at δ 0.9–1.8, and a singlet (9 H) at δ 0.83. The product was not purified further.

Reduction of Monotosylate.—In a nitrogen atmosphere, a solution of 379 mg (1.1 mmol) of crude monotosylate in 3 ml of dry tetrahydrofuran was added dropwise to a stirred slurry of 900 mg (24 mmol) of lithium aluminum hydride in 10 ml of dry tetrahydrofuran. After the mixture had been stirred for 1 hr at room temperature and 3 hr at reflux, addition of ethyl acetate at 0° destroyed excess lithium aluminum hydride. The mixture was diluted with 100 ml of water and extracted with ether. Subsequent drying and concentration *in vacuo* produced 230 mg of crude oil. Vpc analysis[26] of the crude mixture showed two peaks in the ratio of 97:3. The shorter retention time peak (97% isomer) was identified as 1-ethyl-*trans*-4-*t*-butylcyclohexanol (IX) by comparison of retention time and infrared spectrum with that of an authentic sample. The longer retention time peak (3% isomer) was identified as 1-ethyl-*cis*-4-*t*-butylcyclohexanol (X) by comparison of vpc retention time with that of an authentic sample and physical properties and infrared spectral data with the published information.[13]

Reaction of Dimethylthetin Anion with Diisopropyl Ketone.—To a solution of 6.5 mmol of dimethylthetin anion was added 775 mg of diisopropyl ketone. The resulting suspension was stirred for 16 hr at room temperature; however, the suspension remained. It was poured onto ice and acidified to pH 1 with hydrochloric acid. Ether extraction followed by drying and diazomethane treatment produced an oil which exhibited three peaks on vpc.[27] The first peak (73%) was diisopropyl ketone. The

second peak (12%) showed no carbonyl group in its infrared spectrum.[22] The nmr spectrum[22] exhibited a singlet (2 H) at δ 2.45, a multiplet (2 H) at δ 1.96, a doublet (6 H) at δ 0.90 (*J* = 6.5 Hz), and a doublet (6 H) at δ 0.85 (*J* = 6.5 Hz). From this data, the compound is tentatively identified as 1,2-epoxy-2-isopropyl-3-methylbutane (XI).

Anal. Calcd for C₈H₁₆O: C, 74.94; H, 12.58. Found: C, 74.75; H, 12.56.

The third component (14%) showed ester carbonyl stretching absorption (1740 cm⁻¹) in its infrared spectrum.[22] The nmr spectrum[19] exhibited three singlets at δ 3.72, 3.18, and 2.20 in the ratio 3:2:3. These data identify this material as methyl methylthioacetate; comparison with an authentic sample confirmed the assignment.

Registry No.—IIb, 23511-07-1; IIIb, 23511-06-0; V, 23511-08-2; VI, 23511-09-3; VII, 23511-10-6; VIII, 23511-11-7; XI, 23511-12-8; 1-(2-hydroxyethyl)-1-hydroxy-4-*t*-butylcyclohexane, 23511-13-9.

(26) An 8 ft × 0.25 in. 20% diethylene glycol glutarate on Chromosorb P column was employed for this analysis.

(27) An 8 ft × 0.25 in. 20% Carbowax 20M on Chromosorb P column was employed for this analysis.

The Stereochemistry of Electroreductions.
III. Carbon–Oxygen Single Bonds[1]

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Optically active O-benzoylatrolactic acid and methyl O-benzoylatrolactate are reduced electrochemically to 2-phenylpropionic acid with almost complete loss of optical activity. This is in sharp contrast with the electroreduction of the related 2-chloro-2-phenylpropionic acid, which has been reported to undergo reduction with 77–92% inversion of configuration. The exact mechanisms of the two processes must differ.

Numerous workers have investigated aspects of carbon–halogen bond electroreductions. Lambert[2] has attempted a quantitative correlation between polarographic half-wave potentials and Taft polar and steric constants. Several papers have been concerned with the effect of structure on half-wave potentials[3] and mass electrolysis data.[4] Annino, *et al.*,[1] have examined the stereochemical nature of these reductions using cyclopropyl halide derivatives. They explained their results on the basis of the formation and subsequent breakdown of an intermediate electrode complex.

In contrast to carbon–halogen bond reductions, the electroreduction of carbon–oxygen single bonds has received little attention. Wawzonek and Fredericksen[5] examined several mandelonitriles and mandeloni-

trile esters polarographically and reduced I to II in good yield by mass electrolysis. Kabaskalian and
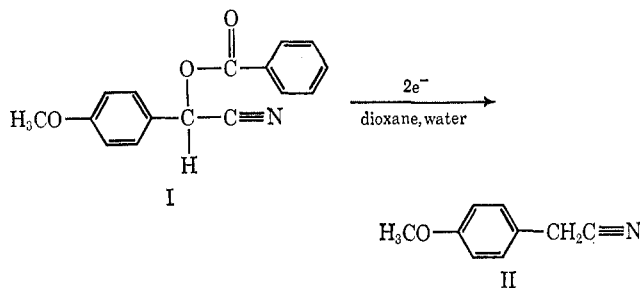
McGlotten reduced a series of hydroxy keto steroids polarographically and followed this study with several controlled potential mass electrolyses.[6]

We report in this paper on the stereochemistry of the electroreduction of atrolactic acid derivatives. The compounds were chosen for initial stereochemical study because (a) analogy with Wawzonek and Fred-

(1) R. Annino, R. E. Erickson, J. Michalovic, and N. McKay, *J. Amer. Chem. Soc.*, **88**, 4424 (1966); R. E. Erickson, R. Annino, M. Scanlon, and G. Zon, *ibid.*, **91**, 1767 (1969).

(2) J. L. Lambert, *J. Org. Chem.*, **31**, 4184 (1966).

(3) F. L. Lambert and K. Kobayaski, *J. Amer. Chem. Soc.*, **82**, 5324 (1960); F. L. Lambert, A. H. Albert, and J. P. Hardy, *ibid.*, **86**, 3155 (1964); J. Zavada, J. Krupieka, and J. Sicher, *Collect. Czech. Chem. Commun.*, **28**, 1664 (1963); P. Zuman, *Talanta*, **12**, 1337 (1965); J. W. Sease, P. Chang, and J. L. Groth, *J. Amer. Chem. Soc.*, **86**, 3154 (1964).

(4) P. J. Elving, I. Rosenthal, and A. J. Martin, *ibid.*, **77**, 5218 (1955); S. Wawzonek, R. C. Duty, and J. H. Wagenknecht, *J. Electrochem. Soc.*, **111**, 74 (1964); G. Klopman, *Helv. Chim. Acta*, **44**, 1908 (1961).

(5) S. Wawzonek and J. D. Fredericksen, *J. Electrochem. Soc.*, **106**, 325 (1959).

(6) P. Kabaskalian and J. McGlotten, *Anal. Chem.*, **31**, 1091 (1959); P. Kabaskalian, J. McGlotten, A. Bosch, and M. D. Yuchs, *J. Org. Chem.*, **26**, 1738 (1961).

ericksen's mandelonitriles[5] suggested that the compounds would be reducible, (b) configurational relationships between atrolactic acid and its reduction product, 2-phenylpropionic acid, are known, and (c) the stereochemistry of the electroreduction of the related halide, 2-chloro-2-phenylpropionic acid, has been determined; therefore direct stereochemical comparisons can be made between carbon–oxygen and carbon–halogen single-bond reductions.

Experimental Section

Materials.—Eastman tetraethylammonium bromide (TEAB) was recrystallized several times from ethanol before use. Undenatured 95% ethanol was used without any further purification. Atrolactic acid was purchased from Pfaltz and Bauer and Aldrich chemical Co.

Atrolactic acid was resolved using α-phenylethylamine[7] (Aldrich) and esterified with diazomethane.[8]

Methyl O-Benzoylatrolactate.—The methyl ester was treated with benzoyl chloride (1:1) in pyridine at room temperature for 12 hr. The resulting solution was poured into water and extracted with ether. The combined ether extracts were washed with dilute hydrochloric acid, dried over anhydrous magnesium sulfate, and distilled under vacuum, bp 172° (2 mm). *Anal.* Calcd for $C_{17}H_{16}O_4$: C, 71.83; H, 5.64; O, 22.53.[9] Found: C, 71.68; H, 5.69; O, 22.63.

O-Benzoylatrolactic Acid.—O-Benzoylatrolactic acid was prepared by treating the parent acid with benzoyl chloride in pyridine as described above. The dried ether extracts were evaporated under vacuum yielding a white solid, mp 130.5–132°. *Anal.* Calcd for $C_{16}H_{14}O_4$: C, 71.11; H, 5.19; O, 23.70. Found: C, 71.30; H, 5.38; O, 23.32.

Atrolactic acid, $[\alpha]^{25}D$ −31° (95% EtOH, 82% resolved),[10] upon esterification and subsequent benzoylation gave the methyl O-benzoylatrolactate derivative having $[\alpha]^{25}D$ −35.33° (95% EtOH). Atrolactic acid, $[\alpha]^{25}D$ 29.78° (95% EtOH, 78.9% resolved), gave an O-benzoyl derivative having $[\alpha]^{25}D$ 31.67° (95% EtOH).

Apparatus.—Polarographic analyses were performed on a Sargent Model XV polarograph in conjunction with a Sargent IR compensator. A Sargent three-electrode Arthur polarographic cell was employed in all determinations. Saturated ethanol calomel electrodes were directly prepared in this cell[11,12] and used as both reference and counter electrodes.

Cyclic voltammetry experiments were performed on a Chemtrix Model SSP-2 single-sweep polarographic analyzer.

In the controlled-potential electrolysis experiments, constant effective potential was maintained with a Model 557/SU potentiostat purchased from Amel Instrument Co., Milano, Italy. Coulometric data was obtained using an Amel Model 558 electronic integrator connected to the potentiostat. Two electrolysis cells, a double-diaphragm model described by Meites[13] and a Model 494 cell from Amel, were employed. The reference electrode in both cases was a commercial saturated calomel electrode. The counter electrode was either a platinum wire or platinum sheet electrode isolated from the sample compartment. A mercury pool electrode was employed as the cathode.

Nuclear magnetic resonance spectra were recorded on a Varian HA-60 recording spectrometer as approximately 15% solutions in chloroform-*d* (CDCl₃).

Optical rotations were measured on an O. C. Rudolph & Sons polarimeter, Model 80. All measurements were made in 95% ethanol using a 10-cm cell.

Polarographic Analysis.—Portions (75 ml) of 0.1 *M* TEAB in 95% ethanol were pipetted into the cell compartment and oxygen was removed by passing nitrogen through the solution for at least 30 min. A 2.00-ml portion of 0.015 *M* ethanolic solution of the

(7) L. Smith, *J. Prakt. Chem.*, **84**, 731 (1911).

(8) "Organic Syntheses," Coll. Vol. IV, John Wiley & Sons, Inc., New York, N. Y., 1963, p 250.

(9) All microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

(10) A. McKenzie and G. W. Clough, *J. Chem. Soc.*, **97**, 1020 (1910).

(11) P. Arthur and H. Lyons, *Anal. Chem.*, **24**, 1422 (1952).

(12) P. Arthur, P. A. Lewis, N. A. Lloyd, and R. K. Vanderkam, *ibid.*, **33**, 488 (1961).

(13) L. Meites, *ibid.*, **27**, 1116 (1955).

compound to be analyzed was added and the solution was polarographed under a nitrogen atmosphere. All data were obtained directly from the recorded polarograms.
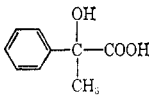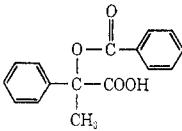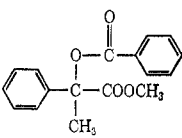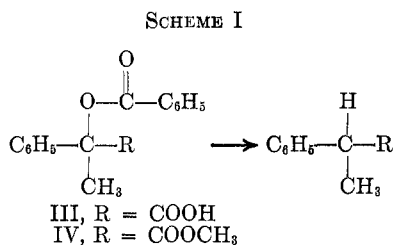
Controlled-Potential Electrolysis.—Electrolyte solution (0.1 *M* TEAB in 95% ethanol) was added to the cell and purged with nitrogen. The mercury pool–solution interface was kept in motion with a mechanical stirrer or a magnetic stirrer. The residual current was recorded at a number of control potentials and the potential at which significant discharge from the supporting electrolyte occurred was noted. The sample (0.5–1.0 g) was dissolved in a minimum amount of ethanol and added to the cell. The solution was again purged with nitrogen and then electrolyzed at the appropriate control voltage. The electrolysis was allowed to proceed until residual current was obtained.

Product Analysis.—The electrolysis solution was poured into three times its volume of water and extracted with ether. In the case of the acid as starting material, the solution was made acidic with concentrated sulfuric acid before extraction. The ether extracts were dried over anhydrous magnesium sulfate and evaporated under vacuum. An nmr spectrum and optical rotation measurements, where appropriate, were obtained on this ether residue. The electrolysis product from O-benzoylatrolactic acid was first chromatographed on silica gel before optical measurement was obtained.

Results and Discussion

Table I summarizes the polarographic data obtained in this study.

TABLE I
POLAROGRAPHIC DATA FOR THE REDUCTION OF CARBON–OXYGEN SINGLE BONDS

Compd	$E_{1/2}{}^a$	$I_d{}^b$	Media
(phenyl)C(OH)(CH₃)—COOH	−1.73		0.1 *M* TEAB in 95% EtOH
	−1.60		
(O–C(=O)–phenyl)(phenyl)C(CH₃)—COOH		2.41	0.1 *M* TEAB in 95% EtOH
	−1.84		
	−1.86		0.1 *M* TEAB in 95% EtOH; equimolar base added
	−1.48		0.1 *M* TEAB in 95% EtOH; equimolar acid added
	−1.84		
(O–C(=O)–phenyl)(phenyl)C(CH₃)—COOCH₃	−1.82	2.03	0.1 *M* TEAB in 95% EtOH
	−1.82		0.1 *M* TEAB in 95% EtOH; equimolar base added
	−1.48		0.1 *M* TEAB in 95% EtOH; equimolar acid added
	−1.82		

a Potentials are in volts relative to saturated ethanol calomel electrode. *b* $I_d = i_d / Cm^{2/3}t^{1/6}$; i_d is the diffusion current measured at the maximum of the instantaneous current.

As can be seen, atrolactic acid exhibits a polarographic wave within the voltage range observed. This represents the reduction of the acidic proton to hydrogen. Polarographic experiments with O-benzoylatrolactic acid (III) and its methyl ester (IV) establish that the first wave in the reduction of III is indeed the reduction of the carboxylic acid proton. Wave height analysis[14] shows that the second wave in III and the wave in IV are both diffusion controlled.

The reductions of III and IV are irreversible as evidenced from cyclic voltammetry experiments. Scan reversal past the cathodic peak at speeds up to 5 V/sec resulted in no evidence of reoxidation.

(14) L. Meites, "Polarographic Techniques," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1965, Chapters 3 and 4.

Controlled-potential electrolysis of both III and IV resulted in cleavage of the carbon–oxygen bond and subsequent carbon–hydrogen bond formation. See Scheme I. Electrolysis of atrolactic acid yielded only the starting acid with no indication of carbon–oxygen bond cleavage.

SCHEME I

$$
\begin{array}{ccc}
& O & \\
& \parallel & \\
& O-C-C_6H_5 & \\
& | & H \\
C_6H_5-C-R & \longrightarrow & | \\
& | & C_6H_5-C-R \\
& CH_3 & | \\
& & CH_3
\end{array}
$$

III, R = COOH
IV, R = COOCH₃

Potential was maintained at −1.80 V for the electrolysis of III and at −1.90 V for IV (vs. sce). Coulometric data for IV indicated that the reduction proceeded via 2e⁻/mol. The number of electrons involved for III were variable owing to the presence of the acid proton wave in this compound.

The products were identified from their respective nmr spectra. The spectrum resulting from reduction of III had a doublet at 1.42, a quartet at 3.63, and a singlet at 7.17 ppm. The spectrum also contained absorption at 8 ppm indicative of the presence of benzoic acid. A triplet at approximately 1.1 and a quartet appearing at 3.65 ppm were shown to represent impurity unrelated to the actual electrolysis product. The product from IV contained a doublet at 1.4 (3 H), an overlapping singlet and quartet at 3.55, (4 H), and a singlet at 7.2 ppm (5 H). The presence of a triplet at 1.15 and a quartet at 4.00 ppm was taken as evidence of ester exchange with concomitant formation of ethyl 2-phenylpropionate. Since the pH of the electrolysis solution varies from 6 to 9 during the reaction period, the assumption of ester interchange is reasonable. The stereochemical data obtained are given in Table II.

This is in contrast to our earlier reductions of cyclopropyl halides[1] in which moderately high stereospecificities (56% inversion to 38% retention) were found. However, analogies to cyclopropyl systems might not be valid owing to the special stereochemical characteristics of the cyclopropyl carbanion. More pertinent to an understanding of the mechanism of carbon–oxygen single bond reductions is a comparison to Czochraloka's work on compound V.[15]
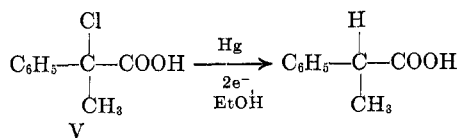
$$
\begin{array}{ccc}
Cl & & H \\
| & Hg & | \\
C_6H_5-C-COOH & \xrightarrow[\text{EtOH}]{2e^-} & C_6H_5-C-COOH \\
| & & | \\
CH_3 & & CH_3 \\
V & &
\end{array}
$$

TABLE II
STEREOCHEMICAL RESULTS

Compd	Electrolyte	$[\alpha]_D$ found, deg	$[\alpha]_D$ calcd,[a] deg	Lit. $[\alpha]_D$, deg
III	0.1 M TEAB in 95% EtOH	−1.0	±35.07[b]	±58[c−f]
IV	0.1 M TEAB in 95% EtOH	−0.15	±47.56[g]	±86.0[c,h]
IV	0.1 M TEAB in 95% EtOH	−0.50	±47.56	±86.0[h]
IV	0.1 M TEAB in 95% EtOH, dilute HAc added to control pH at ca. 7	−4.60	±47.56	±86.0[i]
IV	0.1 M TEAB in 95% EtOH, dilute HAc added to control pH at ca. 7	+0.76	±47.56	±86.0[i]

[a] Calculated based on literature value of ±58° and optical purity of starting material. [b] 77.7% resolved starting material. [c] W. A. Bonner, J. A. Zderic, and G. A. Casaletto, *J. Amer. Chem. Soc.*, **74**, 5088 (1952). [d] E. L. Eliel and J. P. Freeman, *ibid.*, **74**, 923 (1952). [e] W. A. Bonner, *ibid.*, **74**, 1038 (1952). [f] References contained in footnotes c–e. Discrepancies for this value range from ±54.2 to ±81.0°. [g] 82% resolved starting material. [h] Product also contains ethyl 2-phenylpropionate. [i] No evidence of ethyl 2-phenylpropionate in nmr.

Czochraloka reported this electroreduction to proceed with 77–92% inversion of configuration and explained the result in terms of an S_N2-type mechanism. We do not agree that initial attack is on the rear side of the carbon atom and have proposed a fairly complicated mechanism into which Czochraloka's data would fit.[1] *It is obvious, however, that, whatever the true picture of carbon–halogen bond electroreductions is, the mechanism of carbon–oxygen single-bond reductions is different.*

The most obvious difference in the electroreduction of carbon–halogen vs. carbon–oxygen bonds is in the nature of the leaving group. It may be that adsorption of benzoate ion on the electrode is an important factor but we would prefer to defer speculation until we have completed further stereochemical and polarographic investigations.[16]

Registry No.—(+)-O-Benzoylatrolactic acid, 23510-90-9; methyl (−)-O-benzoylatrolactate, 23510-91-0.

(15) B. Czochraloka, *Chem. Phys. Lett.*, **1**, 239 (1967).

(16) Fry and Mitnick [A. J. Fry and M. A. E. Mitnick, *J. Org. Chem.*, **35**, 1232 (1970)] have shown that the stereochemistry of electroreduction of some geminal dihalonorbornanes varies with the addition of surface active species. We thank Professor Fry for a preprint of his publication.