of 1% methyl cellulose (Dow Chemical Co.) in 80% ethanol per liter for maximum suppression. The "pH 13" solutions were 0.1 *M* in tetramethylammonium hydroxide, the "pH 5.2" solutions were 0.1 *M* in ammonium chloride and the "pH 1.9" solutions were 0.01 *M* in hydrochloric acid and 0.1 *M* in tetramethylammonium bromide.

The manual apparatus of Lingane and Kolthoff[8] was adapted to the Kalousek technique by addition of a second polarizing circuit, a three-pole, three-throw switch and a commutator type switch driven by a motor with speed regulation. A diagram of the apparatus is shown in Fig. 10. The commutator switch, X, alternately connects point C with A and B. It is made of an assembly of a brass half-cylinder and a plastic half-cylinder. The brass shaft makes contact to the brass half-cylinder and is connected to point C. Two beryllium–copper flat springs are adjusted parallel to each other as contacts. One of these leads to A; the other to B. For operation, the three-pole, three-position switch, S, is first set for the "formation voltage," (C connected to A) and the potential is checked by balancing the voltage against a Leeds and Northrup student potentiometer. The switch, S, is then turned to the analyzing circuit (C connected to B) and the desired voltage is applied and checked with the potentiometer. The current, read on the galvanometer, G, now is the regular polarographic current. The switch is set so as to connect C to X. The commutator motor is started, and the current read in the galvanometer now is the oxidation or reduction current according to Kalousek. With a galvanometer of 12 to 15 seconds period, aperiodically damped, the oscillations are relatively small and the current can be read accurately. A certain time is needed to establish an equilibrium condition, but with a manual apparatus one can easily wait until the current is stabilized.

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[8] J. J. Lingane and I. M. Kolthoff, THIS JOURNAL, **61**, 825 (1939).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING OF PRATT INSTITUTE AND THE CHEMISTRY DEPARTMENT OF SMITH COLLEGE]

Electrolytic Reduction of 2-Naphthyl Ethers

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A series of 2-naphthyl ethers have been reduced electrolytically to the corresponding enol ethers in high yield. The method offers enhanced selectivity, and this case appears to be one of the first practical reductions of a polynuclear carbocyclic aromatic system by a direct electrochemical process.

Much interest has been shown recently in 2-tetralone and substituted 2-tetralones as intermediates in the possible synthesis of analgesics and substances related to morphine[1,2,3] and in the synthesis of steroid substances.[4] 2-Tetralone, 7-methoxy-2-tetralone and 7,8-dimethoxy-2-tetralone have been obtained previously from the corresponding 2-naphthyl ethers in yields of 52–56%,[2,3] 55%[5] and 31%,[3] respectively, by sodium and alcohol reduction and hydrolysis of the enol ethers.

In the present work, these compounds were prepared much more efficaciously by electrolytic reduction at high cathodic potentials. The reaction appeared to be highly selective and gave the desired enol ethers in excellent yields. These were converted directly to the tetralones without the usual purification *via* the bisulfite adduct.

In the case of 2,7,8-trimethoxynaphthalene, the enol ether was obtained in 95% yield as a well defined crystalline compound which on the basis of its absorption spectrum ($\lambda_{\max}^{\text{cyclohexane}}$ 277.5 mμ, log ε 3.28)[6] is the Δ^2-isomer. The alternative Δ^1-structure would be expected to show a much more intense band in the same region.[7,8] In the reductions of 2-naphthyl ethers the presence of sodium alkoxide would enhance a rearrangement[9] to the Δ^1-enol ether, which was the only type identified.[7]

So far as we can determine, these results represent the first practical electrolytic reduction, suitable for preparative purposes, of a polynuclear carbocyclic aromatic system.[10] In fact, the only direct electrolytic reductions of a benzenoid nucleus previously reported are on phthalic acid and terphthalic acid, in which compounds the presence of the carboxyl groups conjugated with the aromatic system enhances the reduction in the ring.[11] A few other cases in the literature, also dealing with the phthalic system, are considered to be indirect reductions in which the actual agent is potassium

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[1] J. A. Barltrop, *J. Chem. Soc.*, 958 (1946); 399 (1947); H. Andersag and W. Salzer, U. S. Patent 2,271,674 (1942); B. W. Horrom and H. E. Zaugg, THIS JOURNAL, **72**, 721 (1950); H. E. Zaugg, M. Freifelder and B. W. Horrom, *J. Org. Chem.*, **15**, 1197 (1950); *cf.* A. J. Birch, *J. Chem. Soc.*, 430 (1944); G. Stork and E. L. Foreman, THIS JOURNAL, **68**, 2172 (1946); H. Adkins, A. G. Rossow and J. E. Carnahan, *ibid.*, **70**, 4247 (1948).

[2] J. W. Cornforth, R. H. Cornforth and R. Robinson, *J. Chem. Soc.*, 689 (1942).

[3] M. D. Soffer, J. C. Cavagnol and H. E. Gellerson, THIS JOURNAL, **71**, 3857 (1949); M. D. Soffer, R. A. Stewart, J. C. Cavagnol, H. E. Gellerson and E. A. Bowler, *ibid.*, **72**, 3704 (1950).

[4] C. A. Grob and W. Jundt, *Helv. Chim. Acta*, **31**, 1691 (1948); J. W. Cornforth and R. Robinson, *J. Chem. Soc.*, 676 (1946); 1855 (1949); H. M. Cardwell, J. W. Cornforth, S. R. Duff, H. Holtermann and R. Robinson, *Chemistry & Industry*, 389 (1951).

[5] B. W. Horrom and H. E. Zaugg, ref. 1.

[6] The absorption curve is very similar to that of veratrole, except for minor fine structure at the peak of the latter ($\lambda_{\max}^{\text{hexane}}$ 272.7, 278.4, 281.4 mμ, log ε 3.00, 3.38, 3.38; P. Steiner, *Compt. rend.*, **176**, 744 (1923)).

[7] A. Windaus and M. Deppe, *Ber.*, **70**, 77 (1937); *cf.* R. Robinson and F. Weygand, *J. Chem. Soc.*, 386 (1941).

[8] R. A. Morton and A. J. A. de Gouveia, *ibid.*, 916 (1934); R. B. Woodward and R. H. Eastman, THIS JOURNAL, **66**, 674 (1944).

[9] F. Strauss and L. Lemmel, *Ber.*, **46**, 232 (1913); M. Tiffeneau and A. Orekhoff, *Bull. soc. chim. France*, [4] **27**, 782 (1920); W. Hückel and H. Bretschneider, *Ann.*, **540**, 157 (1939).

[10] It has been shown previously (S. Wawzonek and H. A. Laitinen, THIS JOURNAL, **64**, 2365 (1942)) that naphthalene is reducible polarographically in a two-electron reaction proceeding by a 1,4-mechanism, but no product was isolated. It may be in order to point out that since electrolytic reductions under macro conditions may take a different course from that occurring polarographically (S. Wawzonek, *Anal. Chem.*, **24**, 32 (1952); *cf.* M. v. Stackelberg and W. Stracke, *Z. Elektrochem.*, **53**, 118 (1949)) polarographic data alone do not rigidly demonstrate the efficacy of a preparative electrolytic method.

[11] C. Mettler, *Ber.*, **39**, 2933 (1906).

amalgam produced in the reaction.[12] In one other case, the electrolytic reduction of phenol, the process is essentially a catalytic hydrogenation, the hydrogen merely being produced *in situ*.[13,14]

The reductions were carried out at a mercury cathode with tetra-*n*-butylammonium iodide in dioxane–water as both catholyte and anolyte. The cathode potentials were maintained at about 2.5 volts *vs.* S.C.E.

The cell was made by clamping together two sections cut from a rectangular glass tank, a sheet of Cellophane serving both as a gasket and as a diaphragm. The cell was provided with a heating and cooling coil, stirrers, thermometers and nitrogen bubblers; contact with the mercury pool electrodes was made by means of a conventional platinum contact electrode, and a sintered glass bridge[15] almost touching the cathode surface was used to complete the cathode–calomel circuit. A vacuum tube voltmeter was used to measure the cathode potential and the current was recorded by an electronic recording ammeter.

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Experimental

2-Tetralone.—Nitrogen was bubbled through a solution of 600 ml. of purified[16] dioxane and 200 ml. of water containing 44 g. of purified[16] tetra-*n*-butylammonium iodide. Two-thirds of this solution was introduced into the cathode compartment, and the remainder into the anode compartment. The cell temperature was raised to 50° and the residual current at a cathode potential of 2.50 volts *vs.* S.C.E. was 0.08 ampere. At this point 5.01 g. of 2-ethoxynaphthalene was introduced into the cathode compartment causing a drop in the cathode potential to 2.31 volts. The potential was then raised to 2.50 volts. The current increased to about 1.5 amperes and the voltage was maintained at 2.50 volts for about 3 hours after which time the current fell to almost its original residual value.

At this point the catholyte was withdrawn, an equal volume of water was added, and the catholyte was thoroughly extracted with petroleum ether (b.p. 30–50°). Removal of solvent at reduced pressure left the crude enol **ether** as a light colored residual oil (4.85 g., 96%) which on distillation gave the water-white product, b.p. 98° at 1 mm., 4.53 g.; 89.5%.

Anal. Calcd. for $C_{12}H_{14}O$: C, 82.7; H, 8.1. Found: C, 82.3, 82.6; H, 8.2, 8.2.

Hydrolysis of 3.38 g. of the enol ether with dilute hydrochloric acid[2] gave 2.76 g. (89%) of 2-tetralone, b.p. 98–99° at 2 mm. The semicarbazone melted at 189° and gave no depression of the melting point when mixed with an authentic specimen.

7-Methoxy-2-tetralone.—2,7-Dimethoxynaphthalene (3.23 g.) was reduced as described above, giving almost exactly the same electrical data. The catholyte was extracted thoroughly with chloroform and petroleum ether and the washed extract was freed from solvent in a nitrogen atmosphere at reduced pressure. Distillation of the residual oil (3.04 g., 93%) gave the colorless **enol ether**, b.p. 115° at 2.5 mm., 2.61 g., 80%.

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.8; H, 7.4. Found: C, 75.9; H, 7.6.

Hydrolysis[2] of 1.28 g. of the distillate gave 1.11 g. (93%) of the crystalline ketone, m.p. 23–24°. The semicarbazone[3] was prepared by the pyridine method; m.p. and m.m.p. 174–176°.

2,7,8-Trimethoxy-1,4-dihydronaphthalene.—The reduction was carried out in the same way, on 2.55 g. of 2,7,8-trimethoxynaphthalene. Extraction with petroleum ether (b.p. 30–50°) and removal of solvent in vacuum gave 2.45 g. (95%) of the crystalline enol ether, m.p. 55–56°. Recrystallization from petroleum ether (b.p. 20–40°) gave an analytical sample, m.p. 58–58.5°.

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.9; H, 7.3. Found: C, 71.0, 71.0; H, 7.3, 7.4.

7,8-Dimethoxy-2-tetralone.—Hydrolysis[2] of 0.935 g. of the foregoing enol ether gave 0.778 g. (89%) of the ketone in well defined crystals, m.p. 70–72°. Recrystallization from petroleum ether (b.p. 30–50°) gave pure material m.p. 76°. The semicarbazone was identical with an authentic sample[3]; m.p. and m.m.p. 191°.

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(12) F. Fichter and C. Simon, *Helv. Chim. Acta*, **17**, 1219 (1934); V. M. Rodionov and V. K. Zvorykina, *Bull. soc. chim. France*, [5] **5**, 840 (1938).

(13) W. D. Bancroft and A. B. George, *Trans. Electrochem. Soc.*, **57**, 399 (1930).

(14) A reported partial electrolytic conversion of benzoic acid to ethyl 1,2-dihydrobenzoate, in unspecified yield, was not rigorously demonstrated, and the literature is conflicting and confused (F. Somlo, *Z. Elektrochem.*, **35**, 264 (1929); E. Baur and E. Müller, *ibid.*, **34**, 98 (1928)). The electrolytic reduction of benzoic acid and a large number of its derivatives under a variety of conditions has otherwise given no products of reduction in the ring; *cf.* F. Fichter, "Organische Electrochemie," Steinkopf, Dresden, 1942 (Edwards Brothers, Ann Arbor, Mich., 1946) pp. 252–258.

(15) H. A. Laitinen, *Ind. Eng. Chem., Anal. Ed.*, **13**, 393 (1941).

(16) H. A. Laitinen and S. Wawzonek, THIS JOURNAL, **64**, 1765 (1942).