may be attributed to intervention by a complex such as **11**.

Thus it appears that the dependence of the isomeric composition of the product mixture obtained by reduction of 3,3,5-trimethylcyclohexanone or 4-*tert*-butylcyclohexanone with TIBA cannot be attributed to a single cause. At least three minor factors are operative: isomeric equilibration *via* a Meerwein-Ponndorf-Verley type reduction, association of the reducing agent, and complexation of TIBA by the initially formed aluminum alkoxide. Greatest selectivity is attained when TIBA is employed in excess and the reduction is performed in concentrated solution.

Experimental Section

Manipulations of air-sensitive compounds were performed either in a Kewaunee inert atmosphere box or by employing special bench-top techniques.[17] Reagents were transferred in flame-dried syringes which were cooled under nitrogen. Products were analyzed by glc utilizing a 20-ft column packed with 5% Carbowax 20M on Chromosorb G and a Hewlett-Packard Model 700 chromatograph. Ethyl benzoate was employed as internal standard in reduction of 3,3,5-trimethylcyclohexanone, and analyses were performed at 135°. Retention times for ketone, axial alcohol, and equatorial alcohol were 16.0, 25.2, and 31.1 min, respectively. For reduction of 4-*tert*-butylcyclohexanone, 3,3,5-trimethylcyclohexanone was used as internal standard and analyses were performed at 150°. Retention times for ketone, axial alcohol, and equatorial alcohol were 22.6, 25.9, and 31.0 min, respectively.

Materials.—Reagent-grade ether and benzene were refluxed for 24 hr over $LiAlH_4$ and $NaAlH_4$, respectively, distilled through a 3-ft Vigreux column, and stored over sodium–lead alloy (J. T. Baker dri-Na) in a nitrogen atmosphere. Standard solutions of diisobutylaluminum hydride and triisobutylaluminum were prepared from the aluminum compounds as received (Ethyl Corp.). Aluminum analysis of the solutions by EDTA titration were in all cases satisfactory. Hydrolysis of an aliquot and analysis of the gases evolved indicated the presence of 2.7% active hydride in the triisobutylaluminum. 3,3,5-Trimethylcyclohexanone (Chemical Samples Co., 99%) was distilled through a 2-ft glass helices column and the middle fraction was used in this study. 4-*tert*-Butylcyclohexanone (Frinton Laboratories) was sublimed prior to use.

General Procedure for Reduction.—A 50-ml erlenmeyer flask containing a magnetic stirring bar was flame dried and allowed to cool under vacuum in the entry port of an inert atmosphere box. After transfer of the flask into the box, it was sealed with a rubber septum, removed from the box, and connected by means of a needle to a nitrogen-filled manifold equipped with an oil-filled bubbler. A solution of the appropriate ketone (1.00 mmol, *ca.* 1 ml of 1 *M* solution) was introduced into the reaction vessel followed by sufficient solvent to bring the final volume to 10.0 ml except in those cases where TIBA concentration was being studied. Stirring was initiated and the flask was immersed in a water bath at 0° for the reactions to be carried out in ether or at 22° for those to be carried out in benzene. After the flask had come to temperature equilibrium, a solution (*ca.* 1 *M*) of the appropriate organoaluminum reagent was introduced, allowed to react for 2.0 hr, and then quenched by addition of *ca.* 0.5 ml of 5% HCl. Internal standard was added and the product mixture was analyzed by glc.

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Registry No.—**1**, 873-94-9; **2**, 98-53-3; diisobutylaluminum hydride, 1191-15-7; triisobutylaluminum, 100-99-2; axial 3,3,5-trimethylcyclohexanol, 767-54-4; equatorial 3,3,5-trimethylcyclohexanol, 933-48-2; axial 4-*tert*-butylcyclohexanol, 937-05-3; equatorial 4-*tert*-butylcyclohexanol, 937-06-4.

(17) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N. Y. 1969.

The Stereochemistry of Electroreductions. IV. Carbon–Sulfur Single Bonds[1]

CHARLES M. FISCHER AND RONALD E. ERICKSON*

Department of Chemistry, University of Montana, Missoula, Montana 59801

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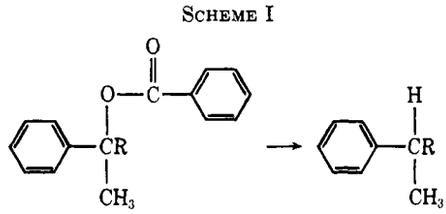
The stereochemistry of the electroreduction of optically active ethyl 2-phenylmercaptopropionate was investigated. Reaction proceeds with the formation of ethyl 2-phenylpropionate of low optical activity (2–4% stereospecificity–inversion of configuration being observed).

In an earlier paper,[1c] we reported the stereochemical features of the electroreduction of atrolactic acid derivatives. Controlled potential electrolysis of both *O*-benzoylatrolactic acid (I) and methyl *O*-benzoylatrolactate (II) resulted in cleavage of the carbon–oxygen bond and subsequent carbon–hydrogen bond formation (see Scheme I). The stereochemical results indicated that the reduction proceeded with almost complete loss of optical activity.

These results were in contrast to earlier reported reductions of cyclopropyl halides[1a,b] in which moderately high stereospecificities (56% inversion to 38% retention) were found. Also, Czochralska found that the electrochemical reduction of 2-chloro-2-phenylpropionic acid proceeded with a very high degree of

SCHEME I



I, R = COOH
II, R = $COOCH_3$

stereospecificity (77% to 92% inversion of configuration).[2]

The present paper reports the results obtained in a study of the stereochemistry of the electroreduction of carbon–sulfur single bond substrates. It was thought

(1) For earlier papers in this series see (a) R. Annino, R. E. Erickson, J. Michalovic, and B. McKay, *J. Amer. Chem. Soc.*, **88**, 4424 (1966); (b) R. E. Erickson, R. Annino, M. D. Scanlon, and G. Zon, *ibid.*, **91**, 1767 (1969); (c) R. E. Erickson and C. M. Fischer, *J. Org. Chem.*, **35**, 1604 (1970).

(2) B. Czochralska, *Chem. Phys. Lett.*, **1**, 239 (1967). We have attempted to repeat Czochralska's work but have been unsuccessful. Yields of the expected product were on the order of 50% and essentially no optical activity was found in the product mixture.

TABLE I

ELECTROCHEMICAL AND STEREOCHEMICAL DATA

Reactant	Reactant α_D (lit.)[a]	$e^{1/2}$,[b] V	E_c,[c] V	e⁻/mol	Product (yield, %)	Product α_D (lit.)[d]
C_6H_5—C(SC$_6$H$_6$)(CH$_3$)—COOH		1.76	1.80–2.0	2.02	Starting material	
C_6H_5—C(SC$_6$H$_6$)(CH$_3$)—COOEt	56.2 ± 1.36° (89.8°)	1.92	1.9–2.0	1.96	C_6H_5—C(H)(CH$_3$)—COOH (90%) + C_6H_5SH (90%)	+4.23 ± 1.84° (45.20)[d]
C_6H_5—C(SC$_6$H$_6$)(CH$_3$)—COOEt	56.2 ± 1.36° (89.8°)	1.92	2.0	2.00	C_6H_5—C(H)(CH$_3$)—COOH (90%) + C_6H_5SH (90%)	+2.20 ± 0.68° (45.20)[d]

[a] Reference 4. [b] All polarograms obtained in 0.1 *M* TEAB in 95% ethanol. Measurements are in volts relative to a saturated ethanol calomel electrode. [c] Potentials are in volts relative to a commercial saturated calomel electrode. E_c symbolizes the value at which the voltage was controlled during electrolysis. [d] Literature[4] indicates an expected value of 72.2° (EtOH) if the ester were optically pure. The 45.2° (EtOH) value is what we would expect for a stereospecific reaction from 62% resolved starting material.

that this data would be valuable in terms of comparison with our earlier work. The compounds chosen for study were 2-phenyl-2-phenylmercaptopropionic acid and its ethyl ester. Studies correlating the configurations of these compounds with their expected reduction products, 2-phenylpropionic acid and its ethyl ester, were available in the literature.[3] Thus, the stereochemical features of the reduction of these substrates could be determined.

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.; *d*-(+)- and 1-(−)-α-methylbenzylamine were purchased from Aldrich Chemical Co.

2-Phenyl-2-phenylmercaptopropionic Acid (III).—This acid was prepared according to the procedure of Bonner[4] in a yield of 72%, mp 100–103° (lit. mp 104.5–105°). The nmr spectrum of this compound in chloroform-*d* had the following signals: δ 1.83 (s), 7.39 (m), >8.00 (s).[5]

The acid was resolved using optically active α-methylbenzylamine according to the procedure of Bonner.[4] The resolved acid had $[\alpha]^{25}D$ +123.5 ± 2.8°, EtOH (lit. $[\alpha]^{25}D$ 165.5°, EtOH).

Ethyl 2-Phenyl-2-phenylmercaptopropionate (IV).—This ester was prepared according to the procedure of Bonner[4] in a yield of 92%. The nmr spectrum of this compound in chloroform-*d* had the following signals: δ 1.21 (t), 1.83 (s), 4.17 (q), 7.33 (m).

Optically active ethyl 2-phenyl-2-phenylmercaptopropionate was synthesized from optically active 2-phenyl-2-phenylmercaptopropionate acid according to the procedure of Bonner.[4] The acid, $[\alpha]^{25}D$ +123.5 ± 2.8° (EtOH), gave the ester having $[\alpha]^{25}D$ +56.2 ±: 1.36° (Et_2O). The literature value for this ester is $[\alpha]^{25}D$ +89.8° (Et_2O).

2-Phenylpropionic Acid.—Ligroin (bp 35–55°) was added to 22.56 g of a sodium hydride–mineral oil (50:50) mixture. This was swirled by hand for approximately 15 min and the liquid was decanted, leaving 11.28 g of sodium hydride.

Benzyl cyanide (50 g, 0.427 mol) was dissolved in dimethylformamide. Sodium hydride (11.28 g, 0.47 mol) and 55.5 g (0.47 mol) of ethyl carbonate were added to this solution. The solution was kept cold until the evolution of hydrogen gas ceased. The solution was then stirred for an additional 1 hr at room temperature.

Methyl iodide (60.6 g, 0.427 mol) was added to the solution, and the reaction mixture was heated in a water bath for approximately 2.5 hr. The reaction mixture was then cooled and poured into water, and the product was extracted with benzene. The benzene extracts were dried with anhydrous magnesium sulfate and the dried extracts were evaporated *in vacuo*. The resulting residue was distilled *in vacuo* and 55.62 g (0.27 mol) of distillate was collected in the range of 109–118° (1–2 mm) [lit.[6] 139–152° (15 mm)]. The nmr data (chloroform-*d*) for 2-phenyl-2-cyanoethyl propionate was δ 1.24 (t), 1.96 (s), 4.23 (q), 7.45 (m).

2-Phenylethyl cyanide (21.1 g) was obtained by hydrolysis of 2-phenyl-2-cyanoethyl propionate according to the method of Delaby, *et al.*, bp 107–110° (12–16 mm) [lit. bp 109° (15 mm)].

2-Phenylethyl cyanide was hydrolyzed to 2-phenylpropionic acid by the method of Campbell and Kenyon,[7] and 15.1 g of the product (23.4% yield) was obtained, bp 153–155° (12–16 mm) [lit.[6] bp 145° (13 mm)]. The nmr data for this compound in chloroform-*d* were δ 1.49 (d), 3.70 (q), 7.23 (s), >8.00 (s).

2-Phenylpropionic acid was resolved using strychnine according to the method of Raper.[8] It has $[\alpha]^{25}D$ ±76.2° ($CHCl_3$). The acid was resolved giving $[\alpha]^{25}D$ +10.7° ($CHCl_3$, 14% resolved).

Ethyl 2-Phenylpropionate.—This ester was prepared from 2-phenylpropionic acid *via* Fisher esterification. 2-Phenylpropionic acid having $[\alpha]^{25}D$ +10.7 ± 1.4° (14% resolved) gave upon esterification the ester having $[\alpha]^{25}D$ +10.0 ± 0.7° (13.9% resolved).

Apparatus.—Polarographic analyses, controlled potential electrolyses, and cyclic voltammetry experiments were carried out as described in an earlier paper.[1c]

Optical rotations were measured on an O. C. Rudolph and Sons polarimeter, Model 80. Two cells were employed, one of 10 cm and the other 5 cm in length. Measurements were performed in the appropriate previously reported solvent.

Nuclear magnetic resonance spectra were recorded on a Varian HA-60 recording spectrometer as approximately 15% solutions in appropriate solvents.

Compounds III and IV were examined under the conditions of cyclic voltammetry.[1c] In both cases, scan reversal past the cathodic peak at speeds up to 5 V/sec resulted in no evidence of reoxidation.

Product Analysis.—In most instances, the electrolysis solution was analyzed immediately upon completion of the experiment. In those cases where this procedure was not followed, the solution was first neutralized with dilute sulfuric acid and was then placed in a refrigerator before analysis.

The procedure employed to isolate the product of reaction consisted of pouring the electrolysis solution into three times its volume of water followed by extraction with ether. When one of the acids was used as a starting material, the solution was made acidic with dilute sulfuric acid before extraction. The ether extracts were dried over anhydrous magnesium sulfate and evaporated under vacuum. Nmr spectra and optical rotation measurements, where appropriate, were obtained on this ether residue.

Results and Discussion

Table I summarizes the important electrochemical and stereochemical data obtained in this study.

(3) W. A. Bonner and R. A. Grimm, *J. Org. Chem.*, **32**, 3022 (1967).
(4) W. A. Bonner, *J. Amer. Chem. Soc.*, **74**, 1034 (1952).
(5) Splitting designations are s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet.
(6) R. Delaby, P. Reynaud, and F. Lily, *Bull. Soc. Chim. Fr.*, 864 (1960).
(7) A. Campbell and J. Kenyon, *J. Chem. Soc.*, 25 (1946).
(8) J. Raper, *J. Chem. Soc.*, **123**, 2557 (1923).

Attempts to determine the electrolysis product of III were unsuccessful. Each time this compound was subjected to controlled-potential electrolysis (−1.76 V), the product isolated was the starting acid. This suggests that the polarographic wave for III at −1.76 V can be attributed to the reduction of the carboxylic acid proton to hydrogen. However, attempts to electrochemically reduce the anion of this acid also resulted in the isolation of starting acid.

The electrochemical reduction of ethyl 2-phenyl-2-phenylmercaptopropionate (IV) proceeded with rupture of the carbon–sulfur bond and subsequent carbon–hydrogen bond formation. The coulometric data in all cases was approximately 2 e/mol. Both of the reduction products, ethyl 2-phenylpropionate and thiophenol, were obtained in high yields and were identified by means of their nmr spectra.

Throughout this series of papers, the basis for investigating the mechanism of electroreductions has been the stereochemistry of the reaction. Bonner and coworkers[3,9] have established that (−)-atrolactic acid and (+)-2-phenylpropionic acid have the same configuration. They have also shown that (−)-2-phenyl-2-phenylmercaptopropanoic acid and (+)-2-phenylpropionic acid have identical configurations. Thus, by synthesizing the appropriate derivative (compound IV) from optically active starting materials *via* routes which do not disturb the configuration about the asymmetric carbon atom (see Experimental Section), the stereochemistry involved in the electroreduction of these substrates could be determined.

As can be noted in Table I, a small degree of inversion of configuration is found for carbon–sulfur single-bond reductions. Our results ranged from 9.35 ± 4.05% to 4.87 ± 1.33% inversion.

By subjecting the product of the reduction of the ester, *i.e.*, ethyl 2-phenylpropionate, to normal electrolysis conditions, it was found that this ester racemizes to some extent. The compound was found to undergo 50% racemization when subjected to conditions of pH 8–9 for 6 hr. However, it is still obvious that the electroreductions examined in this and previous[1c] work proceed with little or no stereospecificity. The value of 50% racemization does not explain the total lack of optical activity in the reduction products for atrolactic acid derivatives, and the percentage inversion for IV is low. Also, the duration of time required to perform the electrolyses of these compounds was usually less than 6 hr and those experiments where the pH was controlled at approximately 7 still resulted in the same relative lack of stereospecificity.

The stereochemical results for compound IV are in accord with the trends found earlier.[1a,b] We reported then a net inversion of configuration to occur in the electroreduction of methyl 1-bromo-2,2-diphenylcyclopropanecarboxylate. Those results were explained in terms of a mechanism involving an intermediate electrode complex with the same configuration as the reactant. The overall stereochemistry of the process was thought to be determined by a stereoselective reaction of a few electrode-shielded carbanions with solvent or proton. Other mechanisms have been suggested[10,11] and we had hoped that some light might be shed on the problem through the use of our substrates. Unfortunately, the picture is more clouded than ever. None of our systems show intermediates such as those found by Webb, Mann, and Walborsky[10] by cyclic voltammetry[12] and the one truly remarkable stereochemical result in the literature[2] could not be repeated.[2,13]

Acknowledgment.—The support of this work by the National Science Foundation is gratefully acknowledged.

Registry No.—(±)-III, 13479-08-8; (+)-III, 42253-92-9; (±)-IV, 42253-93-0; (+)-IV, 42253-94-1; benzyl cyanide, 140-29-4; ethyl carbonate, 105-58-8; methyl iodide, 74-88-4; 2-phenyl-2-cyanoethyl propionate, 15601-34-0; 2-phenyl ethylcyanide, 42253-96-3; (±)-2-phenylpropionic acid, 2328-24-7; (+)-2-phenylpropionic acid, 7782-24-3; ethyl 2-phenylpropionate, 42253-99-6.

(9) W. A. Bonner, J. A. Zdeiec, and G. A. Casaletto, *J. Amer. Chem. Soc.*, **74**, 5086 (1952).

(10) J. L. Webb, C. K. Mann, and H. M. Walborsky, *J. Amer. Chem. Soc.*, **92**, 2042 (1970).

(11) A. J. Fry and R. G. Reed, *J. Amer. Chem. Soc.*, **94**, 8475 (1972).

(12) Fry (ref 11) also found no evidence for organomercurials in the reduction of geminal dihalides.

(13) We are discontinuing work in this area. For those who wish to continue we suggest using substrates which are easily preparable in large quantities so that more time can be spent adjusting the electrochemical experimental parameters.