

This ester shows strong absorption at 1760 cm^{-1} , the high frequency being characteristic of phenolic esters.¹⁴

2-(1-Oxo-2-benzylpropyl)-4,6-dimethylphenol. A mixture of 107 g. (0.4 mole) of the above ester and 160 g. (1.21 moles) of anhydrous aluminum chloride was allowed to stand 20 hr. at room temperature. It was then heated on a steam bath for 2 hr. with vigorous stirring. After hydrolysis of the complex with cold conc. hydrochloric acid, the desired ketone was isolated by filtration and recrystallized from 90% ethanol, m.p. 67–67.5°, yield 43 g. (40%).

Anal. Calcd. for $\text{C}_{18}\text{H}_{20}\text{O}_2$: C, 80.59; H, 7.46. Found: C, 80.37; H, 7.37. An infrared band at 1640 cm^{-1} characteristic of a strongly hydrogen-bonded conjugated ketone¹² was exhibited by this material in cetane solution.

2-(1-Hydroxy-2-benzylpropyl)-4,6-dimethylphenol. The ketone prepared above, 11.0 g. (0.041 mole), was added dropwise to a solution containing 0.9 g. (0.024 mole) of lithium aluminum hydride in 200 ml. of dry ether. After destruction of excess lithium aluminum hydride the mixture was poured on iced 10% sulfuric acid. The ether layer was separated and the aqueous layer was extracted twice with 100-ml. portions of ether. The combined extracts were washed with dilute ammonia, then with water until neutral, and dried. Evaporation of the ether left 10.8 g. (98%) of a crystalline alcohol, m.p. 105–154°. The mixture of diastereomers was separated by crystallization from a 50-50 benzene-hexane mixture. The pure high-melting isomer was obtained from a chloroform eluate from a silicic acid column. It crystallized as fine silky needles, m.p. 157–158°, 4.7 g. (43%).

Anal. Calcd. for $\text{C}_{18}\text{H}_{22}\text{O}_2$: C, 80.00; H, 8.15. Found: C, 80.20; H, 8.12.

This isomer showed two partly overlapping bands in the

(14) J. F. Grove and H. A. Willis, *J. Chem. Soc.* 877 (1951).

OH stretching region at 3360 and 3480 cm^{-1} . No band in the region around 1640 cm^{-1} was observed.

The low melting isomer crystallized as compact crystals, m.p. 104–106°, 3.1 g. (28%) after repeated crystallization from benzene. It showed two well resolved bands in the infrared at 3600 and 3360 cm^{-1} .

Anal. Calcd. for $\text{C}_{18}\text{H}_{22}\text{O}_2$: C, 80.00; H, 8.15. Found: C, 80.05; H, 8.21.

2-(2-Benzylpropenyl)-4,6-dimethylphenol. A mixture of 1.2 g. (0.0044 mole) of 2-(1-hydroxy-2-benzylpropyl)-4,6-dimethylphenol, m.p. 157–158°, and 1.5 g. of freshly fused potassium acid sulfate was heated at 160–170° for 30 min. The product was isolated by ether extraction and purified by distillation, b.p. 124–125° (0.15 mm.), n_D^{25} 1.5795, d_4^{25} 1.0267, 0.96 g. (86%).

Anal. Calcd. for $\text{C}_{18}\text{H}_{20}\text{O}$: C, 85.71; H, 7.93. Found: C, 86.09; H, 8.12.

Mp. Calcd.: 79.18. Found: 80.21.

Similar dehydration of the alcohol, m.p. 104–106°, gave 96% yield of a product with identical physical properties and infrared spectrum. Both samples showed absorption at 805 cm^{-1} and 1645 cm^{-1} characteristic of a double bond and lacked the doublet in the O—H stretching region.

2-(2-Benzylpropyl)-4,6-dimethylphenol. A solution of olefin in glacial acetic acid was reduced at room temperature and atmospheric pressure over palladium-on-charcoal. One mole of hydrogen was absorbed. The solution was poured into water and the product extracted with petroleum ether. The reduced material was isolated in high yield by distillation under reduced pressure. Both the physical properties and infrared spectra were identical with those of the phenolic product from the reaction of the benzyl ether.

Anal. Calcd. for $\text{C}_{18}\text{H}_{22}\text{O}$: C, 84.99; H, 8.70. Found: C, 85.2; H, 8.84.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF OREGON]

Polarographic Reduction of Some Biaryls and Arylalkenes^{1,2}

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Polarographic half-wave reduction potentials of twenty-seven aromatic hydrocarbons (including fifteen conjugated alkenylnaphthalenes, the phenylnaphthalenes, the phenylanthracenes, and the binaphthyls) were obtained under comparable conditions in a solvent-electrolyte mixture of 0.1M tetra-*n*-butylammonium iodide in 75% dioxane-water. In general, among isomeric compounds, the facility of reduction is found to increase with lessened steric restriction to the attainment of coplanarity in the molecule. Notable exceptions to this rule are found in the cases of the vinyl- and cyclopentenyl-naphthalenes, where the 1-naphthyl isomers are reduced at slightly less negative potentials than the sterically less-hindered 2-isomers. Results are interpreted in terms of angles of twist present in the substrate molecules at the time of electron addition (transition state) and inherent conjugative powers of the alkenyl and aryl moieties. Coulometric data are reported for seven compounds.

The polarographic reducibilities of styrene⁴ and biphenyl⁵ are considered manifestations of the

(1) Abstracted (in part) from the Ph.D. dissertation of C. D. Lind, University of Oregon, June, 1956. This research was supported in part by a grant from The Petroleum Research Fund administered by the AMERICAN CHEMICAL SOCIETY and in part through sponsorship by the Office of Ordnance Research, U. S. Army, contract no. DA-04-200-ORD-176. Grateful acknowledgment is hereby made to these donors.

(2) Presented (in part) at the Northwest Regional Meeting of the AMERICAN CHEMICAL SOCIETY, Spokane, Washington, June, 1957. Paper XI in the series on Chemical Reactivities of Arylcycloalkenes. For paper X see ref. 15.

(3) Research Associate, 1957–1958.

general phenomenon of conjugation inasmuch as the π -electronic systems, as present in benzene and ethylene,⁶ are not similarly reducible. In general, one might anticipate that the electroreducibility of any biaryl or arylalkene would depend on at least three inherently different (but closely associated) factors, *viz.* (a) the conjugative powers

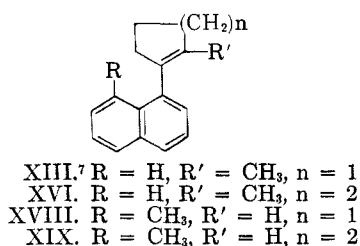
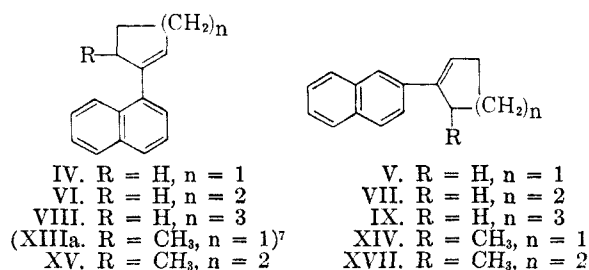
(4) H. A. Laitinen and S. Wawzonek, *J. Am. Chem. Soc.*, **64**, 1765 (1942).

(5) S. Wawzonek and H. A. Laitinen, *J. Am. Chem. Soc.*, **64**, 2365 (1942).

(6) M. v. Stackelberg, *Polarographische Arbeitsmethoden*, W. de Gruyter and Co., Berlin, 1950, pp. 210–211.

of the aryl and alkenyl moieties, (b) the angle of twist in the molecule, and (c) steric hindrance to approach of the substrate to the mercury cathode. This paper reports the results of experiments employing comparable procedures for all compounds used and designed particularly to investigate the influences of factors (a) and (b).

For this study fifteen conjugated naphthylalkenes, the phenylnaphthalenes, the binaphthyls, and the phenylanthracenes (as well as some parent arenes and alkylarenes used for comparison) were reduced polarographically in an electrolyte consisting of 0.1M tetra-*n*-butylammonium iodide in 75% dioxane-water. Data for these compounds are recorded in Table I, examination of which shows that some compounds exhibit only one reduction wave while others exhibit two. For each compound the decision on the number of such waves is based on the following criteria (listed in approximate order of priority): (1) visual appearance of the polarogram, especially where two clearly separated waves are observable, (2) numerical values of the diffusion current constants, and (3) coulometry on a semimicro scale. Criterion (2) was sometimes sufficiently definitive to differentiate between a *bona fide* single wave and two overlapping but visually unresolved waves by comparison with similar



(7) The compound to which we now assign structure XIII is the same one as was previously designated by structure XIIIa. Structure XIIIa was proposed on the basis of chemical degradative studies (*cf.* ref. 21). On the other hand structure XIII (but not structure XIIIa) is consistent with the NMR spectrum of the substance (run in trideuteriochloroform at 60 megacycles using tetramethylsilane as an internal standard, determined and interpreted through the courtesy of Mr. LeRoy Johnson of Varian Associates) which shows a very complex multiplet at *ca.* 450 cycles (aromatic hydrogens) and small spin splittings but no large doubling at *ca.* 91 cycles (methyl group attached to a carbon bearing no hydrogen) and lacks a signal at *ca.* 320 cycles (expected for a hydrogen on a doubly bonded carbon). Structure XIII is also preferred on the basis of the behavior of this compound in studies on rates of catalytic hydrogenation (L. H. Klemm and Roger Mann, unpublished).

data from cases treated successfully by means of criterion (1). Coulometry was interpreted on the basis that ideally each wave for a naphthylalkene should involve two electrons. As justification for this latter interpretation it was found that both the single wave for naphthalene and the first wave (of two visually separated waves of equal height) for IV consumed two electrons. The criteria employed for each compound are noted in Table I. The coulometric procedure and results are discussed later in this paper.

From Table I, it is apparent that the facility of electroreduction increases with decreasing (average) angle of twist, θ , in isomeric biaryls. Thus, one has the orders 2-phenylnaphthalene < 1-phenylnaphthalene; 2,2'-binaphthyl < 1,2'-binaphthyl < 1,1'-binaphthyl; and 2-phenylanthracene < 1-phenylanthracene < 9-phenylanthracene both in θ and in $-E_{1/2}$ (for the first or only wave). Such orders could be ascribed to differences in electrical polarizabilities of the substrate molecules and/or to steric hindrance to adsorption of such molecules on the cathode. Steric hindrance ought to be particularly significant if the transition complex for electroreduction involved a coplanar substrate adsorbed flatwise on the mercury surface. On the other hand these orders are inconsistent with expectations based on relative values of the conjugative power, C_i ,⁸ for the isomeric naphthyl and isomeric anthryl groups. Thus Badger, Pearce, and Pettit⁹ and Braude and Gore¹⁰ have summarized experimental results which indicate that C_i for the 1-naphthyl group is greater than that for the 2-naphthyl group and the Pullmans¹¹ have noted that, in general, C_i for any position on an aromatic hydrocarbon should vary directly with the free-valence number of the position. If, then, C_i were a controlling factor in electroreducibility of these biaryls one would expect to find reverse orders (from those observed) in $-E_{1/2}$ for all three sets of isomers. In this same regard the small differences in $E_{1/2}$ between the pairs 9,9'-bi-anthryl-anthracene (XXVIII and XXIII) and rubrene-naphthacene (XXX and XXIX) have been ascribed¹² to a large deviation from coplanarity in the former member of each pair.

That C_i is important, however, as a determinant of electroreducibility seems apparent if one selects

(8) In a previous paper [L. H. Klemm, H. Ziffer, J. W. Sprague, and W. Hodes, *J. Org. Chem.*, **20**, 190 (1955)] C_i was called the "conjugative effect." The present nomenclature is consistent with that used in ref. 11.

(9) G. M. Badger, R. S. Pearce, and R. Pettit, *J. Chem. Soc.*, 1112 (1952).

(10) E. A. Braude and P. H. Gore, *J. Chem. Soc.*, 41 (1959).

(11) B. Pullman and A. Pullman, *Progress in Organic Chemistry*, Vol. 4, J. W. Cook, ed., Butterworths, London, 1958, Chap. 2, especially pp. 64-65. See also C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.*, **195A**, 188 (1948).

(12) G. J. Hoijtink, *Rec. trav. chim.*, **74**, 1525 (1955).

TABLE I
POLAROGRAPHIC DATA FOR SOME SUBSTITUTED NAPHTHALENES, ANTHRACENES, AND NAPHTHACENES

Compound No.	Substituent(s) on Parent Substrate Molecule	Half-wave Reduction Potential ^a (in v. vs. S.C.E.)		$\frac{i_d}{cm.^2/s^{1/2}}$ (in $\mu\text{-amp.}\cdot\text{mmole}^{-1}\cdot\text{l.-mg.}^{-2/3}\cdot\text{sec.}^{1/2}$)		Criteria for Number of Waves ^b
		First Wave $-E_{1/2}'$	Second Wave $-E_{1/2}''$	First Wave	Second Wave	
On Naphthalene						
I	None	—	2.46	—	2.6	V, D, C
II	1-Vinyl	2.09	2.52	2.5	2.6	V, D
III	2-Vinyl	2.12–2.15 ^c	2.54	2.7–3.9 ^c	2.7	V, D
IV	1-(1-Cyclopentenyl)	2.27	2.53	2.1	2.2	V, C, D
V	2-(1-Cyclopentenyl)	2.30	2.55	2.1	3.4	V
VI	1-(1-Cyclohexenyl)	2.46	2.56	1.7	1.9	C ^d
VII	2-(1-Cyclohexenyl)	2.38	2.56	2.1	3.1	V
VIII	1-(1-Cycloheptenyl)	2.41	2.52	1.9	2.0	C, D ^e
IX	2-(1-Cycloheptenyl)	2.35	2.56	1.7	1.5	V
X	1-Cyclopentyl	—	2.53	—	3.4	V ^e
XI	1-Phenyl	2.40	—	2.5	—	V, D
XII	2-Phenyl	2.30	2.51	2.5	2.6	V, D
XIII	1-(2-Methyl-1-cyclopentenyl)	(2.42)	(2.50)	(1.3)	(1.3)	D ^{e,f}
XIV	2-(5-Methyl-1-cyclopentenyl)	2.37	2.50	1.7	1.4	C ^g
XV	1-(6-Methyl-1-cyclohexenyl)	2.43	2.52	1.8	1.7	D ^d
XVI	1-(2-Methyl-1-cyclohexenyl)	(2.46)	(2.55)	(1.4)	(1.4)	D ^{e,f}
XVII	2-(6-Methyl-1-cyclohexenyl)	2.42	2.50	1.2	1.1	C ^e
XVIII	8-Methyl, 1-(1-cyclopentenyl)	2.36	2.51	1.8	1.8	V, D
XIX	8-Methyl, 1-(1-cyclohexenyl)	(2.42)	(2.49)	(1.1)	(1.1)	D ^{e,f}
XX	1-(1-Naphthyl)	2.33 ^h	2.54	— ^{i,j}	— ^{i,j}	V ^k
XXI	1-(2-Naphthyl)	2.24	2.47	1.1	2.3	V
XXII	2-(2-Naphthyl)	2.17 ^l	2.47 ^m	— ^{j,n}	— ^{j,n}	V
On Anthracene						
XXIII	None	1.96	—	1.9	—	V ^e
XXIV	1-Phenyl	1.89	? ^o	0.8	—	V
XXV	2-Phenyl	1.87	2.58	— ⁿ	— ^{n,p}	V
XXVI	9-Phenyl	1.92	—	1.8	—	V ^e
XXVII	9-Methyl	1.94	—	2.1	—	V ^e
XXVIII	9-(9-Anthryl) ^q	1.97	2.38	3.0	0.9	—
On Naphthacene						
XXIX	None ^r	1.58	1.84	—	—	—
XXX	9,10,11,12-Tetraphenyl ^r	1.55	1.80	—	—	—

^a For a compound showing only one wave, the half-wave potential ($E_{1/2}$) is given under whichever column seems more appropriate. ^b V denotes visual observation of the polarogram; C, coulometry; D, diffusion current constant. ^c The shape of the curve and the high value for the diffusion current constant indicate that this wave may actually consist of two partly superimposed smaller waves—one a minor pre-wave of absolute value <2.09 and the other at -2.15 (diffusion current constant $\cong 2.7$). Gas chromatography of III (conducted by Drs. G. H. Beaven and E. A. Johnson at the Medical Research Council Laboratories, London, England) showed the presence of 10–15% of an impurity therein. ^d Some polarograms show the visual semblance of two waves; others do not. ^e No indication of the presence of more than one wave in the polarogram was visually apparent. ^f In this case the value of the diffusion current constant, as well as other observations, is not definitive for the presence of two waves rather than of one. The numerical data listed are therefore parenthesized. ^g The polarogram shows a slight indication of two waves. ^h One calculates a value of 2.35 on the basis of the results of Hoijtink (ref. 12) using 96% dioxane and assuming a change of $+0.10$ v. in $E_{1/2}'$ (as found for naphthalene) in changing the solvent to 75% dioxane. ⁱ No diffusion current constant is given inasmuch as the characteristics of the capillary used are unknown. ^j The two waves are approximately equal in height. ^k For coulometric results see Table II. ^l A pre-wave of height $1/4$ to $1/3$ of the first wave occurs at ca. -2.01 v. ^m Measured in 0.175M tetra-*n*-butylammonium iodide. ⁿ The concentration of the solution (nearly saturated) was not known quantitatively. ^o Though a second wave is present, the polarogram did not allow determination of $E_{1/2}''$. ^p The height of this wave is 3–4 times that of the first wave. ^q Data of Hoijtink (ref. 12), corrected for effect of solvent as noted in preceding footnote ^h.

series of compounds for which θ -distributions should be equivalent or nearly so and reductions of analogous structural features should ensue (*vide infra*). Thus, one notes that 2,2'-binaphthyl reduces more readily than does 2-phenylnaphthalene. Also, for the 2-alkenylnaphthalenes reducibility is fostered in the order (of alkenyl substituents) vinyl >

cyclopentenyl > cycloheptenyl > cyclohexenyl. The relationship vinyl > cyclopentenyl > cyclohexenyl is in accord with the order of C_i as based on ultraviolet absorption spectra¹³ and Diels-

(13) See ref. in footnote 8.

Alder reactivity.¹⁴ Although the appropriate relative C_r -value for the cycloheptenyl group is not clearly known, it is generally considered to be equal to or less than that of the cyclohexenyl group.^{15,16} On the other hand, one would expect the cyclohexenylnaphthalenes to reduce more readily than their cycloheptenyl homologs if bulkiness of the substituent were the sole pertinent structural factor involved.

For arylalkenes and biaryls one would anticipate that $E_{1/2}'$ would be dependent on θ_p , the angle of twist in the molecule at the time of electron addition, rather than on θ , the angle of twist in the unperturbed molecule present in solution. Electrical polarization and/or preferential flatwise adsorption of the substrate should operate to make $\theta_p < \theta$, if possible. As molecular models indicate little or no steric hindrance to the attainment of coplanarity¹³ in the 2-substituted arenes III, V, VII, IX, XII, XXII, and XXV, we suggest that these molecules are rotated into virtual coplanarity¹⁷ prior to (or in the process of) electroreduction ($\theta_p \cong 0^\circ$). Comparison of $E_{1/2}'$ -values listed in Table I shows that in only two cases (the vinyl-naphthalenes and the cyclopentenyl-naphthalenes) does the 1-isomer reduce more readily than the 2-isomer (as expected on the basis of C_i). It is proposed, therefore, that of the 1-naphthyl compounds studied, only II and IV (where steric hindrance to rotation of the alkenyl group into coplanarity would be least) have $\theta_p \cong 0^\circ$. For all of the other biaryls and arylalkenes listed it is believed that $\theta_p > 0^\circ$.

Seven compounds (*cf.* Table II) were studied by coulometry using an electrolysis cell containing a silver anode, a mercury cathode maintained at a potential 0.08 to 0.15 volt more negative than $E_{1/2}$ (*i.e.* either $E_{1/2}'$ or $E_{1/2}''$ as the case may be), and the same solvent-electrolyte as employed in polarography. The cell was designed to meet the requirements of (a) an inert atmosphere, (b) low internal resistance, (c) efficient mixing of components in the cathode chamber, and (d) a mechanical means of preventing the flakes of silver iodide (arising from reaction at the anode) from contacting the cathode (and being reduced there). Requirement (d) proved the most difficult to satisfy without deleterious effects on (b). It was met by using a diaphragm consisting of a piece of filter paper and a plug of glass wool, suspended (by means of a glass support) between large electrodes in close

(14) L. H. Klemm, W. Hodes, and W. B. Schaap, *J. Org. Chem.*, **19**, 451 (1954).

(15) L. H. Klemm, B. T. Ho, C. D. Lind, B. I. MacGowan, and E. Y. K. Mak, *J. Org. Chem.*, **24**, 949 (1959).

(16) G. Baddeley, *Ann. Repts.*, **LI**, 170-171 (1954); W. M. Schubert and W. A. Sweeney, *J. Am. Chem. Soc.*, **77**, 2297 (1955); O. H. Wheeler, *J. Am. Chem. Soc.*, **78**, 3216 (1956).

(17) Any molecule having an angle of twist between $-\alpha^\circ$ and $+\alpha^\circ$ (*cf.* ref. 13) should be experimentally indistinguishable from one where θ_p is precisely 0° .

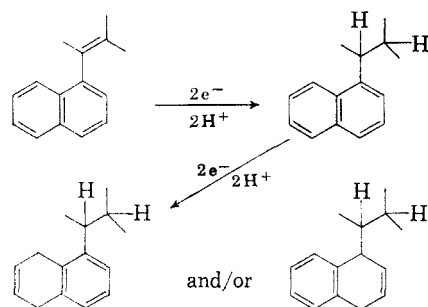
TABLE II

COULOMETRY OF SEVEN HYDROCARBONS IN 0.1M TETRA-*n*-BUTYLAMMONIUM IODIDE IN 75% DIOXANE-WATER

Compound No.	Controlled Cathode Potential (v. vs. S.C.E.)	No. of Trials	Electrons Absorbed per Molecule of Compound	Permanganate Test on Resultant Solution
I	-2.60	4	2.0 \pm 0.2	+
IV	-2.40	1	2.0 \pm 0.2	-
VI	-2.65	2	4.1 \pm 0.3	+
VIII	-2.60	3	4.1 \pm 0.3	+
XIV	-2.65	3	4.1 \pm 0.5	+
XVII	-2.60	3	4.2 \pm 0.2	+
XX	-2.42	1	4.0 \pm 0.2	+
XX	-2.65	3	6.9 \pm 0.5	+

proximity. Even use of a thin, coarse sintered-glass diaphragm raised the internal resistance of the cell so much that successful coulometry could not be achieved. Thus, with the latter diaphragm, onset of electrolysis occurred only at a high potential drop (*ca.* 100 v.) across the cell and was accompanied by excessive heating (even boiling) of the solution as well as by formation of dark suspended particles throughout the cell. Inasmuch as half-wave reduction potentials are known to vary with apparatus and solvent used, our method was standardized against naphthalene which consistently absorbed 2.0 ± 0.2 electrons/molecule when the cathode potential was maintained at -2.60 v. (*vs.* S.C.E.). As noted elsewhere, the first visually observable wave of IV also corresponded to absorption of two electrons per molecule, while the visually singular waves of VI, VIII, XIV, and XVII corresponded to absorption of four. 1,1'-Binaphthyl (XX) absorbed four electrons/molecule when the cathode potential was maintained at a value intermediate between $E_{1/2}'$ and $E_{1/2}''$ or a total of seven electrons/molecule when such potential was held more negative than $E_{1/2}''$ throughout the electrolysis.

Remembering that only conjugated benzene rings and carbon-carbon double bonds are electroreducible and that naphthalene reduces more readily than biphenyl, one can, in certain instances, assign selected polarographic waves to reduction of particular bonds or systems of bonds in the substrate. Thus, the single wave exhibited by 1-phenylnaphthalene may be ascribed to the transformation of this compound to 1-phenyl-1,4-dihydronaphthalene; the two waves of 2-phenylnaphthalene, to double reduction of the substituted ring of the naphthyl moiety to yield 2-phenyl-1,2,3,4-tetrahydronaphthalene; and the single wave for anthracene and 9-substituted anthracenes, to reduction at the 9,10-positions. For the alkenylnaphthalenes reduction should proceed according to generalized Scheme I, which is in agreement with the coulometric results and permanganate tests recorded for IV, VI, VIII, XIV, and XVII in



Scheme I

Table II and with the observation that $E_{1/2}$ for IV is numerically equal to $E_{1/2}$ (single wave) for 1-cyclopentyl-naphthalene (X). It might also be noted that values of $E_{1/2}$ (but not of $E_{1/2}$) for these alkenes are (a) only slightly dependent (maximum deviation from average, 0.03 v.) on the nature of the alkenyl group and its position on the naphthalene ring and (b) more negative than $E_{1/2}$ for naphthalene. Situation (b) may be the result of electron donation by the alkyl group to the naphthyl moiety and/or steric hindrance by such group to preferred orientation of the molecule onto the mercury surface. On the contrary, however, the methyl group (*cf.* our data for the pairs XXIII *vs.* XXVII and IV *vs.* XVIII, as well as those reported for naphthalene *vs.* the mono-methylnaphthalenes¹⁸ and benz[*a*]anthracene *vs.* its 7,12-dimethyl derivative⁵) show little, if any, effect on $E_{1/2}$ ($\Delta E_{1/2} \leq 0.02$ v.), as compared to hydrogen. Clarification of the reason for this discrepancy between the effects of the methyl group and those of the other alkyl groups must await further experimentation.

EXPERIMENTAL

Preparations and/or purifications of all substrates (except XXII), the solvent,¹⁹ and the electrolyte have been described previously.^{14,15,20-22} XXII, obtained as a by-product from

(18) R. A. Burdett and B. E. Gordon, *Anal. Chem.*, **19**, 843 (1947).

(19) Attention should be called to the highly toxic nature of even low concentrations of dioxane in the atmosphere when one is exposed thereto over extended periods of time [*cf.* N. I. Sax, *Dangerous Properties of Industrial Materials*, Reinhold Publishing Corp., New York, 1957, p. 636]. In the interests of safety for laboratory personnel it is strongly recommended that all steps in purification of this solvent or of handling it other than in tightly closed containers should be conducted in a good hood.

(20) L. H. Klemm and W. Hodes, *J. Am. Chem. Soc.*, **73**, 5181 (1951).

(21) L. H. Klemm and H. Ziffer, *J. Org. Chem.*, **20**, 182 (1955).

(22) L. H. Klemm, J. W. Sprague, and H. Ziffer, *J. Org. Chem.*, **20**, 200 (1955).

(23) L. H. Klemm, J. W. Sprague, and E. Y. K. Mak, *J. Org. Chem.*, **22**, 161 (1957).

(24) W. E. Bachmann and L. H. Klemm, *J. Am. Chem. Soc.*, **72**, 4911 (1950).

(25) L. H. Klemm, D. Reed, and C. D. Lind, *J. Org. Chem.*, **22**, 739 (1957).

(26) L. H. Klemm, D. Reed, L. A. Miller, and B. T. Ho, *J. Org. Chem.*, **24**, 1468 (1959).

the reaction of 2-naphthylmagnesium bromide with cyclohexanone, was chromatographed on alumina and recrystallized from ethanol, m.p. 186–188°.

Polarography. The solvent-electrolyte mixture, 0.1M tetra-*n*-butylammonium iodide in 75% (by volume) dioxane in water, was pre-electrolyzed in an H-type cell for 30 min. at an applied potential of 2.8 v. in an atmosphere of purified²⁷ nitrogen. The resultant solution had a pH of *ca.* 9 as measured by a Beckman instrument. Polarography proper was conducted using a Fisher Electrode; an attached potentiometer for measuring *E*, the applied potential, to an accuracy of ± 0.2 mv.; Sargent S-29417 capillary tubing (typical characteristics: $m = 0.6$ – 0.9 mg. per sec., $t = 8$ – 11 sec. at $E = 0$), and a thermostated ($25.0 \pm 0.2^\circ$) three-compartmental cell consisting effectively of an H-cell with an intermediate vertical compartment separated from the cathode compartment by means of a sintered glass disk of medium porosity and from the anode compartment by a similar disk plus an agar-potassium chloride plug. The anode compartment constituted a saturated calomel electrode.²⁸ The intermediate compartment contained saturated aqueous tetra-*n*-butylammonium iodide (renewed for each experiment) to reduce diffusion of potassium ion from anode to cathode and of dioxane in the opposite direction. To the cathode compartment (purified nitrogen atmosphere) were added 5 ml. of pre-electrolyzed solution and 1, 2, or 3 ml. (added in 1-ml. increments to give runs at three different concentrations) of hydrocarbon stock solution, made up by diluting 1 ml. of *ca.* $6 \times 10^{-2}M$ hydrocarbon in 75% dioxane to 10 ml. with pre-electrolyzed solution. The current i was obtained from the average of the minimum and maximum deflections of the damped galvanometer. Values of $E_{1/2}$ were corrected for iR drop ($R = 5000$ ohms) across the cell and generally were within 8 mv. of one another for the various runs on any one compound.

In one case (XVIII) where the polarogram showed some irregularities, i_d , the diffusion current, was ascertained as a function of the effective head of mercury and was consistent with expectations for a diffusion-controlled reduction process.²⁹ Unlike the cases reported by Wawzonek and Laitinen⁵ anthracene and substituted anthracenes showed no special irregularities in diffusion current constants or shapes of polarograms in our studies. Polarographic data are reported in Table I.

Coulometry. The electrolytic cell consisted of a 250-ml. pyrex beaker containing a magnetically stirred lower layer of mercury (cathode), an upper layer of 50 ml. of 75% dioxane containing 0.1M tetra-*n*-butylammonium iodide and (when desired) the reducible hydrocarbon, and an anode compartment (suspended in the electrolytic solution just above the cathode and bearing a horizontal circular silver plate anode) partitioned from the cathode compartment by means of a glass sieve holding a filter paper and a plug of glass wool. The glass sieve was prepared from a glass tube bearing a coarse sintered glass disk sealed flush with the lower end. Several holes were drilled completely through the glass disk in order to decrease internal resistance of the cell. The entire cell was sealed from contact with air by means of a tightly fitting closure plate and rubber stoppers bearing the necessary wires and tubes for operation. Purified nitrogen was passed through the apparatus continuously. The outlet tube of an external, saturated calomel electrode was inserted into the cell in close proximity to the upper

(27) We are indebted to Dr. W. B. Schaap of Indiana University for directions on the construction of a self-regenerating vanadous sulfate-perchloric acid column used in this purification.

(28) O. F. Steinbach and C. V. King, *Experiments in Physical Chemistry*, American Book Co., New York 1950, p. 175.

(29) I. M. Kolthoff and J. J. Lingane, *Polarography*, 2nd Ed., Interscience Publishers, New York, 1952, Vol. I, pp. 85–86.

surface of the mercury cathode. The potential difference between the S.C.E. and the cathode was measured by means of a potentiometer. A gas coulometer³⁰ and a milliammeter were placed in series with the electrolysis cell and a voltmeter was placed in parallel with it. The voltage across the cell was adjusted manually.

In operation the solvent-electrolyte mixture (without hydrocarbon) was pre-electrolyzed by allowing a current of 50 milliamp. to flow through the cell for 15 min. Then a potential difference of 20 v. was maintained across the cell until the cathode had attained the potential desired for the electroreduction. During this time a record of current *vs.* cathode potential was made. When the current had ceased to decrease with time (residual value 2-6 milliamp.), the

initial reading of the coulometer was noted, a sample of 1 ml. of standard 0.1-0.2*M* hydrocarbon substrate in 75% dioxane was added to the cathode compartment, and a timer was started. As the cathode potential immediately became more positive, the overall potential was again raised to 20 v. and the previous procedure of adjusting the voltage was repeated. When the current had reached a steady background value again (1-3 hr.) electrolysis was stopped. The total number of coulombs passed during the electrolysis proper (as calculated from the gas coulometric readings) was corrected for background current-flow (as based both on time of electrolysis and intervening cathode potentials). A sample of the electrolytic solution was withdrawn and tested for unsaturation by means of aqueous permanganate. Results are recorded in Table II.

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EUGENE, ORE.

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

Catalytic Oxidation of Hydrocarbons. Initiation by Ozone

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The isomeric xylenes are readily oxidized to the respective toluic acids with oxygen in acetic acid solvent at reflux temperature. The reaction is catalyzed by cobalt ion and initiated by ozone. *m*-Toluic acid and *p*-toluic acid are oxidized further at a slower rate to the corresponding dibasic acids. When *o*-toluic acid is oxidized the product, *o*-phthalic acid, chelates with cobalt ion and interferes with the chain initiation step, $\text{ROOH} + \text{Co(III)} \longrightarrow \text{ROO}\cdot + \text{Co(II)} + \text{H}^+$, inhibiting the reaction.

Ozone is a powerful oxidant and will oxidize silver (I) ions to silver(II) ions¹ in acid solution. We have found that the characteristic green color of cobalt(III) acetate appears when an ozone-oxygen stream is passed into cobalt(II) acetate solutions in acetic acid. We felt that a more efficient oxidation system might be obtained if the acetaldehyde-oxygen in the Hull oxidation² was replaced by ozone-oxygen. An oxidation of *p*-xylene in acetic acid at reflux temperature was effected by introducing oxygen containing *ca.* 2% ozone into the vigorously stirred system. The reaction rapidly attained the characteristic green color described in the Hull oxidation. However, the product of the reaction is principally terephthalic acid. Furthermore, the ozone can be stopped after the green color is attained and the reaction is self-sustaining, *i.e.* it continues without further addition of ozone. Toluene and some substituted toluenes are also oxidized to the corresponding carboxylic acids. If the water formed is removed continuously then phthalide can be oxidized to phthalic anhydride which does not interfere with the oxidation.

We found that *o*-xylene, unlike the other two isomers, cannot readily be oxidized to the dibasic acid. Initially, we felt that the *o*-phthalic acid formed might be degraded further. Subsequent in-

vestigation showed that *o*-phthalic acid was stable in the reaction mixture. However, when it was present in the reaction in an amount at least equivalent (moles) to the cobalt(II) ion the characteristic green color of cobalt(III) ion could not be obtained even when ozone-oxygen mixtures were passed through continuously. Furthermore, self-sustaining oxidations of any of the xylenes could not be obtained when it was present in appreciable amounts. As a consequence, an *o*-xylene oxidation can be initiated with ozone and the reaction which essentially proceeds stepwise will stop when most of the *o*-xylene is converted to *o*-toluic acid and an amount of phthalic acid equivalent to the cobalt ion in solution is formed. At this point the reaction mixture is no longer green but is the pink color characteristic of cobalt(II) acetate. If the initiator, ozone, is added continuously, more *o*-phthalic acid can be produced at a much reduced rate. The other xylenes are also oxidized to the corresponding dibasic acids in the presence of *o*-phthalic acid at a reduced rate if ozone is added continuously.

Since the intermediate toluic acids have dissociation constants of the same order of magnitude as the solvent acetic acid, they would be expected to have little effect on the catalyst. Isophthalic and terephthalic acids are relatively insoluble in the reaction mixture and also do not interfere with the catalyst. However, *o*-phthalic acid is not only the strongest acid present in the reaction mixture, but it can also form a chelate with cobalt(II) and co-

(1) A. A. Noyes, S. L. Hoard, and K. S. Pitzer, *J. Am. Chem. Soc.* **57**, 1221-9 (1935).

(2) D. C. Hull, U. S. Patent 2,673,217, March 23, 1954.