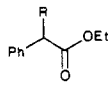
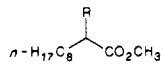
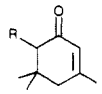
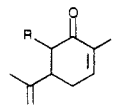
Table I. Reductive Desulfurization with Zn/NH_4Cl

no.[a]	compd	time,[b] h	% yield
1		(a) 32 (b) 1	94 93
2		(a) 24 (b) 3	93 91
3		(a) 24 (b) 1	89 99
4		(a) 24 (b) 3	96 96
5		(a) 72 (b) 3	see text 98
6		(a) 3 (b) 2	95 98
7		(a) 10 (b) 2	96 97

[a] Substrate: (a) R = SPh, (b) R = SOPh. Product: R = H. [b] Maintained at 25 °C.

noteworthy. Phenylthio groups are reduced more slowly than are the corresponding sulfoxides. Phenyl sulfides of purely aliphatic esters are at the limit of the range of this reducing system; ester **5a** was 50% desulfurized after 72 h at 25 °C. However, in the course of our studies in aphidicolin synthesis,[6g] we have found that (phenylthio)-butyrolactone derivatives are reduced efficiently. These examples will be reported separately.[7] These observations are fully in accord with the mechanism postulated by Russell, which involves initial electron donation to the carbonyl group.[4k] Also, according to this mechanism, one would predict that phenylsulfonyl ketones and esters would easily undergo reduction. In fact, 2-(phenylsulfonyl)-4-*tert*-butylcyclohexanone (**1c**) was reduced within 15 min under these conditions to give 1 in 97% yield.

These conditions are mild enough that we have seen no evidence of ester hydrolysis or migration of acid-sensitive olefins. Furthermore, it is of particular interest that even phenylthio groups are completely removed without any competing reduction of α,β-unsaturated ketones (e.g., **6a** → **6**, **7a** → **7**).

This method has been found to be effective in several sensitive situations. We believe that it will be a worthwhile addition to synthetic methodology.

Experimental Section

Proton nuclear magnetic resonance (NMR) spectra were recorded on an IBM WP-270 SY spectrometer at 270 MHz in chloroform-*d* with tetramethylsilane as internal reference. IR spectra were recorded in chloroform solution on a Perkin-Elmer 710B spectrometer. All sulfides and sulfoxides were prepared by literature methods from commercially available ketones or esters 1-7. Melting points were recorded on a hot stage and are uncorrected. Tetrahydrofuran was distilled from lithium aluminum hydride. All other solvents were distilled prior to use.

Activated Zinc.[10] A 20-g portion of zinc dust was ground in a mortar and pestle to remove lumps, then transferred to a fritted glass funnel, and washed with three 50-mL portions each of 4% aqueous HCl, water, methanol, and ether, in that order. The "active" zinc was ground again to remove lumps and then dried, first at 60 °C (20 mmHg) for 15 min and then at 25 °C (0.5 mmHg) for 8 h.

The following experimental procedure is typical for the reduction of **1a,b-7a,b**:

4-*tert*-Butylcyclohexanone (1). To a solution of 139.7 mg (0.533 mmol) of 2-(phenylthio)-4-*tert*-butylcyclohexanone (**1a**) in 7 mL of THF was added 2 g of activated zinc and 7 mL of saturated aqueous ammonium chloride solution. The mixture was stirred vigorously at 25 °C under a nitrogen atmosphere. Progress of the reaction was monitored by TLC, and this analysis indicated that no unreacted **1a** remained after 32 h. The mixture was diluted with 100 mL of a 1:1 mixture of ethyl acetate and hexane. The organic layer was extracted with three 20-mL portions of saturated aqueous sodium bicarbonate solution, dried over sodium sulfate, and evaporated. Flash chromatography of the residue gave 77.4 mg (94%)[9] of 4-*tert*-butylcyclohexanone (1), mp 49-50 °C, identical (^1H NMR, TLC) with an authentic sample.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Public Health Service for their generous financial support of this work.

Registry No. 1, 98-53-3; **1a**, 60774-46-1; **1b**, 107797-38-6; 2, 502-49-8; **2a**, 52190-42-8; **2b**, 55705-18-5; 3, 93-55-0; **3a**, 28403-86-3; **3b**, 69358-42-5; 4, 101-97-3; **4a**, 66693-10-5; **4b**, 107742-82-5; 5, 110-42-9; **5a**, 75280-30-7; **5b**, 107742-83-6; 6, 78-59-1; **6a**, 107742-84-7; **6b**, 107742-85-8; 7, 99-49-0; **7a**, 107742-86-9; **7b**, 107742-87-0.

(10) Zinc activated by this procedure was found to be superior (shorter reaction times) to unwashed zinc dust or zinc powder.

Preparation of Glyceric Acid by Anodic Oxidation of Glycerol at a Silver Oxide Electrode

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Received October 1, 1986

Anodic oxidations of alcohols are well-known.[1,2] Primary alcohols generally yield aldehydes or acids, and secondary alcohols yield ketones. Polyhydroxy compounds tend to give mixtures of products, but under suitable conditions it is sometimes possible to obtain single products. For example, glycerol at a Raney nickel anode in alkaline medium, depending on anode potential and current passed, gives as a major product one of the following substances: dihydroxyacetone, hydroxypyruvic acid, and mesoxalic acid.[3] At a lead anode in aqueous sulfuric acid in the presence of the Mn(II)/Mn(IV) couple, glycerol has been oxidized to glyceraldehyde.[4]

Glyceric acid can be obtained from glycerol by nitrous acid or mercuric oxide oxidations. The present electrocatalytic method for glyceric acid formation is more selective and much "cleaner" than the chemical methods, especially if large-scale synthesis is contemplated. This method oxidizes glycerol to glyceric acid by means of the

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