[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF EMORY UNIVERSITY]

# The Mechanism of the Electrochemical Reduction of Phenyl Ketones to Alcohols

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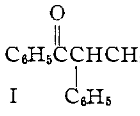
The electrolytic reduction of α-methyldesoxybenzoin has been shown to yield *erythro*-1,2-diphenylpropanol-1. The sodium in alcohol reduction was found to yield a mixture of *erythro*- and *threo*-alcohols. The implications of these findings as to the mechanism of electrolytic reductions of phenyl ketones to alcohols is discussed.

The electrolytic reduction of phenyl ketones to alcohols has been extensively studied in recent years both under polarographic conditions and at a large mercury pool with controlled potential.[1] Many proposals regarding the mechanism of the reduction process have been advanced. The generally accepted picture is that the over-all process is irreversible, although the addition of the first electron under polarographic conditions is reversible, at least in solutions of low *p*H. The irreversibility occurs during the addition of the second electron and proton, and has sometimes been associated with the electron transfer process and sometimes with a subsequent reaction. Studies of stereochemical factors which might contribute to a more detailed understanding of the process occurring at the electrode interface are not available.

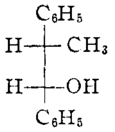
It was apparent that a study of the electrolytic reduction of a phenyl ketone containing an asymmetric center should furnish some information concerning the problem since the reduction could produce either one or two diastereomeric alcohols or a mixture thereof. Since the sodium in alcohol reduction of a ketone to an alcohol has been shown to be governed by equilibrium considerations,[2] a comparison of the reduction products formed *via* electrochemical means with those formed by sodium in alcohol could show whether the same factors determining the outcome of one of these processes are applicable in the other.

Toward this end, α-methyldeoxybenzoin (I) was reduced in two ways, first by sodium in alcohol and then electrolytically. The composition of the reduction products then was determined. It was found, by comparing the infrared spectra of the total crude reaction products with that of pure *erythro*, II, and *threo*, III, alcohols, that whereas sodium in alcohol reduction affords mixture of *erythro*- and *threo*-alcohols (enriched in *erythro* compound in the proportion about 1.8:1), the electrolytic reduction provided primarily the *erythro*-alcohol.[3]

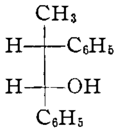


$C_6H_5\overset{\overset{O}{\|}}{C}\underset{\underset{C_6H_5}{|}}{C}HCH_3$

I

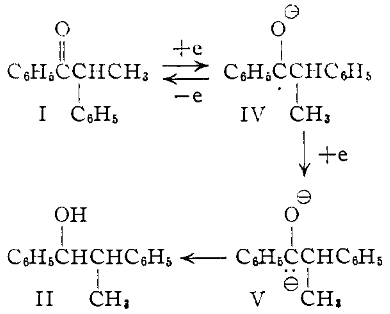


II

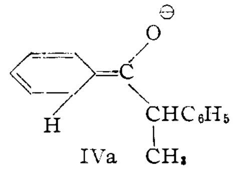


III

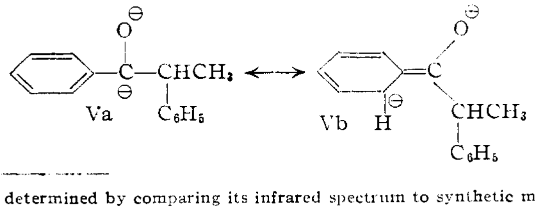
The above finding leads to the conclusion that *the step in the reduction in which the stereochemistry of the alcohol is determined must be rate controlled.* This fact coupled with previous work[1] now allows one to write a complete mechanistic interpretation for the reduction process, namely



This reaction sequence would allow explanation of the fact that the reduction potential is governed by equilibrium factors as the addition of the first electron is depicted as being reversible. It should be noted that in the ion radical IV the carbon atom bearing the free electron has as yet a planar configuration since the resonance forms stabilizing IV, such as IVa, involve double bond character at this carbon and thus a non-asymmetric sp²-hybridization. Therefore it is not until a subsequent stage that the stereochemistry of the resulting alcohol is determined.



The addition of the second electron producing the dianion V now affords the possibility for tetrahedral sp³-hybridization at the new asymmetric center. It is realized however, that the resonance shown below is possible



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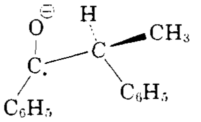
[1] P. J. Elving and J. T. Leone, A. E. C. Report No. 24, January, 1957; R. Pasternak, *Helv. Chim. Acta*, **31**, 753 (1948); M. Ashworth, *Collection Czechoslov. Chem. Communs.*, **13**, 229 (1948); H. J. Gardner, *Chemistry & Industry*, **29**, 819 (1951); R. A. Day, Jr., S. R. Milliken and W. D. Shults, THIS JOURNAL, **74**, 2741 (1952), and leading references therein.

[2] G. Vavon, *Bull. soc. chim.*, [4] **49**, 937 (1931); W. Hückel, *Ann. Chem.*, **533**, 1 (1937).

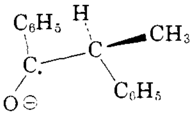
[3] The composition of the sodium in alcohol reduction product was determined by comparing its infrared spectrum to synthetic mixtures prepared from pure *erythro*- and *threo*-alcohols. The product of electrolytic reduction was determined similarly by infrared comparison. In the case of the electrolytic reduction the spectrum was completely identical with that of pure *erythro*-alcohol; however, since we found that it was not possible to detect amounts under 8% of *threo*-alcohol in a mixture of *erythro*- and *threo*-alcohols, we cannot rule out the presence of small amounts of *threo* compound.

Rate controlled protonation of this species could occur in a stereospecific manner[4] and were this to obtain the observed stereospecificity would then follow. There is, however, an alternative which can be put forth that has the advantage of being able to rationalize similar work carried out on the electrolytic reductions of other ketones (ref. 8) as well as being in accord with earlier polarographic studies.[1] The alternate scheme follows if the carbanion V is not free to undergo the type of resonance shown in Va and Vb. This would be so if *the electrons, which have been added to the carbonyl carbon, were still shared by the mercury electrode surface.* It is known that the mercury-to-carbon bond is essentially covalent[5] and hence the electrons involved in such a bond would not be free to participate in resonance leading to structures such as Vb. Electrons at the cathode may then displace this species into the solution which with simultaneous protonation yields II.[6] Thus it is seen that the stereochemistry of the resulting alcohol would be determined during the addition of the second electron.

This picture of the reduction may be further expanded to give a still more detailed physical concept of the process at the electrode surface. The expansion follows from the fact that the *erythro* and not the *threo* configuration was produced and allows one to depict the mode of attachment of IV to the electrode surface. The two most stable conformations for IV are IVa and IVb.



IVa



IVb

These represent rotational isomers about the central carbon to carbon bond where all the groups are coplanar except methyl and hydrogen which protrude from either side of the plane. In IVa the alkoxide anion is staggered with respect to the hydrogen and methyl, whereas in IVb the phenyl is shown in the staggered conformation. One would expect either species to be adsorbed on the mercury surface on its less hindered side and hence electron addition to take place from this less hindered side. This would find IVa giving rise to *erythro*-alcohol and IVb producing *threo*-alcohol. This postulated picture is analogous with that which has been shown to obtain in the lithium aluminum hydride reduction of ketones.[7]

As the *erythro*-alcohol is found to be the product of electrolytic reduction, it must be concluded that the conformation IVa is preferred to that shown in IVb. This indicates that the effective bulk of the alkoxide anion is greater than that of a phenyl group, and hence it tends to exist in the more stable staggered conformation. The explanation for this, in all likelihood, rests in the fact that the oxygen anion exists as a solvated entity or is even itself associated with mercury atoms and hence its effective bulk can easily be greater than that of merely an oxygen atom.[8]

## Experimental

**Apparatus and Reagents.**—The polarographic data were obtained with a Leeds and Northrup Electro-chemograph type E. The macroelectrolyses were carried out using a potentiostat of the Lingane–Jones[9] type. Infrared measurements were made with a Perkin-Elmer model 21 spectrometer. *p*H measurements were made with a Beckman model G *p*H meter.

All inorganic chemicals were reagent grade. Pure samples of the *erythro*- and *threo*-alcohols were kindly furnished by Dr. Donald Cram of the University of California, Los Angeles.

**$\alpha$-Methyldesoxybenzoin** was prepared by the method of McKenzie and Wells.[10]

**Sodium in Alcohol Reduction.**—One-half gram of ketone was placed in a 50-ml. flask which was connected to a reflux condenser; 10 ml. of absolute ethanol was added and the solution was brought nearly to boiling. Then, over a period of 1.5 hours, 0.8 g. of sodium was added. After the solution cooled, water was added and the solution was extracted with two 25-ml. portions of ether. The ether was washed twice with dilute hydrochloric acid, then twice with water. The water layer was discarded and anhydrous sodium sulfate was added to dry the ether layer. The ethereal solution was decanted into a 100-ml. flask and the ether evaporated on a hot water-bath. Carbon tetrachloride was added and concentrated to dryness twice. The residue was taken up in carbon tetrachloride and the infrared spectrum then was recorded.

**Procedure for Polarographic Reduction.**—The stock solution of ketone was 0.002 *M* and contained 75% by volume ethanol, 25% water; 10 ml. of this stock solution was combined with 10 ml. of the appropriate buffer. The final concentration of ketone was 0.001 *M*. The solution was added to the polarographic cell, nitrogen was passed through for 10 minutes and the polarogram was recorded. The drop time in all cases was 5.0 seconds with an open circuit. The temperature was ambient room temperature, normally around 25°.

**Procedure for Macroelectrolyses.**—Approximately 0.2 g. of ketone was dissolved in 37.5 ml. of ethyl alcohol; 57.5 ml. of a veronal buffer (*p*H 8) was added and the solution was placed in the electrolysis cell. Nitrogen was passed through the solution continuously during the electrolysis which was carried out at −1.85 volts. The reduction was allowed to continue for 12 hours, the ketone concentration being followed by polarographic analysis. Following the reduction, the solution was made distinctly alkaline with 10% sodium carbonate and was then extracted twice with ether. The ether was dried with anhydrous sodium sulfate and then concentrated to dryness on a hot water-bath. The residue was taken up in carbon tetrachloride and the infrared spectrum was then recorded.

Infrared spectra of the pure *erythro*- and *threo*-alcohols were recorded and used as reference spectra for estimating the relative percentages of the alcohols formed in the sodium in alcohol reduction of $\alpha$-methyldesoxybenzoin and also for identification of the controlled potential electrolysis reduction product.

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[4] H. E. Zimmerman, THIS JOURNAL, **79**, 6554 (1957).

[5] N. V. Sidgwick, "The Chemical Elements and their Compounds," Oxford University Press, London, 1950, p. 301.

[6] That this process should proceed with retention of configuration is indicated by the work of S. Winstein, T. G. Taylor and C. S. Garner, THIS JOURNAL, **77**, 3741, 3747 (1955), and S. Winstein and T. G. Taylor, *ibid.*, **78**, 2597 (1956), in their studies of the electrophilic replacement of organomercury compounds.

[7] D. J. Cram and F. A. Abd Elhafez, THIS JOURNAL, **74**, 5828 (1952).

[8] This latter fact would lead one to expect the possibility of a different stereochemical result (*i.e.*, *threo*- rather than *erythro*-alcohol being produced) were the reduction carried out in acidic media, where it would be less likely for the alkoxide anion to be formed, but rather a hydroxyl group. The "effective bulk" of a free hydroxyl should be less than that of the more heavily solvated alkoxide anion and thus the above stereochemical analysis could be reversed. Interestingly this explanation allows rationale of the findings of H. Lund, *Acta Chem. Scan.*, **11**, 283 (1957), where different stereoisomers were found to be produced in the electrochemical reduction of $\Delta^4$-keto-3-steroids depending on whether the reduction medium was acidic or basic. The hypothesis could not be tested directly in the present case as under acidic conditions reductive coupling occurs.

[9] J. J. Lingane and S. L. Jones, *Anal. Chem.*, **22**, 1169 (1950).

[10] A. McKenzie and G. O. Wells, *J. Chem. Soc.*, **127**, 283 (1925).