Synthesis and Polarographic Reduction of Strained Phenanthrenequinones. The Buttressing Effect[1-3]

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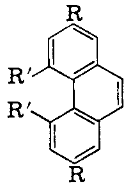
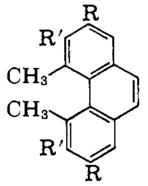
Abstract: The syntheses of 2,7-dimethyl- ($\mathrm{I_q}$), 4,5-dimethyl- ($\mathrm{II_q}$), 2,4,5,7-tetramethyl- ($\mathrm{III_q}$), and 3,4,5,6-tetramethyl-9,10-phenanthrenequinones ($\mathrm{IV_q}$) are described. The half-wave reduction potentials of these quinones have been measured in 75% dioxane at 28 ± 2° in order to obtain a measure of the steric effect of methyl groups on conversion of quinones to hydroquinones. The order of increasing difficulty of reduction is $\mathrm{I_q}$, $\mathrm{II_q}$, $\mathrm{III_q}$, and $\mathrm{IV_q}$ (see Table I).

In earlier work, the difference in strain energies of 2,7-dimethylphenanthrene (I) and 4,5-dimethylphenanthrene (II) was shown to be 12.6 ± 1.5 kcal/mol by measurement of the heats of combustion.[4] In order to get an estimate of the "buttressing" effect[5] of two methyl groups in the 3 and 6 positions, the combustion of 2,4,5,7-tetramethylphenanthrene (III) and 3,4,5,6-tetramethylphenanthrene (IV) was carried out.[6] The buttressing effect of the 3- and 6-methyl groups was estimated to be 7.2 ± 1.4 kcal/mol.



I, R = CH_3; R' = H
II, R = H; R' = CH_3



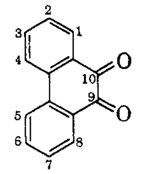
III, R = CH_3; R' = H
IV, R = H; R' = CH_3

In order to obtain more information about the effect of strain in polycyclic compounds on reactivity we have studied the polarographic reduction of the 9,10-quinones $\mathrm{I_q}$–$\mathrm{IV_q}$ to the corresponding hydroquinones $\mathrm{I_{hq}}$–$\mathrm{IV_{hq}}$.

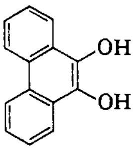
Quinones $\mathrm{I_q}$ and $\mathrm{II_q}$ were prepared by oxidation of I[7] and II[8] with chromic oxide in 42 and 27% yields. Part of the II used in this work was produced by the lithium aluminum hydride–aluminum chloride reduction of the cyclic ether of 4,5-dihydroxymethylphenanthrene.[9] In the oxidation of I, a 17% yield of 2,7-dimethyl-1,4-phenanthrenequinone was also obtained. To our knowledge, this is the first case in which a quinone other than a 9,10-quinone has been isolated from the oxidation of a phenanthrene.

Quinones III and IV were obtained by treatment of dimethyl 4,4',6,6'-tetramethyldiphenate[6] and dimethyl 5,5',6,6'-tetramethyldiphenate[6] with sodium in refluxing xylene–*p*-cymene and xylene, respectively.[9]

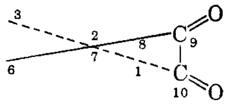
To illustrate our concept of the steric factors involved in the reduction, the exaggerated projection formula, P, for the quinones, A, is provided. In this projection the eye is in the plane defined by carbons 2 and 7, and the midpoint of the C_9–C_{10} bond. The dotted lines represent bonds away from the eye (1–4 ring) while the solid lines represent bonds near the eye (5–8 ring).



A



B



P

In the quinones, A, the 9,10 bond is essentially a single bond. The strain introduced by methyl groups in the 4 and 5 positions may be relieved by having the aromatic rings twist out of planarity. The twist causes the dihedral angle between the carbonyl bonds to increase as shown.[10] When reduction occurs to hydroquinones, B, the molecule flattens and the 9,10 bond is essentially a double bond. By measuring the increase in energy required to reduce certain quinones, a measure of the steric effect of methyl groups in the 4 and 5 positions and a measure of the buttressing effect[5] of methyl groups in the 3 and 6 positions has been provided.

Experimental Section[11]

2,7-Dimethyl-1,4-phenanthrenequinone and 2,7-Dimethyl-9,10-phenanthrenequinone ($\mathrm{I_q}$). A solution of 2.0 g of 2,7-dimethylphenanthrene[7] and 5.0 g of chromic oxide in 120 ml of acetic acid and 20 ml of water was heated at 65–70° for 20 min. The crude solid obtained on dilution with 100 ml of water was chromatographed over 150 g of silica gel using 1:1 chloroform–benzene. From the first yellow-orange band there was isolated 0.40 g (17%) of yellow crystals of 2,7-dimethyl-1,4-phenanthrenequinone, mp 206–208°, by recrystallizations from ethanol–benzene, 19:1. From the analysis, failure to give a quinoxaline derivative with *o*-phenylenediamine and nmr spectrum (singlet at τ 7.5, 7-CH_3; doublet

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(1) This research was supported by Grant CA-07394 of the National Institutes of Health.

(2) Taken in part from the Ph.D. thesis of H. A. K., The Ohio State University, 1965.

(3) Taken in part from the M.S. Thesis of M. L. R., The Ohio State University, 1966.

(4) M. A. Frisch, C. Baker, J. L. Margrave, and M. S. Newman, *J. Amer. Chem. Soc.*, **85**, 2356 (1963).

(5) For a discussion of the buttressing effect see F. H. Westheimer in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p 552.

(6) H. A. Karnes, B. D. Kybett, M. H. Wilson, J. L. Margrave, and M. S. Newman, *J. Amer. Chem. Soc.*, **87**, 5554 (1965).

(7) For a recent synthesis of I see M. S. Newman and P. Zeelen, *Ohio J. Sci.*, **65** (4), 187 (1965).

(8) M. S. Newman and H. Whitehouse, *J. Amer. Chem. Soc.*, **71**, 3664 (1949).

(9) G. Wittig and H. Zimmerman, *Ber.*, **86**, 629 (1953), prepared $\mathrm{II_q}$ in 36% yield by this method.

(10) Even in 9,10-phenanthraquinone there is undoubtedly a nonzero dihedral angle between the carbonyl groups because of dipole–dipole interaction.

(11) All melting points were taken with standardized thermometers and are uncorrected. Microanalyses were done by the Galbraith Microanalytical Laboratories, Knoxville, Tenn.

at τ 7.85, J = 1.7 cps, 2-CH_3[12]) the structure of 2,7-dimethyl-1,4-phenanthrenequinone was assigned to this compound.

Anal. Calcd for $C_{16}H_{12}O_2$: C, 81.4; H, 5.2. Found: C, 81.3; H, 5.0.

Further elution of a dark band yielded an orange solid which on recrystallizations from benzene–ethanol, 9:1, yielded 0.97 g (42%) of orange crystals, mp 230.6–231.8°, of I_q.[13]

4,5-Dimethyl-9,10-phenanthrenequinone (II_q). To a solution of 40 g of anhydrous $AlCl_3$ in 80 ml of dry ether was added 7.6 g of $LiAlH_4$ in portions and then 4.4 g of the cyclic ether[8] of 4,5-dihydroxymethylphenanthrene. The resulting stirred mixture was heated and ether allowed to distil until the temperature reached 66–68°. After 42 hr (20 ml of ether added after 18 hr to facilitate stirring) 400 ml of ether was added to the cooled mixture and the whole filtered through a bed of diatomaceous earth. The filtrate and ether washings were washed with dilute acid and alkali and filtered through a bed of anhydrous $MgSO_4$. Chromatography over 75 g of alumina using 1:1 hexane–benzene afforded 2.7 g of a pale oil which contained II (54%) and dihydropyrene (42%) by glpc. This mixture was stirred at reflux in xylene with 2 g of 5% palladium on charcoal for 18 hr. The resulting oil (46% II, 46% pyrene) was chromatographed over 175 g of alumina using hexane as eluent to yield in the second main cut 1.2 g of II better than 97% pure by glpc. One recrystallization from ethanol yielded 1.1 g (27%) of II, mp 77.2–78.4°.

On adding in portions a warm solution of 1.4 g of chromic oxide in 20 ml of acetic acid and 10 ml of water to a solution of 1.0 g of II in 40 ml of acetic acid at 52° the temperature rose to 57°. After stirring for 12 min without external heating the temperature dropped to 53°. The mixture was then added to water and the organic product isolated by ether–benzene extraction. Two crystallizations of the product from 3:2 benzene–hexane, followed by sublimation under vacuum, yielded 0.3 g (27%) of II_q,[9] mp 163.0–164.5°, infrared bands at 5.92 and 5.95 μ.

2,4,5,7-Tetramethyl-9,10-phenanthrenequinone (III_q). Dimethyl 4,4′,6,6′-tetramethyldiphenate, mp 155.5–156.5°, was prepared by acid-catalyzed esterification of the corresponding acid.[6]

Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.6; H, 6.8. Found: C, 73.4; H, 6.6.

In a 500-ml flask (dried by distillation of xylene) equipped with high-speed stirrer, distilling-reflux condenser, and nitrogen inlet were placed 50 ml of xylene (mixture of isomers), 110 ml of *p*-cymene, and 7.0 g of sodium. To the sodium dispersion produced at reflux and cooled to 140° was added at once a solution of 5.0 g of the above ester in 100 ml of boiling *p*-cymene. The temperature rose to 160° and the color turned to red. After 1 hr at 153–157° the mixture was cooled to 20° and treated with 60 ml of methanol (in portions). The neutral portion (3.9 g) of the reaction products, isolated by usual methods, was thrice recrystallized from 9:1 ethanol–benzene to yield 1.8 g (45%) of III_q as orange needles, mp 199–200°, after softening at 195°, infrared bands at 5.88 (weak) and 5.90 (strong) μ. When this reaction was attempted in xylene alone, only unreacted starting ester was recovered.

Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.8; H, 6.1. Found: C, 81.7; H, 6.0.

The yellow quinoxaline derivative, mp 230–230.5°, was formed in high yield.

Anal. Calcd for $C_{24}H_{20}N_2$: N, 8.3. Found: N, 8.2.

3,4,5,6-Tetramethyl-9,10-phenanthrenequinone (IV_q). Dimethyl 5,5′,6,6′-tetramethyldiphenate, mp 106–107°, was prepared by esterification of the corresponding acid.[6]

Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.6; H, 6.8. Found: C, 73.5; H, 6.7.

The above ester (5.0 g) was cyclized with sodium (6.0 g) in refluxing xylene (225 ml) much as described for III_q. A 3-hr reaction time was optimal. The IV_q was obtained in 38% yield as yellow fine crystals, mp 195–196°, having only one strong carbonyl band at 5.92 μ. When this reaction was carried out in xylene–*p*-cymene at 145–150°, neither starting ester nor IV_q was obtained.

Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.8; H, 6.1. Found: C, 81.6; H, 6.1.

The yellow quinoxaline derivative, mp 181–181.5°, was formed in high yield.

Anal. Calcd for $C_{24}H_{20}N_2$: N, 8.3. Found: N, 8.2.

Polarographic Determinations

Dioxane purified as described[14] was kept in a distilling flask containing $LiAlH_4$ and was distilled as needed for each experiment after refluxing for 20 min. The condenser led into a dry nitrogen-swept polyethylene glove bag, in which all manipulations of the sample, including polarography, were conducted. This procedure eliminated any trace of a peroxide wave from the polarographic residual current.

Buffer constituents and supporting electrolyte salts were ordinary reagents. Sodium biphthalate, used because of its increased solubility in water–dioxane mixtures, was prepared by dissolving phthalic acid in a solution of sodium hydroxide. Phthalic acid was prepared by crystallization from an acidified solution of potassium biphthalate. The product was purified by recrystallization from an acidified solution.

Values of pH quoted herein are simply meter readings for the individual solutions in water–dioxane solvent. Although the pH meter was standardized with aqueous buffer solutions in the usual manner, no significance in terms of hydrogen ion activity can be attached to the readings for the mixed solvents.

Apparatus. Because the results of this study depended on highly precise current–voltage data, the applied voltages had to be corrected for *iR* drop in the rather poorly conducting water–dioxane mixtures either by (1) use of the three-electrode technique, or (2) use of a conventional two-electrode technique supplemented by precision measurements of R_s, the resistance of the test solution between the working electrodes. Because of technical difficulties in positioning the reference electrode, occasioned by working in the glove bag, the latter course was chosen. Thus, a simple tubular cell, equipped with nitrogen inlets above and below the solution level and a side compartment separated from it by a fine-porosity sintered-glass disk, was used. In the side compartment a platinum foil working anode of about 1-cm² area, curled to fit the tube, and a fiber-type sce reference electrode were inserted. The tip of the reference electrode was close to the platinum working electrode. The dropping mercury electrode was placed in the cell as usual. Polarograms were recorded on an ORNL-1988 A instrument (Indiana Instrument and Chemical Corp., Bloomington, Ind.) with the sce connected to the "reference" lead.

At the end of a polarographic experiment, with the test solution still in the cell, R_s, the series resistive component of the infinite-frequency cell impedance, was measured as follows. The polarographic working electrodes were connected to the "unknown" arm of a capacitance bridge set up to yield series resistance values directly. The bridge and detector systems, which have been fully described elsewhere,[15] were very similar to those previously employed.[16–18] Since the component of cell impedance due to the pure resistance of the electrolyte was needed, the dependence of R_s upon the frequency, f, of the ac signal used to power the bridge was investigated. R_s was found to vary linearly with

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[12] The methyl group in 2-methyl-1,4-naphthalene quinone shows a doublet at τ 7.83, J = 1.5 cps.

[13] R. Haworth, C. Mavin, and G. Sheldrick, *J. Chem. Soc.*, 454 (1934), give mp 224–225° for I_q.

[14] K. B. Wiberg, "Laboratory Technique in Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1960.

[15] D. W. Imhoff, Ph.D. Dissertation, The Ohio State University, 1966.

[16] D. C. Grahame, *J. Amer. Chem. Soc.*, **71**, 2975 (1949).

[17] P. Delahay and I. Trachtenberg, *ibid.*, **79**, 2355 (1957).

[18] T. Biegler and H. A. Laitinen, *J. Phys. Chem.*, **68**, 2374 (1964).

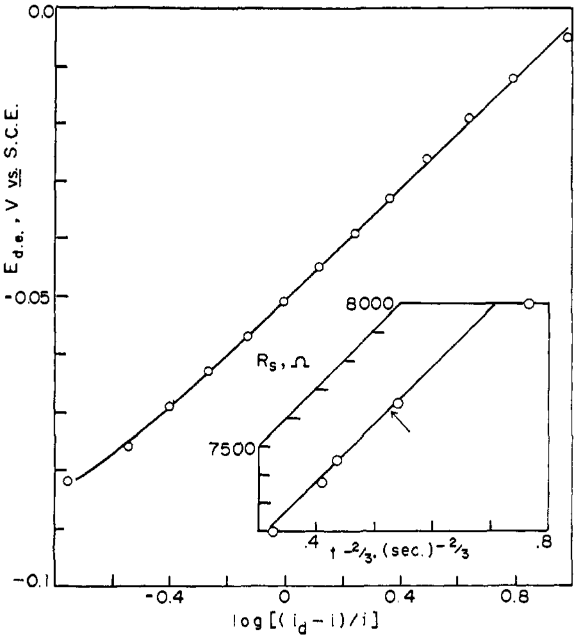

Figure 1. Typical log plot. Test solution was 2.23 mM in III_q; solvent 75% dioxane, pH 2.71, 0.1 M $NaNO_3$; temperature 27.5° t_d 6.54 sec. Inset: R_s as a function of $t^{-2/3}$. The arrow indicates the R_s corresponding to a drop 2.60 sec old, *i.e.*, $0.397t_d$, when the instantaneous current was equal to tne average current.

f^{-1}, and the value obtained at 7500 Hz was between 5 and 10% of the value obtained by extrapolation to $f^{-1} = 0$. For this reason a single impedance measurement at 7500 Hz was used for obtaining the infinite-frequency value of R_s in routine polarographic work.

The area of the drop issuing from the dropping mercury electrode, and hence its age, affected R_s. The geometry of a spherical drop suggests that R_s should be proportional to $t^{-2/3}$. In order to get a value of R_s valid for the time when the instantaneous current, i_t, equalled the average current, i_{av}, the usual one-sixth power dependence of current on time was postulated and eq 1 resulted.

$$t_{i_t = i_{av}} = 0.397t_d \qquad (1)$$

Bridge balance was made at the end of the drop life; the drop time was recorded; the drop time was changed, and the process was repeated. For each run a plot of R_s *vs.* $t_d^{2/3}$ was constructed, and the R_s to be used for iR corrections was obtained for the time when the instantaneous current equalled the average current by interpolation from this plot and application of eq 1. Typical R_s values, used in calculating iR corrections, were 1100 ohms for 40% dioxane to 7600 ohms for 75% dioxane. The largest corrections were 40 to 50 mV.

R_s, the resistive component of the cell impedance, was postulated to be the resistance contributed by the electrolyte under the exact conditions of the experiment. The validity of this assumption derives from studies[19] of the impedance of electrolytes as a function of frequency. In the present instance, it led to resistance values which, although systematically different from infinite frequency values by 5–10%, were precise to *ca.* ±1.0%. These values, used to correct applied voltages data, yielded plots of E_{dme} *vs.* log $[(i_d - i)/i]$ usable over a wide range.

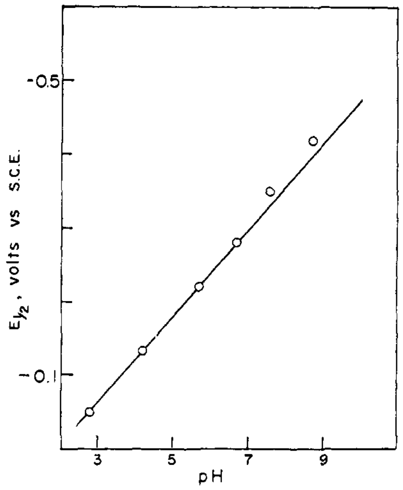

Figure 2. Half-wave potential as a function of pH. Reduction of III_q in 75% dioxane.

A maximum in the polarographic wave, which was accentuated at low pH and as concentration of the quinone increased, presented some problem in obtaining good current–potential data. Maximum suppressors were not tried, and the portion of the wave obviously influenced by a maximum was not used in analyzing the wave.

An example of the use of the data is given in Figure 1. This logarithmic plot is noteworthy for the range it covers with but slight departure from linearity. The points shown include values of current corresponding from 9 to 85% of the diffusion current. The slope of this plot is 0.049 V. Details of the exacting procedure employed in handling samples and data are available.[3]

Results

Effect of Composition of Solvent and pH on Polarographic Waves. As the fraction of dioxane in the solvent decreased, the two-electron reduction wave of the four quinones more closely approximated that of a reversible process without complicating steps. This is shown in Table I, where the slope of the log plots is seen to tend toward 0.030 V as the dioxane content decreases. Data comparing the four quinones in 40% dioxane are shown in Table II. The change in $E_{1/2}$ with pH was close to 60 mV/pH unit in all the dioxane–water mixtures studied. Data for III_q are shown in Figure 2, and results from exactly similar plots for compounds I_q, II_q, and IV_q are 0.063, 0.060, and 0.061 V/pH unit, respectively. The empirical coefficient $\Delta E_{1/2}/\Delta$pH may be used to normalize half-wave potential data for comparison purposes, a procedure used in calculating values for the last columns of Tables I and II.

Character of Polarographic Waves. For all quinones studied in 75% dioxane, $E_{1/2}$ was independent of drop time but dependent on concentration. Plots of E_{dme} *vs.* log $[(i_d - i)/i]$ had slopes intermediate between the theoretical values for one- and two-electron reductions and showed some sigmoid shape. It was concluded that the electrode process was reversible but might in-

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(19) For example see G. Jones and S. M. Christian, *J. Amer. Chem. Soc.*, 57, 272 (1935).

Table I. Effect of Solvent Composition on Polarographic Parameters[a]

% dioxane	pH	$E_{1/2}$, V, *vs.* sce	$\frac{i_d}{Cm^{2/3}t^{1/6}}$	Slope of log plot,[b] V	$E_{1/2}$ at pH 2.80, V, *vs.* sce
75	2.80	−0.067	2.44	0.045	−0.067
65	2.58	−0.050	2.08	0.036	−0.063
55	2.40	−0.043	2.13	0.034	−0.067
40	2.24	−0.032	2.04	0.033	−0.065

[a] Compound III_q electrolyzed at dme with $m^{2/3}t^{1/6}$ = 1.51 mg$^{2/3}$ sec$^{-1/2}$. Supporting electrolyte: 0.4 *M* $NaNO_3$; solutions buffered with 0.05–0.1 *M* malonic acid. [b] An average of three runs at various drop times.

Table II. Characteristics of Polarographic Waves, 40% Dioxane[a]

Compd	Concn, m*M*	Slope of log plot,[b] V	$\frac{i_d}{Cm^{2/3}t^{1/6}}$	$E_{1/2}$, V, *vs.* sce[b]
I_q	1.35	0.032	2.10	+0.072
II_q	1.34	0.034	2.00	0.000
III_q	1.29	0.033	2.02	−0.010
IV_q	1.27	0.033	2.04	−0.029

[a] Solution pH 2.19 in 0.12 *F* malonic acid buffer; 0.4 *M* $NaNO_3$. [b] An average of three runs at various drop times.

volve dimerization.[20] A formal treatment of Brdicka[21] was applied to the data which takes into account the dimerization equilibrium constant defined by eq 2.

$$q = [\text{dimer}]/[\text{quinone}][\text{hydroquinone}] \qquad (2)$$

Values of q for each current were computed using relationships derived by Brdicka.[21] Although highly imprecise, they indicated a downward trend with decreasing pH and concentration of quinone and did not vary significantly for the several quinones at a given pH and concentration. Thus, shifts in half-wave potential among the quinones are not due to greatly different positions of the dimerization equilibrium. Details of these results are available elsewhere.[3]

Discussion

The appearance of the polarographic waves of the quinones related to phenanthrene and their tendency toward more reversible behavior as the water content of the solvent was increased are in accord with previous studies of quinones.[22,23] The present study is also consistent with earlier studies on the effect of substituents on the ease of reduction of quinones[24–27] which most recently have correlated increased ease of reduction of a substituted quinone with the electron-attracting power of the substituent.

The interest in the present data is the effect of the position of substituents on the ease of reduction of 9,10-quinones related to phenanthrene. The difference of 0.072 V for $E_{1/2}$ of compounds I_q and II_q (see Table II) is equivalent to a difference of 3.3 kcal/mol in the free energy of the reduction process. Thus this result shows that whereas the heat of combustion data (12.6 kcal/mol) reflects the entire extent of methyl–methyl repulsion, the polarographic results (3.3 kcal/mol) reflect only the different extent of repulsions in hydroquinones relative to quinones. (The more positive $E_{1/2}$ indicates the stronger oxidant.) Since in the reduction product the 9,10 bond is a double bond, the difference in the free energy for the two reactions may be thought of as the energy required to force the nonplanar quinone into a more nearly planar configuration favored by the aromatic system. In the case of the quinones, III_q and IV_q, the same reasoning applies, except that the difference in this pair reflects the increased crowding at the 4,5 positions caused by the "buttressing effect"[5] of methyl groups in the 3,6 positions. The buttressing effect for the conditions employed in this study is 0.9 kcal/mol. The buttressing effect inferred from the present work is not directly comparable to that obtained for the parent hydrocarbons.[6] One reason for this is the mutual repulsive effect of the *o*-carbonyl groups of the quinones, which introduces more distortion into the quinone compounds. Another is the lack of thermodynamic data necessary to relate free energies of the reduction of quinones to enthalpies of formation.

Acknowledgments. We thank D. Shishir K. Jain for preparing the quinoxaline derivatives of III_q and IV_q.

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(21) R. Brdicka, *Z. Elektrochem.*, **47**, 314 (1941).

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