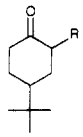
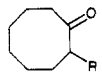
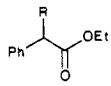
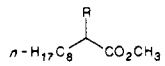
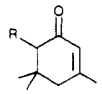
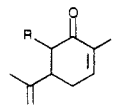
Table I. Reductive Desulfurization with Zn/NH_4Cl

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.

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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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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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(2) Kyriacou, D. K. *Basics of Electroorganic Synthesis*; Wiley-Interscience: New York, 1981.
(3) Siemens-Schuckertwerke, A. G. (Varta Pertrix Union Gmbh) Br. Pat. 1 051 614, 1966.
(4) Lang, W., U.S. Pat. 808 095, 1905.

0022-3263/87/1952-2318$01.50/0

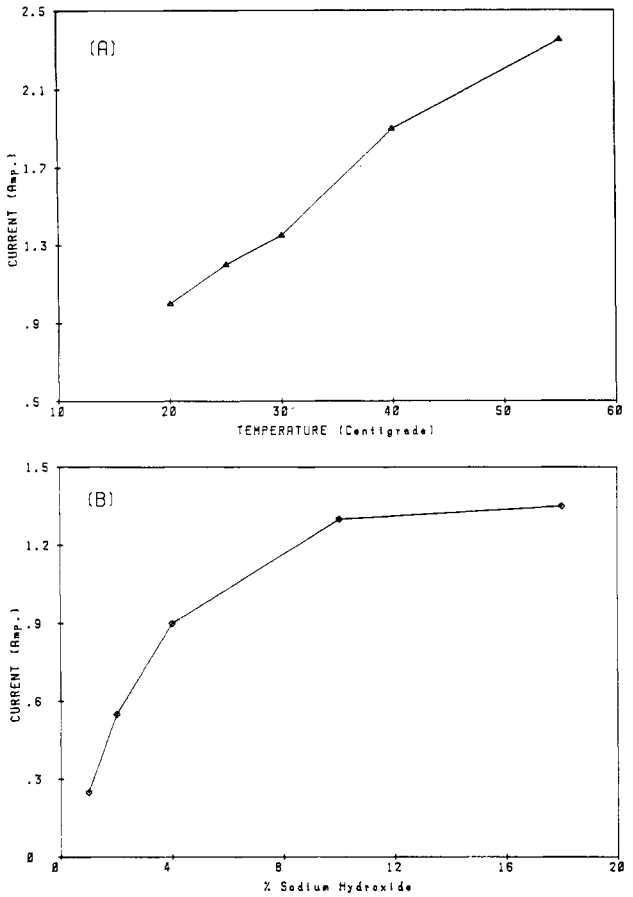

Figure 1. Influence of temperature and hydroxide concentration on rate of oxidation of glycerol. (A) Observed oxidation current as a function of temperature. Stirred solution of 5 g of glycerol/100 mL of 18% aqueous NaOH, electrolyzed at 0.2 V. vs. SCE. (B) Observed oxidation current as a function of hydroxide concentration. Stirred solution of 5 g of glycerol/100 mL solution, electrolyzed at 0.2 V vs. SCE, 30 °C.

in situ formed silver oxide on a silver electrode.

Results and Discussion

The oxidation of glycerol to glyceric acid occurs in aqueous basic medium when a potential of 0.2–0.6 V vs. a saturated calomel reference electrode (SCE) is applied to a silver foil working electrode. A potential of +0.2 V is most suitable for avoiding side reactions such as oxygen evolution or overoxidation of glycerol. Through measurement of the current, the oxidation rate is observed to be dependent on both hydroxide concentration and temperature and in general increases as either of these factors increase. The temperature effect was observed by using thermostated solutions. Interestingly, this effect is roughly linear over the region examined (Figure 1A). We have no plausible explanation for this at this time. We prefer temperatures below 45 °C because some decarboxylation seems to occur above this temperature as evidenced by CO_2 evolution upon acidification of the electrolyzed solution. The effect of hydroxide concentration is dramatic up to a concentration of about 10% above which the rate is not significantly altered (Figure 1B). In neutral or acidic media the desired oxidation does not occur. The oxidation takes place in either divided or undivided cells. The only reactions observed at the potentials used are the oxidation of glycerol at the anode and hydrogen evolution at the cathode. The oxidation is believed to be a typical heterogeneous electrocatalytic reaction involving in situ formed silver oxides at the anode surface. Mechanisms via such surface oxides have been proposed.[5] Although a silver mirror test for aldehyde was positive during the electrolysis, no aldehyde was detected in the isolated products. Other possible side products were negligible, as evidenced from the IR spectrum of the calcium salt and the almost stoichiometric yield of the salt referred to the starting amount of glycerol. As regards the speculated mechanism, it should be noted that when the black oxide surface of the anode was exposed to the solution, with the circuit open, the blackness quickly disappeared, most probably as a result of chemical reaction of the oxide with glycerol. However, this did not happen in the absence of glycerol.

Experimental Section

An undivided three-electrode cell was employed, with a Princeton Applied Research Corp. potentiostat, Model 371 (20 V compliance and current limit of 7 A). Typically, 12 g (0.13 mol) of glycerol was dissolved in 100 mL of water containing 10 g (0.25 mol) of NaOH. The solution was electrolyzed at an anodic potential of 0.2 V vs. SCE at 25–35 °C with constant stirring. A cylindrical silver foil, ~100 cm^2 exposed area, served as anode and a graphite rod, cocentric with the anode, as cathode. The reference electrode, Luggin capillary, was almost touching the inner part of the anode. After the theoretical coulombs had passed (~10 h, initial current ~4 A, final current ~0.08 A) the electrolysis was stopped. The solution was brought to pH 8 with concentrated HCl, and the water was evaporated at 50–80 °C from a petri dish. The white crystals thus obtained were washed with 35 mL of acetone and then with 35 mL of methanol and were dried at ~50 °C. Thus, 25 g of white crystals were obtained, consisting of sodium glycerate and sodium chloride. From this mixture glyceric acid can be recovered upon acidification as a syrupy liquid. However, great care should be exercised during water removal in order to avoid interesterification of the glyceric acid.

The infrared spectrum of the calcium salt of the produced glyceric acid was identical with a standard spectrum (*Aldrich Library of Infrared Spectra*). The identity of the Ca salt was confirmed by melting point [mp 130–135 °C (lit. mp 137–139 °C)]: ^1H NMR (decoupled in D_2O) δ 8.41 (OH, s), 4.62 (CH(OH), 1 H, s), 3.91 (CH_2OH, 2 H, s) [lit. for glyceric acid (polysol), δ 5.41 (OH, s), 4.12 (CH(OH), 1 H, t), 3.72 (CH(OH), 2 H, d)]; ^{13}C NMR (decoupled in D_2O) δ 62.3 (CH_2OH), 171.8 (CH(OH)), 180.4 (CO_2H).

Acknowledgment. We acknowledge the help of Dr. Edwin G. E. Jahngen in obtaining and interpreting the NMR data.

Registry No. NaOH, 1310-73-2; glycerol, 56-81-5; sodium glycerate, 70333-81-2; glyceric acid, 473-81-4.

(5) Fleischmann, M.; Korinek, K.; Pletcher, D. *J. Chem. Soc., Perkin Trans. 2* **1972**, 1396.

Activation and Coupling of Pyrrole-1-carboxylic Acid in the Formation of Pyrrole *N*-Carbonyl Compounds: Pyrrole-1-carboxylic Acid Anhydride

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The preparation of pyrrole *N*-carbonyl compounds typically are based on the nucleophilic coupling of 1,1′-carbonyldipyrrole[2] or the selective N-acylation of pyrrole

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