TABLE II

THE HYDROLYSIS OF PROPIONITRILE IN HYDROCHLORIC ACID SOLUTION

$T = 59.6°, (K)_0 = 2.53$

M_{HCl}	$\log \frac{a_{\mathrm{HCl}}}{a_{\mathrm{H_2O}}}$	$v_A/z + v_B/z$ hr.$^{-1}$		
		Obsd.	Calcd., $\beta = 0$	Calcd., $\beta = -0.1$
0.509	$\bar{1}.18$	0.00026	0.00026	0.00026
1.00	$\bar{1}.85$	.00058	.00061	.00060
2.00	0.72	.0015	.0017	.0017
4.00	1.97	.0067	.0083	.0080
4.55	2.29	.012	.013	.013
5.02	2.57	.017	.020	.020
6.48	3.42	.10	.096	.093
8.47	4.52	1.2	.95	1.0
10.13	5.43	8.3	6.8	8.0

to be −7105 cal., the same as for the corresponding reaction of aniline.[29] To obtain the constants b and $(k_9')_0$ in equation (23), necessary for the evaluation of k_9', reaction by Path B was assumed negligible in comparison to that by Path A for $M_{\mathrm{HCl}} \leq 2$. The ratio $a_{\mathrm{HCl}}/a_{\mathrm{H_2O}}$ was assumed to be the same at 59.6° as at 25°, for which temperature figures are given in the second column of the table.[30]

The values of the first-order constant in the fourth column of the table were obtained by taking β in equation (17) as zero, and $(k_{11})_0$ as 1.60×10^{-5} liter/mole/hour; those in the fifth column, by taking β as −0.100, and $(k_{11})_0$ as 1.23×10^{-5}. This very rough computation shows that in hydrochloric acid solution hydrolysis probably takes place by two paths, and that, in consequence, the parameters of the Arrhenius equation

$$k = k_{\mathrm{obs.}}/M_{\mathrm{acid}} = Ae^{-E/RT}$$

have no theoretical significance.

Acknowledgment.—The writer wishes to express her appreciation of stimulating discussions with Professors E. C. Wagner and Martin Kilpatrick.

Summary

A mechanism has been proposed to account for the fact that, of the strong acids, the halogen acids are least effective in hydrolyzing cyanamide, but are most effective in hydrolyzing the aliphatic nitriles. In the case of the nitriles, hydrolysis probably occurs by two paths in the solution of a halogen acid; the kinetic equations set up giving the rate of reaction by each path are supported by the experimental results of Rabinovitch, Winkler and Stewart on the hydrolysis of propionitrile. The mechanism is in harmony with the experimental results of Krieble and his co-workers.

PHILADELPHIA, PA. RECEIVED AUGUST 12, 1946

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[29] Pedersen, *Kgl. Dansk Videnskab. Selskab.*, **14**, No. 9, 3 (1937).

[30] "International Critical Tables," Vol. VII, p. 233.

[CONTRIBUTION FROM PULP MILLS RESEARCH PROJECT, UNIVERSITY OF WASHINGTON]

Oxidation Potentials of Some Compounds Related to Vanillin

BY D. M. RITTER

The ease with which phenols are oxidized to the corresponding free radicals can be considered a measure of how readily electrons are removed from a specific point in the molecule. The oxidation potential is related to the availability of electrons at that point, and thus to the general distribution of electron density throughout the molecule. Fieser[1] has demonstrated that, though the over-all oxidation of phenols is irreversible, the reaction occurs in steps of which one, the electron transfer, appears to be a reversible process. Certain groups were found to alter the ease with which electrons are removed from phenols. This property, shared by electron-attracting groups such as the nitro group, is a characteristic found not only in the phenols, but is also a property of substituents in compounds of the quinone–hydroquinone types which form reversible oxidation-reduction systems. Conversely, groups such as methoxyl, which repel electrons, lower the normal potentials and the related critical oxidation potentials (E_c) of phenolic substances.[2]

For several reasons determination of the critical oxidation potentials of guaiacyl derivatives should prove interesting. Vanillin and other *p*-hydroxyaldehydes undergo carbonyl addition reactions at retarded rates.[3,4] The similarly lowered reactivity of other guaiacyl derivatives may possibly be ascribed to the influence on the class B side chain reactions of electron-repulsion by the *p*-hydroxyl substituent. Vanillin was found to possess a higher potential (E_c = 1.080 v.) than guaiacol (E_c = 0.868 v.), indicating the displacement of electrons toward the side chain which should retard reaction with nucleophilic reagents. The extent to which electron donation by the hydroxyl group has occurred should be reflected in the oxidation potentials and these should thus furnish a means of predicting the side chain reactivity of other guaiacyl derivatives.

In addition to such considerations concerning side chain reactivity vanillin is only a fair antioxidant. ' Correlations between antioxidant efficiency and critical oxidation potentials for pro-

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[1] Fieser, THIS JOURNAL, **52**, 5204–5241 (1930).

[2] Fieser and Fieser, "Organic Chemistry," D. C. Heath and Company, Boston, 1944, p. 729.

[3] Vavon and Montheard, *Bull. soc. chim.*, **7**, 551, 560 (1940).

[4] Geissman, "Organic Reactions," vol. 2, John Wiley and Son, New York, N. Y., 1944, p. 94.

tection of rubber[5] and gasoline[6] show that this mediocrity is to be expected. With the view of preparing guaiacyl compounds with improved antioxidant action, it should be useful to have a knowledge of the effect on the critical oxidation potentials produced by variation of the atoms linked to the side chain.

In the course of this work several Schiff base-type compounds were prepared. Except that they were adapted to the study in progress, they depart little in general character from similar compounds previously synthesized from vanillin and a variety of aromatic amines.[7]

Experimental Part[8]

Preparation of Known Compounds.—Substances which have been reported previously were prepared as follows:

Vanillin, Eastman Kodak Co., m. p. 81–82° was used without further purification.

Vanillic acid was prepared by hydrolysis of vanillonitrile[9] and recrystallized from hot water, m. p. 207°.

Vanillonitrile was prepared by the hot concentrated hydrochloric acid hydrolysis of acetovanillonitrile and recrystallized from aqueous ethanol, m. p. 86–87°.

Vanillic acid *n*-butyl amido ester chloride and vanillic acid amide, m. p. 153–154°, were prepared from vanillonitrile as described in a previous communication.[10]

Vanillal aniline was prepared as described by Carre and Baranger.[7a] After recrystallization from chloroform the product melted at 155–156°.

Benzal aniline was prepared from aniline and benzaldehyde and recrystallized from petroleum ether and aqueous ethanol, m. p. 50.5–51.5°.

Vanillal *p*-Hydroxyaniline.—This compound was prepared by heating at the boiling point for thirty minutes a solution in 95% ethanol of *p*-aminophenol (10 g., 0.092 mole) and vanillin (14 g., 0.092 mole). The alcoholic solution was poured into 600 cc. of water. The oil which separated crystallized slowly to an orange-brown mass weighing 19 g., an 85% yield of crude product. Yellow-brown crystals were obtained from 95% ethanol, m. p. 200.5–202°.

Anal. Calcd. for $C_{14}H_{13}O_3N$: N, 5.76. Found: N, 5.63, 5.50.

Vanillal α-Naphthylamine.—α-Naphthylamine (10 g., 0.07 mole) and vanillin (10.6 g., 0.07 mole) were dissolved in 50 cc. of 95% ethanol and refluxed for three hours. Concentration of the solution gave a sirup soluble in benzene, chloroform and petroleum ether–ethanol mixtures, and immiscible with petroleum ether, but obtainable as crystals from none of the solvents. The oil was mixed with an excess of vanillin (1.0 g.) dissolved in 25 cc. of 95% ethanol. After evaporation of the solvent on the steam-bath the chloroform solution of the mixture was extracted with 10% sodium bisulfite solution. Slow addition of petroleum ether to the chloroform solution until cloudiness appeared gave a small amount of oil which was rejected. The chloroform solution was evaporated; the solid was dissolved in boiling benzene and petroleum ether was added slowly. Upon cooling pale yellow to tan crystals (9.0 g., 46% yield) were deposited, m. p. 107–108°.

Anal. Calcd. for $C_{18}H_{15}O_2N$: N, 5.05. Found: N, 5.17, 4.93.

Vanillal β-Naphthylamine.—β-Naphthylamine (10 g., 0.07 mole) and vanillin (10.6 g., 0.07 mole) were dissolved in 50 cc. of 95% ethanol and the solution was heated to boiling with reflux for three hours. The yellow crystals (17 g., 88% yield) obtained upon cooling the solution were recrystallized from a 40–100 mixture of chloroform–petroleum ether, m. p. 148–149°.

Anal. Calcd. for $C_{18}H_{15}O_2N$: N, 5.05. Found: N, 4.93.

Potential Measurements.—The critical oxidation potentials were determined by the method developed by Fieser[1] with a few convenient modifications.

The poising systems were potassium molybdo–molybdicyanide, potassium tungsto–tungsticyanide and potassium ferro–ferricyanide.

The solvent for the cells was the 36% ethanol sodium–potassium phosphate buffer solution recommended by Fieser. When 50 ml. of buffer solution was evaporated to dryness and made up to the same volume with water the *p*H was 7.03.

The hydrogen electrode potential in the buffer solution was found subject to drift caused by change in solvent composition. A saturated calomel half-cell was found much more manageable as a reference electrode. It was joined to the cell through an agar bridge made up in saturated potassium chloride solution. Potential values were corrected to the hydrogen half-cell reference state by adding to the observed potentials the value 0.702 v.[11]

The potassium molybdicyanide solutions were analyzed by electrometric titration with standard potassium ferrocyanide solution. The normal potentials calculated for the titration data proved so dependent upon concentration that the Mo^{IV}/Mo^{V} ratio could not be accurately determined by reference to the titration curve. Therefore, the molybdicyanide ion always present in potassium molybdicyanide solution was determined separately by electrometric titration in 1 *N* sulfuric acid solution using standard potassium permanganate. Daily determinations were made while the molybdicyanide reagent was in use.

The ferro–ferricyanide systems were adjusted to the desired potential by mixing appropriate quantities of standard potassium ferrocyanide and potassium ferricyanide solutions.

All measurements were made at 25.00° with the electrode vessels immersed in a water-bath held at constant temperature to within ±0.001°.

Many of the substances were studied at potentials where the poising systems are almost completely in the oxidized state. Since in those ranges small changes in redox ratio produce large changes in potential, the measurements were necessarily carried out with great care. Particularly, all sources of potential drift were eliminated, and measurements were made only after no drift was observed in the poising potential during a period comparable with the duration of a determination.

The normal potential E_0 of vanillal *p*-hydroxyaniline was estimated by application of Fieser's method of discontinuous electrometric titration.[12]

Results and Discussion

The critical oxidation potentials and the data from which they were determined are given in Table I, and in Table II the E_c values are collected for comparison.

Vanillin was studied to test the reproducibility to be expected, and the success of the method can be judged by the argreement between the result reported here and the value 1.080 v. found by

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(5) Doede, *Rubber Chem. Tech.*, **12**, 287 (1939).

(6) Lowry, Egloff, Morrell and Dryer, *Ind. Eng. Chem.*, **25**, 804 (1933).

(7) (a) Carre and Baranger, *Bull. soc. chim.*, **43**, 73–74 (1920); (b) Schlögel, *J. prakt. Chem.*, **88**, 215–216 (1913); (c) Wheeler, THIS JOURNAL, **35**, 976 (1913); (d) Raiford and Hilman, *ibid.*, **49**, 1571 (1927); (e) Hann, Jamieson and Reid, *ibid.*, **51**, 2586 (1929).

(8) All melting points are uncorrected.

(9) *Cf.* Raiford and Potter, THIS JOURNAL, **55**, 1682 (1933).

(10) D. M. Ritter, *ibid.*, **68**, 2738 (1946).

(11) The potential of the cell

$$\mathrm{Pt}\ |\ \mathrm{H_2}\ \left|\ \begin{array}{c}36\%\text{ ethanol phosphate}\\ \text{buffer } p\mathrm{H}\ 7.0\end{array}\ \right\|\ \begin{array}{c}\mathrm{KCl}\\ \text{satd.}\end{array}\ \left\|\ \begin{array}{c}\mathrm{Hg_2Cl_2},\text{ satd.}\\ \mathrm{KCl},\text{ satd.}\end{array}\ \right|\ \mathrm{Hg}$$

has been determined by electrometric titration of molybdicyanide solution to be 0.702 v.

(12) Fieser, THIS JOURNAL, **52**, 4915–4940 (1930).

Fieser. When estimating the accuracy of the data the fact should be noted that the E_c values for vanillin, vanillic acid amide, and vanillal *p*-hydroxyaniline occur at such potentials as to permit extrapolation to E_c over an extensive range of oxidation percentage. The reproducibility of E_c values for those compounds can be estimated as about ± 2 mv. The E_c values for the other compounds could be determined only by extrapolation over small degrees of oxidation. These values are estimated to be liable to uncertainties approximating ± 5 mv.

TABLE I

DATA FOR DETERMINATION OF CRITICAL OXIDATION POTENTIALS

Vanillin
Oxidant Mo

Volts	% oxid.
1.131	63.3
1.117	49.2
1.107	32.8
1.099	12.2
1.092	6.0
1.086	4.7

Cor. = -2.0 mv.
E_c = 1.082 v.

Vanillic acid amide
Oxidant Mo

Volts	% oxid.
1.131	35.7
1.109	16.6
1.104	14.5
1.095	8.1
1.091	5.8

Cor. = -2.7 mv.
E_c = 1.085 v.

Vanillal aniline
Oxidant W

Volts	% oxid.
0.989	3.1
.947	1.8
.930	1.3
.923	0.9

Cor. = -5.5 mv.
E_c = 0.892 v.

Vanillal
β-naphthylamine
Oxidant Fe

Volts	% oxid.
0.928	0.25
.910	.20
.898	.15
.876	.10
.858	.0

Cor. = -4.6 mv.
E_c = 0.858 v.

Vanillonitrile
Oxidant Mo

Volts	% oxid.
1.163	2.8
1.150	1.4
1.138	0.7
1.129	0.0

Cor. = -2.3 mv.
E_c = 1.133 v.

Vanillic acid *n*-butyl amido ester chloride
Oxidant Mo

Volts	% oxid.
1.178	2.0
1.175	1.8
1.172	1.2
1.168	0.2
1.148	.7
1.137	.2

Cor. = $+0.8$ mv.
E_c = 1.131 v.

Vanillal
p-hydroxyaniline
Oxidant Mo

Volts	% oxid.
0.797	30.6
.766	22.5
.740	10.8
.725	6.3

Cor. = -2.2 mv.
E_c = 0.707 v.

Vanillal
β-naphthylamine
Oxidant W

Volts	% oxid.
0.908	1.1
.872	0.3
.859	0.0

Cor. = -5.8 mv.
E_c = 0.858 v.

Vanillic acid
Oxidant Fe

Volts	% oxid.
0.913	1.9
.897	1.4
.887	0.9
.879	.6
.860	.0

Cor. = -1.2 mv.
E_c = 0.865 v.

Benzal aniline
Oxidant Mo

Volts	% oxid.
1.175	3.6
1.162	1.3
1.158	0.6
1.44	0.0

Cor. = -2.6 mv.
E_0 = 1.155 v.

Vanillal
α-naphthylamine
Oxidant Fe

Volts	% oxid.
0.973	1.4
.914	0.5
.901	.3
.888	.2
.878	.0

Cor. = -5.0 mv.
E_c = 0.879 v.

TABLE II

CRITICAL OXIDATION POTENTIALS

Compounds	E_c, v.	E_0, v. calcd.	ΔE_c, v.
Vanillin	1.082	1.218	+0.214
Vanillonitrile	1.133	1.269	+ .265
Vanillic acid	0.865	1.001	.000
Vanillic acid amide	1.085	1.221	+ .217
Vanillic acid *n*-butyl amido ester chloride	1.131	1.267	+ .263
Vanillal aniline	0.892	1.028	− .190[a]
Vanillal *p*-hydroxyaniline	.707	0.843	− .375[a]
Vanillal *α*-naphthylamine	.879	1.015	− .203[a]
Vanillal *β*-naphthylamine	.858	0.994	− .224[a]
Benzal aniline	1.155	1.291	

[a] Based on vanillin.

For the simple vanillin derivatives E_0 values can be calculated by adding Fieser's[1] empirical value of 136 mv. to the critical oxidation potentials. In these cases a single electron change is assumed. For the vanillal derivatives a more close scrutiny is required before the electron change upon oxidation can be arrived at. The E_c value for benzal aniline is so high as to suggest that the azomethine center is not oxidized at lower potentials.

Vanillal *p*-hydroxyaniline has a formal structural resemblance to *p,p'*-dihydroxystilbene and in the critical oxidation experiments it displayed properties suggesting the formation of a radical with a short but measureable half-life. Table III contains the data on the discontinuous titration of that compound in the neutral buffer solution using the S.C.E. as a reference. Beyond the mid-point of the titration, where the oxidant is in excess over the reductant, difficulty was experienced in reproducing the potentials. From the individual observed values the constant "C" was calculated from the equation

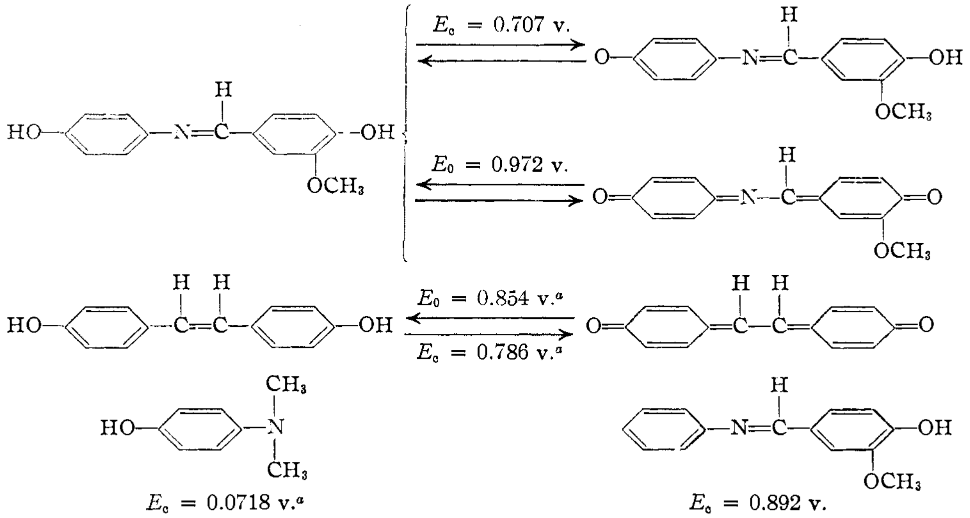
$$E - E_0 = 0.0295\, C \log \frac{O}{R} \tag{1}$$

The data were plotted to form a titration curve and with values taken from the curve at 0.025 milliequiv. intervals normal potentials were calculated. The average of eight values was 0.270 v. with deviations of 0.0016 v. average and 0.004 v. maximum. The agreement among the

TABLE III

DATA ON DISCONTINUOUS TITRATION OF VANILLAL *p*-HYDROXYANILINE REDUCTANT ADDED AS 5 ML. OF 0.03 *M* SOLUTION

Milliequiv. Mo^{V}	E_1 volts	E_2 volts	t, sec.	Decay constant sec.$^{-1}$ × 10^2	C
0.047	0.239	0.232	45	1.13	1.43
.048	.236	.228	50	1.17	1.60
.070	.244	.235	60	1.21	1.73
.072	.242	.233	60	1.21	1.90
.094	.253	.240	60	1.61	1.69
.118	.260	.248	60	1.59	1.80
.143	.267	.261	40	1.21	2.50
.167	.278	.256	60	1.53	2.70
.190	.285	.263	90	1.85	2.10
.244	.300				1.59
				Av. 1.52	1.74



[a] Values from Fieser.

Fig. 1—Comparison of vanillal *p*-hydroxyaniline and *p*,*p*′-dihydroxy stilbene oxidation.

decay constants calculated from the equation for a first order reaction is only fair. This is not surprising when the half-life is found to be about forty seconds. The complete reversible oxidation of vanillal *p*-hydroxyaniline is seen to involve a two-electron change and within the range of potentials from 0.240 v.–0.400 v. *vs.* S.C.E. the azomethine center is not oxidized. A difference between this situation and that found by Fieser for *p*,*p*′-dihydroxystilbene must be noted. The regularly occurring difference of 68 mv. between the normal and the critical potentials found for the hydroquinones is not characteristic of at least the Schiff base studied here. The difference between E_0 and E_c is 265 mv. The probable reason for this large difference is easily found. During the discontinuous titration measurements, those individual experiments where the ratio of reductant to oxidant was large (> 2.5) the decay curves were composite. The linear portion, which could be extrapolated to zero time to obtain the potentials in Table III, extended over a period of about fifty to one hundred seconds. After that the potential dropped precipitously during thirty to sixty seconds and finally became stabilized in another region of decay linear with the time. These lower values, which could be extrapolated only roughly, reached zero time at potentials near 0.07–0.12 v. *vs.* S.C.E. This suggests a single electron change with a normal potential in the region of 0.8 v. *vs.* the hydrogen half-cell; not far from the value of 0.843 obtained by adding Fieser's constant difference, 136 mv., to E_c for the vanillal *p*-hydroxyaniline derivative.

A comparison of the systems established by oxidation of vanillal *p*-hydroxyaniline and of *p*,*p*′-dihydroxystilbene is illustrated in Figure 1. The potential values shown there indicate that the phenolic group originating from *p*-aminophenol is the first group oxidized since the value for E_c = 0.707 v. is very close to E_c = 0.718 v. for *p*-dimethylaminophenol. Before the midpoint has been reached in oxidation to the free radical product formed between 0.71 and 0.84 v., oxidation to the quinone form has begun. The E_c value for the second step in the oxidation of vanillal *p*-hydroxyaniline is inaccessible experimentally. The value 0.836 v. can be calculated from E_0 = 0.972 v., based on vanillin ΔE_c = 0.246 v. Thus the hydroquinone–quinone-like structure in this azomethine appears less mobile than the stilbene system; its oxidation at low potentials occurs in steps, and the change observed when determining E_c involves a single electron. Fieser's constant difference can therefore be applied to two-electron changes only when the potential of the second oxidation step is lower than that of the first step, as is the case with the hydroquinones.

Berliner[13] has recently summarized the views on the relation between oxidation–reduction potentials of hydroquinone–quinone type compounds and their structure. Similar considerations of the proportionality between potentials and resonance energies doubtless apply to the phenolic compounds upon which these measurements were made, but the same opportunity is not available for testing the relationship with systems giving unstable oxidation states. Less quantitative comparisons, but ones closely connected with electron distribution and the reactivity of guaiacyl derivatives can be made with the data at hand. Taking guaiacol as the reference substance, groups which raise E_c can be considered to drain electrons from the ring. The carbon atom in the new substituent should have decreased electrophilic character and the rates of class B reactions should be retarded.

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[13] Berliner, THIS JOURNAL, **68**, 49 (1946).

In Table IV are compared the effects upon the critical oxidation potential produced by introduction of different substituents on the side chain carbon atom.

TABLE IV

EFFECT OF SIDE CHAIN SUBSTITUTION ON CRITICAL OXIDATION POTENTIAL

State of substitution in side chain	ΔE_c	State of substitution in side chain	ΔE_c
—CN	+0.308	—CH=N—R	+0.040
—COOH	+ .040	$—CH_2—CH=CH_2$	− .068[a]
$—CONH_2$	+ .260	$—CH=CH—CH_3$	.00[a]
$—C(OR)NH_2$	+ .306	$—CH_3$	.00[a]
—CHO	+ .255		

[a] Based on E_c values from Fieser.

Complete hydrogen substitution is taken as the reference point, creosol the reference compound. Only substitution of a vinyl group (isoeugenol) lowers the potential; substituents in all of the other compounds examined raise the E_c values. Comparison between the potential for vanillin and the rate data of Vanon and Montheard suggests, though by no means proves, that vanillonitrile, vanillic acid amide, vanillic acid esters[14] and vanillic acid amido ester salts should undergo class B reactions at retarded rates. Assuming the rate dependent steps in the reactions concerned to be attack by nucleophilic reagents, these increased potentials, indicating as they do a decreased electrophilic character for the side chain carbon atom, explain the failure to obtain vanillic acid amide by careful hydrolysis of vanillonitrile and by ammonolysis of methyl vanillate.[10]

Addition of an aromatic amine to the carbonyl group in vanillin lowers E_c sufficiently to place the values for the azomethines in the range of potentials requisite for antioxidant activity.

Absence of an effect by the carboxyl group in vanillic acid is worthy of note. The same group in 1-naphthol-2-carboxylic acid raises E_c 0.267 v. from the value for α-napthol,[1] while in anthroquinone 2-carboxylic acid the increase in E_0 caused by the carboxyl group is 0.067 v.[15]

Acknowledgment.—The author wishes to thank Dr. V. Sivertz and Dr. E. C. Lingafelter for loan of much of the equipment with which this investigation was carried out.

Summary

The critical oxidation potentials have been determined for several compounds derived from vanillin.

The normal oxidation-reduction potential of vanillal p-hydroxyaniline has been determined by discontinuous electrometric titration.

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[14] Vanillic acid esters were not examined but their potentials should be close to those for vanillic acid amide.

[15] Conant and Fieser, THIS JOURNAL, **46**, 1858 (1924).

SEATTLE 5, WASHINGTON RECEIVED JUNE 10, 1946

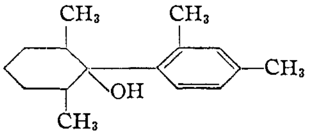
[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER AND OF THE CARNEGIE INSTITUTE OF TECHNOLOGY]

The Dehydration of a Hindered Tertiary Alcohol

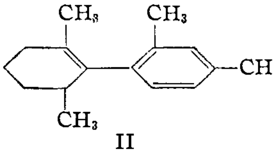
BY ROBERT B. CARLIN AND DOROTHY ANN CONSTANTINE

It has been reported[1] that 1-(2,4-dimethylphenyl)-2,6-dimethyl-1-cyclohexanol (I) is not dehydrated by the action either of potassium acid sulfate at 190–200° or of boiling acetic anhydride. It is the purpose of this paper to describe the conditions under which the dehydration has been successfully accomplished and to indicate some properties of the dehydration product.

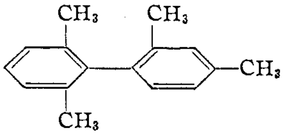
Dehydration was accomplished in 88% yield by heating I at 200–220° with anhydrous oxalic acid for one hour. The comparative resistance of I to dehydration was indicated by its stability toward anhydrous oxalic acid at 130°, a temperature at which Zelinsky and Zelikow[2] were able to bring about the dehydration of a number of open-chain and cyclic secondary and tertiary alcohols with the same reagent.



I



II



III

Although the composition of the product of dehydration of I is in accord with the structure 1-(2,4-dimethylphenyl)-2,6-dimethyl-1-cyclohexene (II), it was recognized that the action of oxalic acid at comparatively high temperatures on I might produce isomers of II. However, the occurrence of carbon skeleton rearrangements during the dehydration of I appeared unlikely in view of the fact that the product was dehydrogenated to 2,2′,4,6′-tetramethylbiphenyl (III) by the application of the same conditions under which I has been shown[1] to be directly converted to III. Had a rearrangement of the hydroaromatic

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[1] Carlin, THIS JOURNAL, **67**, 928 (1945).

[2] Zelinsky and Zelikow, *Ber.*, **34**, 3249 (1901).