[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE SPRAGUE ELECTRIC COMPANY]

The Chemical, Catalytic and Polarographic Reduction of 2,2′-Dinitrobiphenyl and its Reduction Products

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With sodium sulfide 2,2′-dinitrobiphenyl can be reduced stepwise to 2,2′-dinitrosobiphenyl and benzo(c)cinnoline-5-oxide but not to benzo(c)cinnoline. Low pressure catalytic reduction of the dinitro compound leads only to 2,2′-diaminobiphenyl. Under similar conditions, benzo(c)cinnoline is not reduced further, and 2,2′-dinitrosobiphenyl and benzo(c)cinnoline-5-oxide are reduced to benzo(c)cinnoline. 2,2′-Dinitrobiphenyl, 2,2′-dinitrosobiphenyl, benzo(c)cinnoline-5-oxide and benzo(c)cinnoline were studied polarographically at three apparent *p*H's. The Kalousek technique was used to study the anodic oxidation of dihydrobenzo(c)cinnoline. The structural relationships between these compounds as members of a series derived by progressive reduction from the parent compound, 2,2′-dinitrobiphenyl, is confirmed by the polarographic experiments. The end product of the reduction is, in every case, dihydrobenzo(c)cinnoline. This compound can be reoxidized polarographically to benzo(c)cinnoline but not further, as shown by the fact that a two electron oxidation is observed in the Kalousek diagrams of all four compounds, while two, four, six and ten electron steps, respectively, are observed for the reductions of these compounds.

In a previous publication from this Laboratory,[1] it was shown that the sodium sulfide reduction of 2,2′-dinitro-4,4′-bis-(trifluoromethyl)-biphenyl proceeds stepwise to yield the 2,2′-dinitroso-4,4′-bis-trifluoromethyl)-biphenyl, 3,8-bis-(trifluoromethyl)-benzo(c)cinnoline-5-oxide and 3,8-bis-(trifluoromethyl)-benzo(c)cinnoline and that catalytic hydrogenation results in a mixture containing 2,2′-diamino-4,4′-bis-(trifluoromethyl)-biphenyl in addition to the above benzo(c)cinnoline and benzo(c)-cinnoline oxide. The reduction of 2,2′-dinitrobiphenyl (I) has been studied extensively,[2] but the interest was largely preparative and structural. Our own interest was in a comparison of the reduction of I with the reduction of the previously studied 2,2′-dinitro-4,4′-bis-(trifluoromethyl)-biphenyl, and we have studied the chemical, catalytic and polarographic reduction of I.

The sodium sulfide reduction of I leads to either 2,2′-dinitrosobiphenyl (II) or benzo(c)cinnoline oxide (III). Our results are summarized in Table I. The oxide III cannot be reduced further with this reagent—a marked contrast to our previous experience with 2,2′-dinitro-4,4′-bis-(trifluoromethyl)-biphenyl, which is readily reducible to the corresponding benzo(c)cinnoline.

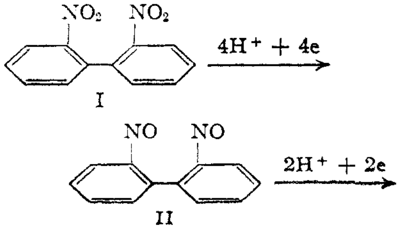
TABLE I

Moles $Na_2S \cdot 9H_2O$/mole nitro group	Mole NaOH/liter of reaction mixture	Reaction time (hours)	Yield, % I	Yield, % II	Yield, % III
0.125	0.25	4	60	2.5	Trace
.25	.25	4	41	10	Trace
.50	.25	4	20.6	24.3	29.2
1.0	.25	4			94
2.5	.25	24			96

The results of low pressure hydrogenation of I present an even more striking contrast. The only product obtained on reduction of I is 2,2′-diaminobiphenyl. Benzo(c)cinnoline (IV) is not reduced further by low pressure hydrogenation in the presence of Adams catalyst. The dinitroso compound, II, and III are both reduced quantitatively to IV, but not further. It is, therefore, certain that II, III and IV are not intermediates in the reduction of I to the diamine. Thus, only that reaction path which leads to the diamine and obviates the formation of compounds containing the benzo(c)cinnoline ring system is followed in the catalytic reduction of I.

These differences are probably attributable to the presence of the two trifluoromethyl groups in 2,2′-dinitro-4,4′-bis-(trifluoromethyl)-biphenyl and their absence in I. The inductive effect of two trifluoromethyl groups in 3,8-bis-(trifluoromethyl)-benzo(c)cinnoline-5-oxide makes the central ring more positive and more subject to attack by a reducing agent. The effect of the trifluoromethyl groups on the catalytic reduction is more speculative. The two reduction paths that prevail with the trifluoromethyl substituted dinitrobiphenyl were explained[1] in terms of the two extreme orientations which are possible on the catalyst surface; the orientation with the two nitro groups *trans* leading to the diamine and the orientation with the two nitro groups *cis* leading to the compounds containing the benzo(c)cinnoline ring system. To be consistent we would have to attribute the single reduction path that prevails for I to the absence, on the catalyst surface, of those configurations of I in which the nitro groups are *cis* to one another. The permissible or favored orientations of the substrate on the catalyst surface are determined by the lattice spacing of the catalyst and the points of attachment available on the substrate, and the function of the trifluoromethyl groups, in this case, may be to supply alternate points of attachment and make more orientations permissible or favorable.

The polarographic reductions of I, II, III and IV were studied at apparent *p*H's of 1.9, 5.2 and 13 in solutions containing 80% ethanol (by volume) and an electrolyte of 0.1 molarity. II, III and IV are all possible stages in the stepwise reduction of I, and these compounds may be interrelated as



I

II

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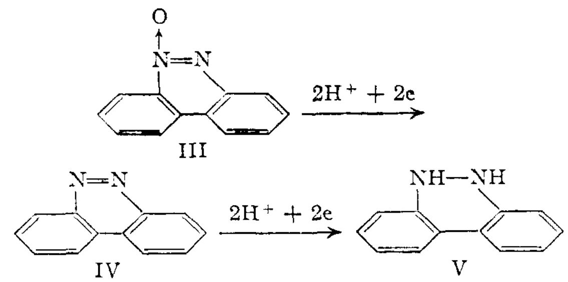
[1] S. D. Ross and I. Kuntz, THIS JOURNAL, 74, 1297 (1952).

[2] For references to this work see reference 1.



The ratio of the diffusion currents, at all three *p*H values, makes it evident that the end-product of the reduction is dihydrobenzo(c)cinnoline (V), (Table II).

TABLE II

Compound		$E_{1/2}$ vs. 0.1 *N* C.E.	I_D (μa./10^{-3} *M*)	n^a	μa./$10^{-3}M \times n$
		*p*H 1.9			
I		0.51	25.4	10	2.54
II		.48	14.9	6	2.48
III		.48	10.0	4	2.50
IV		.41	4.88	2	2.44
		*p*H 5.2			
I		0.83	26.6	10	2.66
II		.80	16.0	6	2.67
III		.88	11.73	4	2.94
IV		.67	5.52	2	2.76
		*p*H 13.0			
I		0.90	24.3	10	2.43
II	1st wave	0.92	3.7	2	1.85
	2nd wave	1.20	10.8	4	2.70
III		1.20	11.3	4	2.82
IV		1.08	5.35	2	2.68

[a] *n* = no. of electrons involved in the reduction.

At "*p*H 13" (0.1 *M* tetramethylammonium hydroxide) a single wave is obtained for IV at a less negative half-wave potential than that obtained for the oxide, III. Under these circumstances resolution of the polarogram of III into double waves was not expected, and it was not observed. The dinitrosobiphenyl II, however, is reduced stepwise: first in a two electron step to III and then in a four electron step to V. The half-wave potential of the second wave coincides with the half-wave potential of the benzo(c)cinnoline oxide reduction, supporting the stepwise reduction scheme indicated above. The dinitrobiphenyl I is reduced at a considerably more positive potential than II, III or IV, and these compounds do not appear as intermediates in this reduction. However, the number of electrons involved indicates that again V is the end-product (Fig. 1).

At "*p*H 5.2" the half-wave potentials of II, III and IV have moved closer together and to more positive values, and the reduction of II is no longer resolved into two waves. The half-wave potential of I at this apparent *p*H is now more negative than that of IV (Fig. 2). The proportionality between the current and the concentration was checked at this apparent *p*H for benzo(c)cinnoline over the concentration range of 1 × 10^{-4} to 4 × 10^{-3} and was satisfactory within experimental error. The half-wave potential is, however, a function of the concentration (Fig. 3). The half-wave potentials obtained with the automatic Sargent polarograph

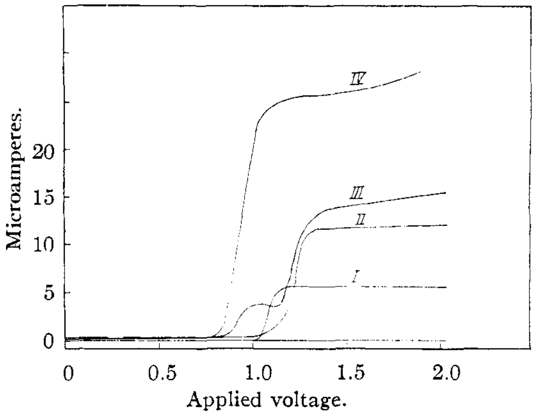


Fig. 1.—Polarographic reduction waves at an apparent *p*H of 13 (0.1 *M* tetramethylammonium hydroxide) in 80% ethanol by volume containing 0.01% methyl celluose for maximum suppression: I, 1.053 × 10^{-3} *M* benzo(c)-cinnoline; II, 1.028 × 10^{-3} *M* benzo(c)cinnoline-5-oxide; III, 1.003 × 10^{-3} *M* 2,2'-dinitrosobiphenyl; IV, 1.072 × 10^{-3} *M* 2,2'-dinitrobiphenyl.

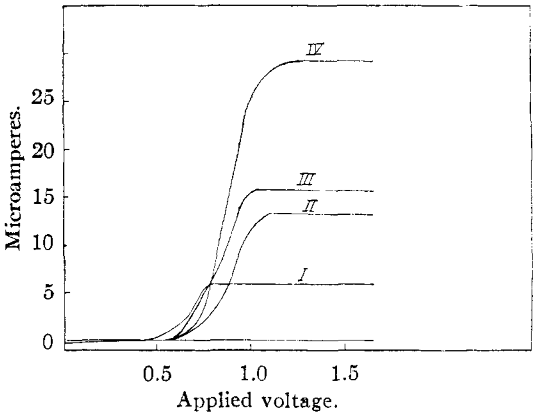


Fig. 2.—Polarographic reduction waves at an apparent *p*H of 5.2 (0.1 *M* ammonium chloride) in 80% ethanol by volume containing 0.01% methyl cellulose for maximum suppression: I, 1.104 × 10^{-3} *M* benzo(c)cinnoline; II, 1.131 × 10^{-3} *M* benzo(c)cinnoline-5-oxide; III, 0.981 × 10^{-3} *M* 2,2'-dinitrosobiphenyl; IV, 1.097 × 10^{-3} *M* 2,2'-dinitrobiphenyl.

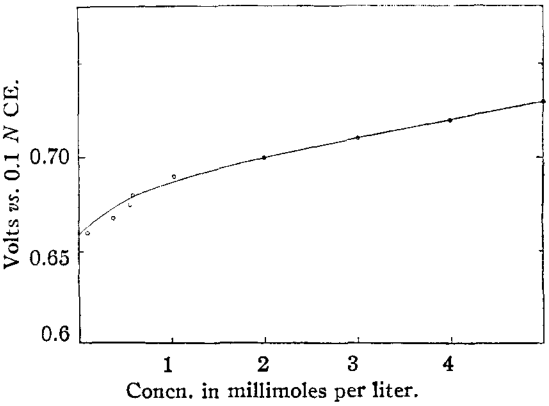


Fig. 3.—Half-wave potential *vs.* concentration of benzo(c)-cinnoline at an apparent *p*H of 5.2.

were corrected for *IR* drop, and the observed values were checked with the half-wave potentials obtained with a manual polarograph. Calculation of the diffusion coefficient of benzo(c)cinnoline in this medium from Ilkovic's equation resulted in a value of 4.26 × 10^{-6} cm.^{2} sec.$^{-1}$ at 25°, assuming that two electrons are involved in this reaction.

At "*p*H 1.9" further shifts of the half-wave potentials to more positive values have taken place, obscuring any stepwise reductions that may have occurred (Fig. 4).

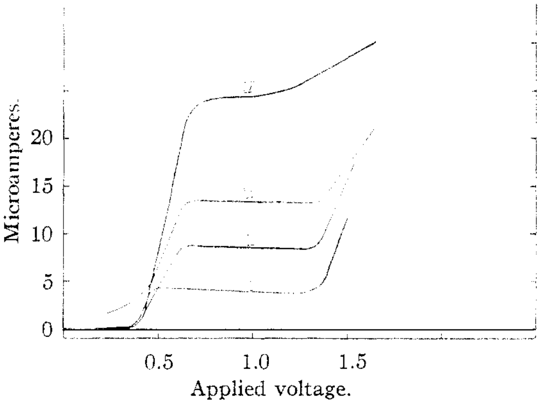


Fig. 4.—Polarographic reduction waves at an apparent *p*H of 1.9 (0.01 *M* hydrochloric acid and 0.1 *M* tetramethylammonium bromide) in 80% ethanol by volume containing 0.01% methyl cellulose for maximum suppression: I, 0.816 × 10^{-3} *M* benzo(c)cinnoline; II, 0.852 × 10^{-3} *M* benzo(c)cinnoline-5-oxide; III, 0.904 × 10^{-3} *M* 2,2'-dinitrosobiphenyl; IV, 0.958 × 10^{-3} *M* 2,2'-dinitrobiphenyl.

The plot of log $i/i_d - i$ *versus* the cathode potential, *E*, for IV at "*p*H 5.2" gave a straight line (Fig. 5). The slope of this line, 0.096, is however far from the theoretical for a reversible reaction. Also, no oxidation waves were obtained with I, II, III or IV.

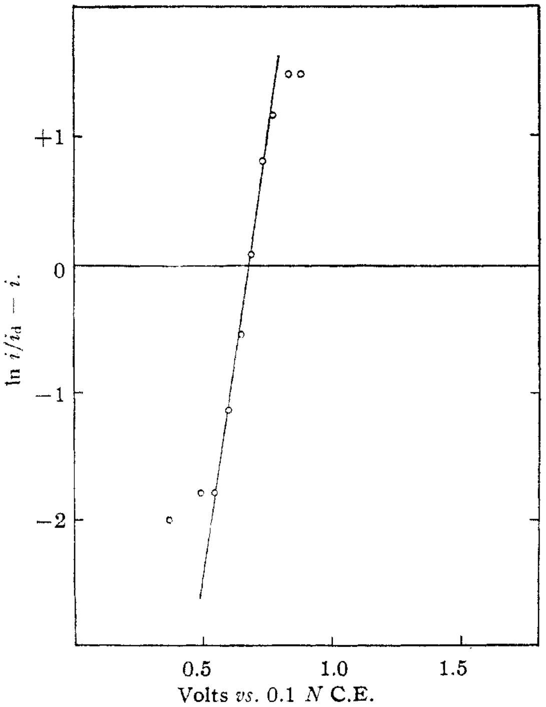


Fig. 5.—Log $i/i_d - i$ *vs.* cathode potential of 1 × 10^{-3} benzo(c)cinnoline at an apparent *p*H of 5.2

Since dihydrobenzo(c)cinnoline (V) proved too unstable to handle by conventional techniques, we used the Kalousek[3] technique to study the benzo(c)cinnoline–dihydrobenzo(c)cinnoline oxidation reduction system at the dropping mercury electrode at "*p*H 5.2." The Kalousek technique permits the application of two voltages alternately to the dropping mercury electrode. Using scheme II of Kalousek, one potential, the formation potential, was kept constant at a voltage at which the diffusion current of benzo(c)cinnoline is reached. Thus, during one part of the cycle, all of the benzo(c)cinnoline reaching the dropping mercury electrode was reduced to dihydrobenzo(c)cinnoline. The other potential was varied over the usual range and the current–voltage curve in this branch of the circuit was obtained in the usual manner.

The curve obtained for benzo(c)cinnoline is shown in Fig. 6 and shows an oxidation wave for dihydrobenzo(c)cinnoline. The value of the oxidation current indicates that the oxidation proceeds to benzo(c)cinnoline. However, the observed oxidation half-wave potential is slightly more positive than the reduction half-wave potential. We conclude, therefore, that the system is thermodynamically irreversible as indicated by the slope of the log $i/i_d - i$ *vs. E* plot.

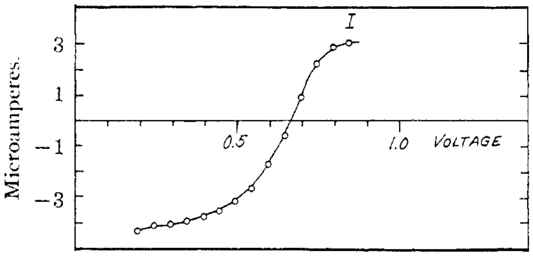


Fig. 6.—Kalousek curve at 1.5 cycles per second obtained for 1 × 10^{-3} *M* benzo(c)cinnoline at an apparent *p*H of 5.2.

Benzo(c)cinnoline oxide, run with the Kalousek technique at 1.5 cycles per second, gave an oxidation reduction wave corresponding to reduction by four electrons to V and reoxidation by two electrons to IV (Fig. 7). Similarly II showed a six electron reduction to V and a two electron reoxidation to IV (Fig. 8). The dinitrobiphenyl II gave an oxidation wave which was less than 50% of the value obtained for IV. Two processes, rather than an improbable one-electron oxidation, may be responsible for this result. The first is chemical interaction of V with I; the second, losses due to convection at the electrode. These processes should become less significant at lower concentrations, and, in fact, when the concentration of I was reduced to 2.5 × 10^{-4} *M* from 1 × 10^{-3} *M* the ratio of the oxidation to reduction current was closer to the theoretical. Also, an increase in the frequency of potential switching would be expected to minimize

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[3] M. Kalousek, *Collection Czechoslov. Chem. Commun.*, **13**, 105 (1948).

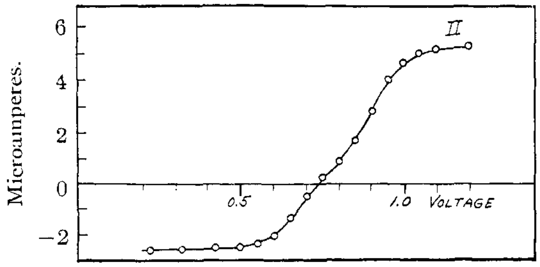

Fig 7.—Kalousek curve at 1.5 cycles per second for 1×10^{-3} *M* benzo(c)cinnoline-5-oxide at an apparent *p*H of 5.2.

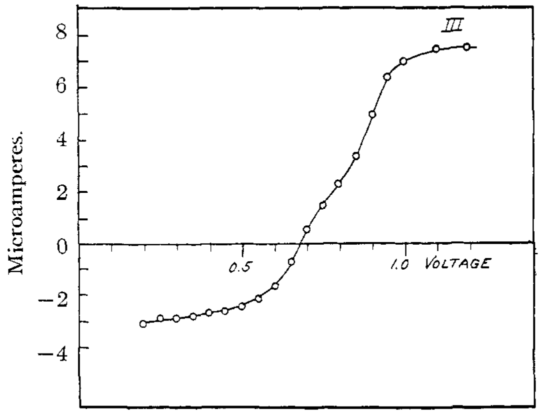

Fig. 8.—Kalousek curve at 1.5 cycles per second for 1×10^{-3} *M* 2,2'-dinitrosobiphenyl at an apparent *p*H of 5.2.

these effects. As anticipated, the oxidation current for I at 30 cycles per second had the same value as that observed for the benzo(c)cinnoline–dihydrobenzo(c)cinnoline at 1.5 cycles per second (Fig. 9). However, at the higher frequency, the effect of the charging current was strongly noticeable in the increase of the anodic current when starting at 0.3 volt and going toward more positive potentials.

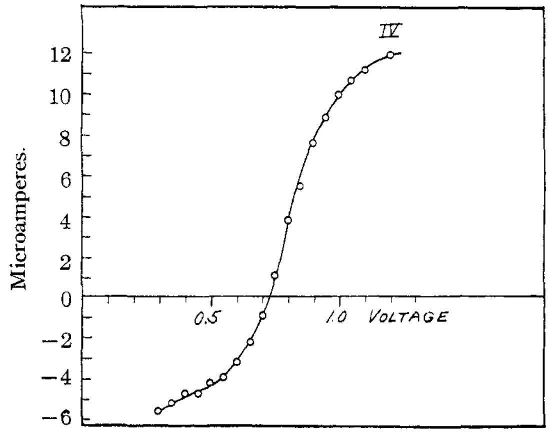

Fig. 9.—Kalousek curve at 30 cycles per second for 1×10^{-3} *M* 2,2'-dinitrobiphenyl at an apparent *p*H of 5.2.

Experimental

Reduction of I with Sodium Sulfide.—The sodium hydroxide and sodium sulfide nonahydrate in water (50 cc.) were added slowly at 60° to 2,2'-dinitrobiphenyl[4] in ethanol (250 cc.) and the mixture was refluxed. The quantities of reagents and reaction times are those indicated in Table I. After the reflux period, the alcohol was removed, and the crude mixture was crystallized from ethanol to effect separation into its components. The results are summarized in Table I. In the experiment using 0.5 mole of $Na_2S \cdot 9H_2O$ per mole of NO_2, the separation was effected chromatographically by adsorbing the total crude product on aluminum oxide and eluting portionwise with benzene containing increasing percentages of ethanol. I was eluted with pure benzene; III with 5–20% ethanol; II with 50–100% ethanol. The 2,2'-dinitrosobiphenyl II[5] had m.p. 233–236°.

Anal. Calcd. for $C_{12}H_8O_2N_2$: C, 67.91; H, 3.80. Found: C, 67.66, 67.88; H, 4.19, 4.00.

The benzo(c)cinnoline-5-oxide (III)[6] had m.p. 139–140°.

Anal. Calcd. for $C_{12}H_8ON_2$: C, 73.45; H, 4.11. Found: C, 73.95, 73.78; H, 4.07, 4.20.

The identity of both compounds was further corroborated by comparing their ultraviolet spectra with the known spectra of these compounds.[1]

Catalytic Hydrogenation of 2,2'-Dinitrobiphenyl (I).—A solution of I (12.2 g., 0.05 mole) in ethyl acetate (150 cc.) and absolute ethanol (50 cc.) was shaken in a Parr low-pressure hydrogenation apparatus at 2–3 atmospheres pressure with 0.1 g. of platinum oxide catalyst at room temperature. There was a rapid pressure drop of 24.8 lb. The solvent was removed, and the crude 2,2'-diaminobiphenyl[7] was crystallized from ethanol; m.p. 80–81°; yield 8.8 g. (96%).

Catalytic reduction of II in ethanol led to an 81% yield of IV. Similarly, reduction of III in ethanol led to an 84% yield of IV. IV was not reduced further under the same conditions.

The polarograms were obtained on a Sargent Polarograph Model XXI and with a manual apparatus, which was adapted for Kalousek's technique as described below. The polarographic cell was an H cell of the Lingane–Laitinen type with sintered glass discs and agar plugs separating the compartments. Two capillaries were used. The first had a drop time of 3.5 sec. in 0.1 *N* KCl without applied potential and with a mass of mercury, m = 2.36 mg./sec., flowing through the capillary per second. The second had a drop time of 2.55 sec. in 0.1 *N* KCl and m = 2.65 mg./sec. The resistance of the cell measured with a General Radio bridge, was 3000 ohms with 0.1 *M* ammonium chloride in 80% ethanol.

The solutions were all made with reagent grade chemicals in 80% ethanol by volume. All solutions contained 10 cc.

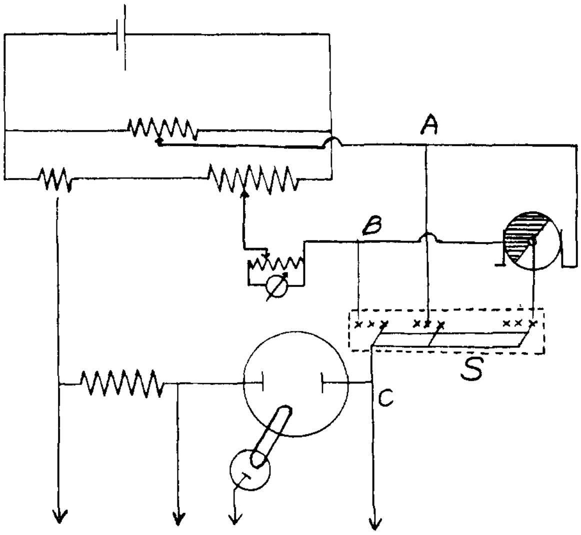

Fig. 10.—Schematic diagram of Lingane and Kolthoff manual polarograph adapted to Kalousek technique (see reference 8).

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[4] R. C. Fuson and E. A. Cleveland, *Org. Syntheses*, **20**, 45 (1940).

[5] E. Tauber, *Ber.*, **24**, 3081 (1891). This compound is usually named benzo(c)cinnoline dioxide. For the considerations which led to the reassigned structure see reference 1.

[6] F. Ullmann and P. Dieterle, *ibid.*, **37**, 23 (1904); F. E. King and T. J. King, *J. Chem. Soc.*, 824 (1945).

[7] E. Tauber, *Ber.*, **24**, 198 (1891).

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

BY GEORGE B. DIAMOND AND MILTON D. SOFFER

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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).