sentially the same. In effect, these assumptions preclude the A2 mechanism. For hydrolysis reactions of aliphatic acetals and ketals,[2] and ortho esters,[10] an overwhelming body of evidence excludes the A2 mechanism. It seems reasonable to conclude that acid-catalyzed hydrolysis reactions of acetals, ketals, and ortho esters rarely if ever occur by the A2 mechanism.

A possible exception to this generalization is the hydrolysis of 2-aryl-4,4,5,5-tetramethyl-1,3-dioxolanes.[3] Fife observed buffer catalysis of 2-(*p*-methoxyphenyl)-4,4,5,5-tetramethyl-1,3-dioxolane hydrolysis in formate buffers at 40°, and concluded on the basis of this and other data on hydrolyses of 2-aryl-4,4,5,5-tetramethyl-1,3-dioxolanes that these compounds hydrolyze by an A2 mechanism. We believe that the experimental evidence is too ambiguous to justify this conclusion.

First, the value of k_{D^+}/k_{H^+} for this reaction is 2.4, which is typical of SE2 reactions but considerably larger than the values of 1.3–1.7 characteristic of A2 reactions. Second, the slope of a plot of log k_{obsd} *vs.* log $C_{H_3O^+}$ for one of these 2-aryl-1,3-dioxolanes is 2.0, rather than approximately 1.0 as expected for an A2 reaction. A Bunnett plot of (log $k_{obsd} + H_0$) *vs.* log a_{H_2O} is strongly curved, with an average slope of +2. The curvature, together with the lack of knowledge of *w* values for established SE2 reactions, makes it inadvisable to interpret the average *w* value for this reaction. The entropy of activation for hydrolysis of 2-phenyl-4,4,5,-5-tetramethyl-1,3-dioxolane is −14 eu, which, although more negative than entropies of activation for 2-aryl-1,3-dioxolane hydrolyses[23] (which probably occur by an A1 mechanism), is substantially more positive than entropies of activation observed for authentic A2 reactions.[27] The surprisingly small reactivity of the 2-aryl-4,4,5,5-tetramethyl-1,3-dioxolanes relative to benzaldehyde ethylene ketals may be due either to diminished basicity of the conjugate acid (due to steric hindrance to hydration), or to steric hindrance to concerted attack by hydrated protons ($H_9O_4^+$) on dioxolane oxygen, or possibly even to reversible carbonium ion formation.[28] In summary, none of the evidence clearly requires an A2 mechanism for hydrolysis of these hindered dioxolanes, and much of it is more compatible with an SE2 mechanism.

Kinetic solvent isotope effects on SE2 reactions involving rate-limiting proton transfers from acids to oxygen may at first seem surprising, since they frequently lead to k_{D^+}/k_{H^+} values characteristic of secondary rather than primary solvent isotope effects.[29] It was noted above that orthocarboxylate hydrolysis typically has k_{D^+}/k_{H^+} values ranging from 2 to 2.7, and we observed $k_{D^+}/k_{H^+} = 2.6$ for hydrolysis of 2,2-diphenyl-1,3-dioxolane at 30°. If these reactions involve rate-limiting proton transfer from hydronium ion to the reactant, one might expect an important primary isotope effect.

The observed isotope effect arises, of course, from the effect of replacing protium oxide by deuterium oxide on the free energy difference between the reactants and the rate-limiting transition state. The observed large Brønsted catalysis law α values ($\alpha \simeq 0.7$) for ortho ester hydrolysis and the fact that water is much more basic than ortho esters or ketals both suggest that the proton is nearly completely transferred from hydronium ion to substrate oxygen in the transition state. The transition state structurally resembles the conjugate acid, and therefore has a large zero point vibrational energy due to strong hydrogen bonding to water. Since the rate-limiting transition state for the SE2 mechanism has the same composition as the rate-limiting transition state for the A1 mechanism, and differs from it only slightly in charge distribution, bond lengths, and hydrogen-bonded interactions with solvent, it is natural that the two mechanisms should exhibit similar kinetic solvent isotope effects. The fact that k_{D^+}/k_{H^+} is somewhat smaller for the SE2 reactions than for the A1 reactions is understandable, since the proton is completely transferred to substrate oxygen in the A1 transition state, and only mostly transferred in the SE2 transition state.

Registry No.—2,2-Diphenyl-1,3-dioxolane, 4359-34-6; 2,2-di(*p*-methoxyphenyl)-1,3-dioxolane, 19018-64-5; 2,2-di(*p*-tolyl)-1,3-dioxolane, 19018-65-6; 2,2-di(*p*-chlorophenyl)-1,3-dioxolane, 19018-66-7; benzophenone diethyl ketol, 6397-77-9.

Acknowledgment.—The authors are indebted to the Committee on Research, University of California at Santa Barbara, and to Biomedical Sciences Support Grant USPHS-FR-07099, for generous support of this research.

[27] F. A. Long, J. G. Pritchard, and F. E. Stafford, *J. Amer. Chem. Soc.* **79**, 2362 (1957).

[28] B. Capon and D. Thacker, *J. Chem. Soc., B,* 185 (1967).

[29] C. A. Bunton and V. J. Shiner, *J. Amer. Chem. Soc.*, **83**, 3207, 3214 (1961).

Substituent Effects in the Polarography of Aromatic Diazonium Salts

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Polarographic reduction of a number of substituted benzenediazonium tetrafluoroborates in the aprotic solvent, sulfolane, has been carried out. The most positive wave is a reversible one-electron step. The half-wave potential of this wave correlates well with Hammett σ values and is defined by the equation $E_{1/2} = 0.229\sigma + 0.314 \pm 0.024$ V.

The polarographic activity of diazotized aromatic amines was first reported by Elofson and Mecherly,[1] who used the facile reduction of diazonium salts at the dropping mercury electrode in a series of amperometric titrations of diazonium salts with coupling agents. In

[1] R. M. Elofson and P. A. Mecherly, *Anal. Chem.*, **21**, 565 (1949).

subsequent papers Elofson, *et al.*,[2] and Atkinson, *et al.*,[3] independently described the polarographic behavior of diazotized aromatic amines in aqueous solution. Both groups of workers found two waves, one at about -0.2 V *vs.* sce and independent of pH and one, a much larger wave, at more negative potentials and dependent on pH. The first group of workers concluded from the height of the over-all waves that four electrons were involved in the reduction—presumably to produce phenylhydrazines. However, coulometric analyses in the hands of Atkinson, *et al.*,[3,4] gave results corresponding to the consumption of two electrons. Later Kochi[5] undertook a brief study of the effect of substituents on the half-wave potential of the more positive wave. No consistent relationship could be demonstrated between the σ value of the substituents and the half-wave potentials as measured at pH 4 in aqueous media. Instead, as demonstrated by Zuman,[6] an apparently complicated and abnormal relationship existed between the Hammett σ constants of substituents and the half-wave potentials.

In 1958, Elofson[7] demonstrated that four electrons were required in the reduction and that the normal product of reduction at the dropping mercury electrode was indeed phenylhydrazine. Stirring of the electrode in the experiments of Atkinson, *et al.*, and of Kochi had introduced side reactions resulting in consumption of fewer electrons. Moreover it was demonstrated that the more positive wave in the polarography of diazonium salts in aqueous solutions, while due to a one-electron step, was influenced by adsorptive effects. This may have explained the failure of Kochi to observe normal substituent effects on the half-wave potential. In this paper we wish to report the results of a polarographic study of a considerable number of diazotized aromatic amines in tetramethylene sulfone (sulfolane) using tetrabutylammonium perchlorate as the supporting electrolyte. It will be demonstrated that a good correlation does indeed exist between the half-wave potential of the reversible one-electron reduction and σ values under these aprotic conditions. This and subsequent papers will demonstrate that the course of the reduction under aprotic conditions follows the course

$$\mathrm{ArN_2^+} + \mathrm{e} \longrightarrow \mathrm{ArN_2\cdot} \longrightarrow \mathrm{Ar\cdot} + \mathrm{N_2} \qquad (1)$$

of eq 1. Later papers will bear on the importance of this reduction in a number of reaction systems.

Experimental Section

The aromatic amines were diazotized by standard procedures in acidic aqueous media. Sodium tetrafluoroborate solutions were added to the reaction media and the resulting highly stable diazonium tetrafluoroborates were removed by filtration.[8] This material was dissolved in methanol and recrystallized by addition of cold ether. Sulfanilic acid and *p*-aminobenzoic acid were diazotized and precipitated as the zwitterion salts. Attempts to produce the tetrafluoroborates of the latter compounds were unsuccessful. Percentages of active materials in the resulting salts were established by coupling reactions with α-naphthol and by amperometric activity.[1]

Sulfolane "tetrahydrothiophene 1,1-dioxide" supplied by the Shell Development Corp., Emeryville, Calif., was fractionally distilled from sodium hydroxide under vacuum, bp 98° (0.1 mm), mp 28°.

Polarograms were run with a Leeds and Northrup electrochemograph, type E, using as anode a saturated calomel electrode connected through a porous glass bridge. Because of the high melting point of sulfolane, polarograms were run at 25° where the solutions were liquid, instead of at the more normal temperature of 0° for diazo studies. The value of m was 3.7 mg/sec. At 0.2 V in 0.1 M $(\mathrm{C_4H_9})_4\mathrm{NClO_4}$ in sulfolane the drop time was 2.51 sec.

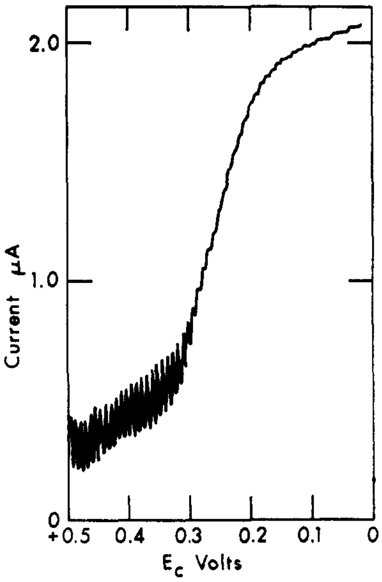

Figure 1.—Polarogram of first wave of *p*-methylbenzenediazonium tetrafluoroborate 9×10^{-4} M in sulfolane containing 0.1 M $(\mathrm{C_4H_9})_4\mathrm{NClO_4}$.

Results

Figure 1 presents a polarogram of the more positive reduction wave of *p*-methylbenzenediazonium fluoroborate, 9×10^{-4} M, in 0.1 M tetrabutylammonium perchlorate in sulfolane. This wave was shown to be diffusion controlled by the fact that the ratio of height at 80–40-cm pressure at 2.9×10^{-4}, 9.0×10^{-4}, and 2.3×10^{-3} M was 1.40, 1.40, and 1.38, respectively. Analysis of the wave shown in Figure 1 gave an inverse slope of 0.064 V (Figure 2), indicative of the usual one-electron reversible reduction found in aprotic solvents.[9] Comparison of the diffusion current with that of benzophenone under the same conditions also pointed to a one-electron reduction. The diffusion current of *p*-methylbenzenediazonium tetrafluoroborate was linear with concentration over the range 1×10^{-4} to 1.66×10^{-3} M with an I_d/C of 1.35 μA/mmol. Very similar I_d/C values were noted for the remainder of the compounds but no calibration curves were made. At concentrations in excess of 3.3×10^{-3} M, maxima in the waves occurred. No attempt was made to suppress maxima since they did not occur at the concentration of about 9.0×10^{-4} M which was used to determine the effect of substituents.

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(2) R. M. Elofson, R. L. Edsberg, and P. A. Mecherly, *J. Electrochem. Soc.*, **97**, 166 (1950).

(3) E. R. Atkinson, H. H. Warren, P. I. Abel, and R. E. Wing, *J. Amer. Chem. Soc.*, **72**, 915 (1950).

(4) E. R. Atkinson, C. E. Garland, and A. F. Buller, *ibid.*, **75**, 983 (1953).

(5) J. K. Kochi, *ibid.*, **77**, 3208 (1955).

(6) P. Zuman, "Substituent Effects in Organic Polarography," Plenum Press, New York, N. Y., 1967, p 98.

(7) R. M. Elofson, *Can. J. Chem.*, **36**, 1207 (1958).

(8) A. Roe in R. Adams, *et al.*, "Organic Reactions," John Wiley & Sons Inc., New York, N. Y., 1949, p 202.

(9) P. H. Given and M. E. Peover in I. S. Longmuir, "Advances in Polarography," Vol. III, Pergamon Press, New York, N. Y., 1960, p 948.

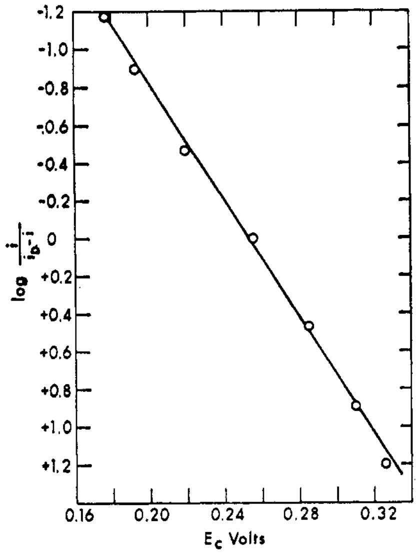

Figure 2.—Test of the equation of the wave of *p*-methylbenzenediazonium tetrafluoroborate (Figure 1).

All of the diazonium compounds examined showed this more positive reduction wave. Further reduction occurred at voltages approximating −0.5 to −1.0 V but it was erratic and varied greatly from compound to compound and with rate of flow of mercury and drop time. Maxima were common and, especially at low flow rates of mercury, desorption phenomena were observed at more negative potentials, resulting in no net additional current. Elucidation of the nature of these waves is not included in this paper and would not appear to be a profitable undertaking.

Table I presents the half-wave potentials of the diazotized aromatic amines used in this investigation together with the Hammett constants selected from Hine.[10] Since the diazonium group is the most powerful electron-withdrawing group listed it was felt justified to use σ^+ values[11] for the *para* substituents capable of resonance electron donation. In Figure 3 the half-wave potentials of *meta* and *para* derivatives have been plotted as a function of σ or σ^+ of the substituents. The equation of the best fit line becomes

TABLE I

THE HALF-WAVE POTENTIALS OF BENZENEDIAZONIUM SALTS IN SULFOLANE (9×10^{-4} *M* DIAZONIUM SALT IN 0.1 *M* TETRABUTYLAMMONIUM PERCHLORATE IN SULFOLANE)

Substituents	Compound no. (Figure 1)	σ value[a]	$E_{1/2}$ *vs.* sce
p-NO_2	1	+0.778	+0.450
p-CN	2	+0.660	+0.433
m-Cl	3	+0.373	+0.410
p-Cl	4	+0.114[b]	+0.350
o-Cl		+0.400[c]	+0.410
2,5-DiCl		+0.790[c]	+0.495
m-Br	5	+0.391	+0.429
p-Br	6	+0.150[b]	+0.383
p-I	7	+0.135[b]	+0.383
p-CO_2^-	8	0.000	+0.328
None	9	0	+0.295
p-SO_3^-	10	0.090	+0.297
m-CH_3	11	−0.069	+0.285
p-CH_3	12	−0.311[b]	+0.250
o-CH_3		−0.390[c]	+0.228
p-OCH_3	13	−0.778[b]	+0.140
o-OCH_3		−0.710[c]	+0.153
p-$N(CH_3)_2$	14	−1.70[b]	−0.095

[a] See ref 10. [b] σ^+ value used (see ref 11). [c] Calculated from Figure 3.

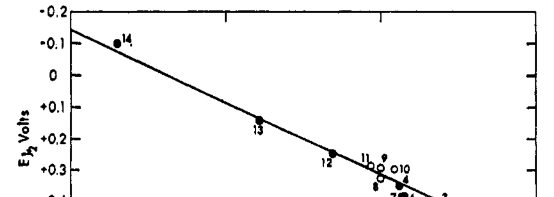

Figure 3.—Relation of half-wave potentials *vs.* sce for the reduction of substituted benzenediazonium salts in sulfolane to Hammett substituent constants: ○, σ constants used; ●, σ^+ constants used.

$$E_{1/2} = 0.229\sigma + 0.314 \pm 0.024 \text{ V} \tag{2}$$

Using this graph the values of σ for *o*-chloro, *o*-methoxy, and *o*-methyl become +0.38, −0.65, and −0.35, respectively. For 2,5-dichlorobenzene–diazonium chloride the σ constant is +0.740 indicating that the effect of two *o*-chloro substituents is nearly twice that of one.

Discussion

Unlike the results in aqueous media,[5] the effect of substituents on the half-wave potentials in sulfolane is distinctly normal. Electron-donating substituents make the half-wave potentials more negative while electron-attracting substituents make the diazonium cation easier to reduce. Since *o*-chloro and *o*-methoxy give more positive and *o*-methyl a more negative σ value than those for the corresponding *para* substituents, it is suggested that direct field effects rather than steric factors are responsible for these *ortho* effects. This conclusion is further supported by the fact that if Taft's value[12] for the polar substituent constant σ^* for *ortho* substituents is multiplied by Taft's constant 2.48 and inserted instead of the values deduced here, a reasonable correlation is still obtained. $E_{1/2}$ then agrees with eq 2 for *o*-chloro and *o*-methyl and deviates by only about 50 mV for the *o*-methoxy group. The validity of all these results is reinforced by the clear demonstration that these reduction waves are diffusion controlled and involve one-electron transfers. We assume from the work of Aten, Buthker and Hoijtink, but did not prove here, that the waves are reversible.[13]

The very positive values of the reduction potentials reported here are noteworthy. The values are much more positive than those determined in aqueous media. When acetonitrile was used as the aprotic solvent,

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(10) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., Chapter IV.

(11) H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4979 (1958).

(12) R. W. Taft in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., New York, N. Y., 1963, p 619.

(13) A. C. Aten, I. C. Buthker, and G. J. Hoijtink, *Trans. Faraday Soc.*, **55**, 324 (1959).

somewhat more negative half-wave potentials were obtained. The values are, in fact, indicative of considerable oxidizing power on the part of diazonium cations. The electrode reaction studied here apparently involves the reversible addition of an electron to the diazonium cation to produce a diazonium radical, eq 1, which may either be reduced further, reacts, or more often decomposes with the release of N_2 to produce a phenyl radical. The existence of the phenyl diazonium radical, $C_6H_5N_2\cdot$, is attested to by the composition of the tar $(C_6H_5N_2)_n$ found by Kochi.[5] It is also supported by the fact that phenylhydrazine is the normal product of polarographic reduction of diazonium compounds.[7] The ready decomposition of these diazonium radicals, when further reduction does not take place, to phenyl radicals will be the subject of the next paper in this series.

Registry No.—Tetrabutylammonium perchlorate, 1927-70-2; sulfolane, 77-79-2.

The Synthesis of Bilobanone

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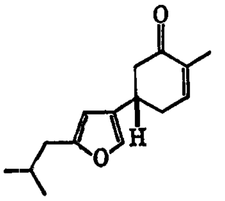
Received October 9, 1968

Oxidation of (+)-carvone with selenium dioxide in alcohol solution gave the optically active aldehyde **5**, the optically inactive tertiary alcohol **7**, and dehydrocarvacrol (**6**). The mechanism of oxidation is discussed. Condensation of the aldehyde **5** with the Grignard reagent from 3-methyl-1-butyne produced the secondary alcohol **16**. Oxotropic rearrangement to the primary alcohol **20** followed by mercuric ion catalyzed cyclization completed the synthesis of bilobanone (**1**). Two minor products, **22** and **23**, are formed concurrently and their origin is discussed.

Bilobanone, a constituent of the heartwood of *Ginko biloba* L., is a sesquiterpene with structure **1**.[1] It became of interest to evaluate bilobanone (**1**) as a potential raw material in perfumery and in this paper we describe its synthesis.



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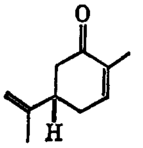
(+)-Carvone was an obvious starting material and selenium dioxide appeared to be a suitable reagent for introducing a functional group into the isopropenyl side chain. This oxidizing agent attacks the most nucleophilic double bond in polyolefins[2,3] and the rules of Guillemonat[4] predict the alcohol **13** to be the major product of oxidation. Our enthusiasm for this approach was temporarily dampened by reading a paper on the oxidation of carvone (**2**) with selenium dioxide to a mixture of the aldehyde **3** and the diosphenol **4**.[5] The structural arguments presented, however, were far from convincing and we decided to reinvestigate the reaction.



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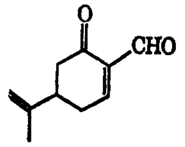

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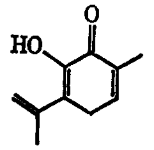

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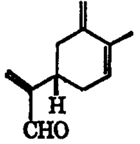
In our hands this oxidation gave a product mixture of which approximately 20% could be distilled under a high vacuum. Extraction of the volatile portion with aqueous sodium hydroxide followed by distillation of the nonacidic portion gave an optically active substance, mp 25–26° (6% yield), whose spectral properties (see Experimental Section) demand structure **5**. The base-soluble material consisted of essentially pure dehydrocarvacrol (**6**). Analysis of the volatile portion of a crude oxidation mixture by gas chromatography *prior* to extraction with aqueous sodium hydroxide revealed the presence of approximately 10% aldehyde **5**, only 8% phenol **6**, and 70% optically inactive hydroxy ketone **7**. Hence, the major volatile product formed in the oxidation of carvone (**2**) with selenium dioxide is not the primary alcohol **13** nor the corresponding aldehyde **5** but, contrary to the "rules",[4] the tertiary alcohol **7** which was indeed transformed to the phenol **6** by brief exposure to sodium hydroxide.



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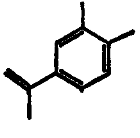

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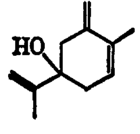

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The formation of the three products can be rationalized in terms of a mechanism proposed by Wiberg and Nielsen.[6] Addition of the conjugate acid of selenous acid to the isopropenyl group of carvone (**2**)

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[1] H. Irie, H. Kimura, N. Otani, K. Ueda, and S. Uyeo, *Chem. Comm.*, 678 (1967); H. Kimura, H. Irie, K. Ueda, and S. Uyeo, *Yakugaku Zasshi*, **88**, 562 (1968).

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[4] A. Guillemonat, *Ann. Chim.* (Paris), **11**, 143 (1939).

[5] K. K. Chakravarti and S. C. Bhattacharyya, *Perfum. Essent. Oil Rec.*, **46**, 341 (1955).

[6] K. B. Wiberg and S. D. Nielsen, *J. Org. Chem.*, **29**, 3353 (1964).