2.8 *M* Li) and analyzing the reaction mixture by glpc[16] we have found a ratio for $k_{\mathrm{indanol}}/k_{\mathrm{tetralol}}$ of 1.26,[7] indicating a considerably smaller rate difference for the phenolic systems than for the hydrocarbons. This may be rationalized as follows. The difference in bond angle strain which is reflected in the greater rate of reduction of indan with respect to tetralin becomes insignificant in the case of the corresponding phenols in view of the much greater energy barrier to reduction resulting from the like charges of the reacting species.

As representatives of the phenolic estrogens[17] we have subjected estrone and its 17-ethylene ketal, mp 171–172°,[11] $[\alpha]^{31}\mathrm{D}$ +30°, to Birch reduction in 0.014 *M* solution and an initial Li concentration of 4.3 *M*. Estrone furnished in 95% yield a product which consisted of 77% of $\Delta^{5(10)}$-estrene-3α,17β-diol (VI)[18] and 23% of a faster moving component (glpc analysis). The former was obtained by direct crystallization, mp 205–207°, and identified by comparison with an authentic sample.[19] The faster moving component could not be separated in pure form, but analysis of the mass spectra of mixtures of the latter with VI indicated that it must be a 5,10-dihydro derivative of VI.[20] Similarly, reduction of estrone 17-ethylene ketal furnished a 4:1 mixture of the ketal VII and its 5,10-dihydro derivative, mp 135–136°,[11] M$^+$ 318 and 320, which on hydrolysis with dilute acid afforded the corresponding 17-ketone VIII.[19] We have considered the possibility that the phenolic ring might be reduced at a slower rate in the case of estrone than of its ketal because of a possible long-range electrostatic effect of the 17-hydroxylate anion (formed on reduction of the 17-keto group of estrone) on the rate of electron addition to the phenolic ring. A competition experiment[21] involving these two substrates (0.01 *M* in each, 2.8 *M* Li) gave $k_{\mathrm{ketal}}/k_{\mathrm{estrone}} = 1.73$, suggesting that such long-range interactions may indeed be operative.

We consider it most likely that the above reductions take place in the bronze phase of the metal–ammonia system, which exhibits electron mobility characteristic of the metallic state and is known to contain solvated and at highest concentrations unsolvated electrons in equilibrium with dimeric or even polymeric metal species.[22] It is possible, therefore, that it is merely the higher concentration of electrons which drives the reaction. On the other hand, the possibility of contact ion-pair formation between phenolate and metal ions favored by high concentrations of the latter, thereby reducing electrostatic repulsion between substrate and the electron-carrying species, must also be considered.

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(16) Column temperature 110°; retention times (minutes) 5-indanol, 4.4; *ar*-2-tetralol, 8.4; IV, 1.6; V, 3.3; Both IV and V contained 20% of a faster component at 1.4 and 2.6 min, respectively, which may represent dihydro derivatives of the former. *Vide infra.*

(17) *Cf.* C. Djerassi, "Steroid Reactions," Holden-Day, Inc., San Francisco, Calif., 1963, p 267 ff.

(18) J. A. Hartmann, *J. Am. Chem. Soc.*, 77, 5151 (1955). For correct stereochemistry at C-3, see S. B. Levine, N. H. Eudy, and E. C. Farthing, *Tetrahedron Letters*, 1517 (1963), and W. F. Johns, *J. Org. Chem.*, **29**, 1490 (1964).

(19) We wish to thank Dr. W. F. Johns of G. D. Searle and Co. for a sample of this compound.

(20) Of the possible structures we prefer that of 5α-estrane-3α,17β-diol, since exposure of pure VI to Li–NH_3 under the conditions employed for estrone led to a mixture showing the same ratio of components on glpc as the product obtained from estrone.

(21) Glpc at 210°; retention times (minutes): estradiol, 7.4; estrone 17-ethylene ketal, 11.5; VI, 4.8; VII, 7.8. Extraction with base separated estradiol from VII, but, surprisingly, left estrone ketal in the neutral fraction.

(22) "Solvated Electrons," Advances in Chemistry Series, No. 50, American Chemical Society, Washington, D. C., 1965.

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Book Reviews

Principles of Polarography. By Professor Jaroslav Heyrovsky, Nobel Prize Laureate of Chemistry, 1959, and Jaroslav Kuta, D.Sc. Academic Press Inc., 111 Fifth Ave., New York, N. Y. 1966. 581 pp. 17 × 24.5 cm. $19.50.

The appearance of an English edition of this book, originally published in the Czech language in 1963, has been awaited with great interest. Given a subject in which many thousands of papers have been written over a period of forty years, authors who represent the founder of the method and one of his outstanding collaborators, and the limitations of a single volume addressed primarily to third-year undergraduates, what topics are to be covered, and in what depth? Perhaps even more important, what topics are to be omitted, and what complications are to be avoided?

The authors have taken the approach of eliminating complex mathematical details, minimizing experimental descriptions, showing experimental results that stress basic principles, and discussing the results in relation to theory. It is difficult to quarrel with this approach, although we may wish for differing degrees of emphasis on the various topics, which often reflect the particular viewpoint of the Czech school. Thus a special chapter, "The Kalousek Commutator (Switch) and Related Methods" by J. Weber, serves to give due credit to Kalousek for his pioneering experiments, but it relegates to 4.5 pages (out of 18) the square wave and pulse polarographic methods which have the advantage of minimizing charging currents.

The organization of the book causes odd scattering effects on subjects not included in classical polarography. For example, chronopotentiometry is buried in Chapter XXII, entitled "Oscillographic Polarography," and linear voltage sweep voltammetry is covered partly in that same chapter, partly in Chapter VII, "Equation for a Reversible Polarographic Wave," and partly in Chapter XIV, "Irreversible Electrode Processes."

Overwhelming emphasis is placed on various forms of mercury electrodes. Although there is an excellent 3-page description of the Levich rotated disk electrode, little mention is made of this powerful tool for studies of kinetics and mechanisms.

Topics that are very briefly covered include pen and ink recording polarographs (barely mentioned), limiting current (amperometric) titrations (4 pages), polarography of organic substances (4.5 pages), alternating current polarography (barely mentioned), and polarography in nonaqueous solvents and melts (9 pages of text, 3 pages of references).

Topics covered exceptionally well include diffusion to the dropping electrode including depletion effects with successive mercury drops, equations of reversible polarographic waves, kinetic currents, and current–time behavior during individual drop formation, as complicated by adsorption and other factors.

Although there are many simplifications of mathematical treatment, there are few errors. One time-honored error that is perpetuated in this book is the treatment of migration current in the reduction of anions. In the absence of supporting electrolyte, such a reduction process results, not in the simple diminution of total salt concentration in the diffusion layer as in the electrodeposition of a metal, but in the formation of ionic products, *e.g.*, $IO_3^- + 6e^- + 3H_2O \rightarrow I^- + 6OH^-$, which act as a supporting electrolyte in the diffusion layer. Equation (11), p 69, therefore does not describe a real situation. Another treatment that lacks justification is the use of the reciprocal of the mean conductance (4/3 of the minimal resistance) as the mean resistance for correction of current–voltage curves for ohmic voltage drop (pp 62–63). This quantity, originally derived by Ilkovic in 1932, is used with validity only for *resistance* limited currents and not for *diffusion* limited ones. Moreover, it ignores the time-invariant component of resistance due to all resistive elements except those in the immediate vicinity of the growing drop.

Altogether, this book, serving as a convenient single volume source, should prove particularly useful as an introductory reference for students and research workers and as a guide to the research literature through its numerous, critically selected references. Its price may act as a deterrent to its use as a text.

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