poorly and much material was lost through sulfonation. Three grams of the pleiadenedione was quickly stirred into a solution of 160 cc. of concentrated sulfuric acid and 80 cc. of water preheated to 170°. The initially yellow-red solution soon turned brown and after three minutes it was poured into boiling water, and after boiling the mixture to coagulate the red precipitated material this was collected and washed; yield 0.9 g. The material was purified through the acetate which crystallizes from glacial acetic in cottony clusters of canary-yellow needles, m. p. 218–219°. This was hydrolyzed with alcoholic alkali giving, after dilution, an intensely blue solution of the sparingly soluble sodium salt from which the hydroxyquinone separated on acidification as a fiery red precipitate of hair-like micro-needles. From alcohol the substance crystallized as orange-red plates, m. p. 256–258°, dec. Treated with sodium hydrosulfite, the blue alkaline solution gives a transient red color and then an orange-yellow vat.

Anal. Calcd. for $C_{19}H_{12}O_3$: C, 79.14; H, 4.20. Found: C, 78.84; H, 4.66. Acetate, calcd. for $C_{21}H_{14}O_4$: C, 76.34; H, 4.27. Found: C, 76.42; H, 4.39.

Summary

By using 2-alkyl-3-hydroxy-1,4-naphthoquinones having reference groups in the aromatic ring it has been possible to prove that the substituents in the 2- and 3-positions exchange places in the course of the Hooker oxidation in exactly the manner predicted by the discoverer of the reaction. Hooker's view that the quinone ring is opened in the first step of the process has been substantiated by the isolation of products evidently arising from the type of intermediate postulated.

Converse Memorial Laboratory
Cambridge, Massachusetts Received April 16, 1936

[Contribution from the Chemical Laboratory of Harvard University]

The Electron Affinity of Free Radicals. X. A Potentiometric Method for Determining ΔF for the Addition of Sodium to an Organic Compound[1]

By H. E. Bent and N. B. Keevil

Most compounds containing sodium are very stable. A reaction leading to the formation of a compound involving the pure metal goes so nearly to completion that it is not possible to obtain an equilibrium constant from the concentration of unreacting material. Such reactions can be studied, however, with the aid of mercury.[2] Sodium forms compounds with mercury which are so stable that it is possible to remove sodium from other compounds by shaking them with mercury or a dilute amalgam. By choosing an amalgam of the proper concentration an equilibrium can be established favorable for analysis and the computation of an equilibrium constant. At equilibrium the reaction may be considered as a distribution experiment, the sodium in the mercury being in equilibrium with the sodium in the solution of the compound being studied. Since the thermodynamic properties of amalgams have been rather thoroughly studied, it is possible to calculate the free energy change which would have accompanied the reaction if solid sodium had been used.

The method is capable of quite general application but has certain disadvantages. In the first place the range of concentration of sodium amalgams which are liquid at room temperature is small. The increase in temperature necessary to extend the range of concentration appreciably would be so great as to decompose many organic compounds. The consequence of this rather narrow range of liquid amalgam is that only compounds which have a correspondingly narrow range of stability can be studied by this method. A second difficulty was encountered when studying reactions characterized by a large activation energy. Sometimes many months were required for the establishment of substantially equilibrium concentrations. The potentiometric method to be described seems likely to be free from these objections.

Both difficulties are inherently absent in a potentiometric method since a reaction does not need to proceed to the equilibrium point. The potential is a measure of the distance the system is from equilibrium and hence one might expect to be able to study with the aid of liquid amalgams reactions which would require solid amalgams by the analytical method. Furthermore, a reaction which proceeds very slowly might be expected to supply sufficient energy for a delicate electrical measurement while requiring years for substantial completion. Preliminary calculations indicated this to be the case.

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[1] Presented before the Division of Physical and Inorganic Chemistry at the 91st meeting of the American Chemical Society, Kansas City, Mo., April 13–17, 1936.

[2] Bent, This Journal, **52**, 1498 (1930).

The very delicacy of a potentiometric method, however, introduces new difficulties. The amounts of materials necessary to give a detectable e. m. f. are so small that traces of impurities are capable of producing side reactions which may be confused with the reaction being studied. Furthermore, the course of the reaction cannot be determined by an analysis of the products of the reaction. These difficulties may be overcome to a great extent by varying the concentrations of the substances involved in the reaction and noting the corresponding variation in the e. m. f. of the cell. As a further check on the reliability of the potentiometric method we have studied certain reactions by both methods. The compounds which have been studied in the greatest detail by the analytical method are organic free radicals. We have chosen three free radicals to study by the potentiometric method.

A cell is constructed in which the over-all reaction is the addition of sodium to an ethane to give two molecules of the sodium derivative of a free radical. These cells are constructed with one electrode of liquid sodium amalgam and the other of bright platinum. The electrolyte is an ether solution of the product of the reaction, that is, the sodium addition compound, NaR, R representing a free radical. The ethane is enclosed in a small glass capsule directly over the bright platinum electrode. When the cell has been brought to constant temperature in a thermostat and is ready for measurement the capsule is broken, thus saturating the electrolyte in the neighborhood of the platinum electrode with the ethane. A sintered Pyrex disk prevents the amalgam and solution in contact with the amalgam from coming in contact with the platinum. After some time the ethane diffuses through the ether to the amalgam but this is a process which is sufficiently slow to give no trouble. The over-all cell reaction may be considered as involving two primary reactions. At the amalgam electrode the reaction is $Na \longrightarrow Na^+ + \Theta$ while at the platinum electrode the reaction is $R_2 + 2\Theta \longrightarrow 2R^-$. These reactions are followed by the combination of the ions to form ion pairs.

An unexpected difficulty arose from certain fluctuating potentials which were observed before the capsule containing the free radical was broken. These potentials and the methods of eliminating them are discussed in the experimental section of the paper.

Materials

Details of the preparation of materials have been given in previous papers. The appropriate carbinol is first converted by hydrochloric acid into the chloride and this then converted either into the free radical or the sodium derivative of the free radical. All preparations were carried out in closed glass systems in the final stages. A slight improvement in technique has been developed. The sodium derivatives are prepared by shaking chloride with dilute sodium amalgam and then decanting the solution into a second tube and from there into small capsules, which are finally sealed off. In order to calculate the concentration of the resulting solution from the original amount of chloride introduced and the volume of ether it is necessary to avoid distillation during the final step of sealing off the capsules. In order to prevent decomposition of ether in contact with the hot glass it is also necessary to cool the capsules in liquid air or dry ice. This cooling may be accomplished quite readily without distillation by closing each tube leading to the capsule with a steel ball bearing which fits a seat previously ground in the glass by the same size ball bearing. These ball bearings may conveniently be moved around in the apparatus by means of a horseshoe magnet.

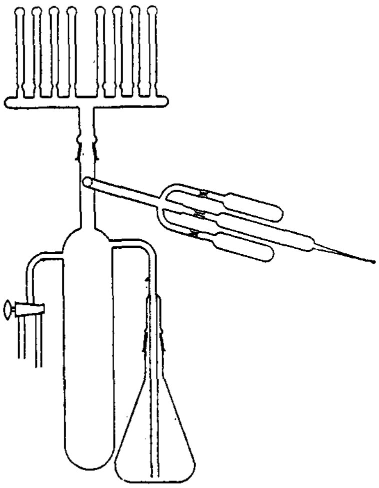

Fig. 1.

The apparatus shown in Fig. 1 was used in the preparation of the free radical. The operation of the apparatus is almost self-evident. The bulb containing the ring seal is used for the initial preparation of the free radical from the chloride and lead amalgam. By controlling the pressure, using nitrogen where necessary, the solution may be decanted over into the second tube without tipping or disturbing the precipitate of metallic chloride. This first tube may then be cleaned and refilled with suitable solvents for recrystallizing and washing, always flushing the tube with nitrogen. The capsules above the second tube are for three purposes. In two capsules solution saturated with free radical is removed for the purpose of determining the solubility and in another a sample is removed for determining the purity by oxygen absorption. After these samples have been removed the solvent is removed and the dry material loosened if necessary from the sides of the container by removing the ground joint and scraping with a steel wire, again using a counter stream of nitrogen. Finally the top of the apparatus is again attached and the solid free radical distributed between the small round-bottomed capsules. The ends of these capsules are sufficiently thin to allow crushing with a magnetic hammer in the final cell.

The apparatus for determining the purity of the free radical by oxygen absorption has been previously described.[3]

Experimental Procedure

The design of the cell was changed frequently in the course of the research. The last type to be used is illustrated in Fig. 2. A sintered glass disk[4] prevents rapid diffusion of the free radical from the platinum electrode to the amalgam where it would react. The disk also permits construction of a cell with relatively small resistance as the amalgam can flow against the disk without danger of passing through. It is important to have a notch filed in the top of the disk two or three millimeters in diameter in order to have a vapor connection between the two sides of the cell. If this is not done slight changes in temperature will cause surging of the liquid and consequent stirring.

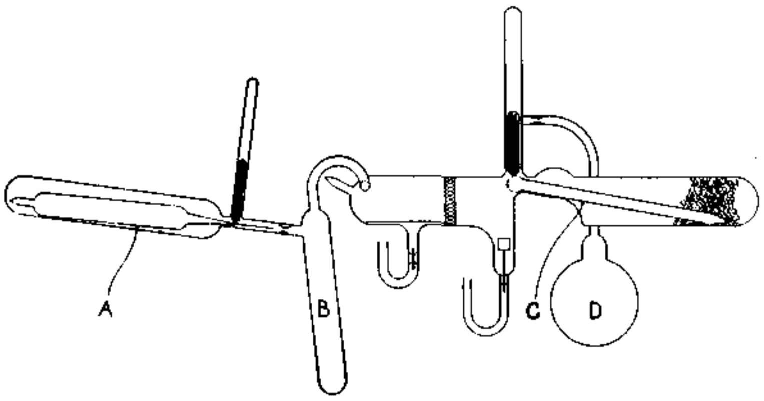

Fig. 2.

The sodium addition compound dissolved in ether, and free radical, are contained in capsules so arranged as to be broken by magnetic hammers. The cell is first baked and sparked as much as is possible without warming the organic materials. The amalgam is then introduced and then the electrolyte. The cell is placed in a thermostat and kept dark in order to avoid any possible effect of light on the free radical. Next tests are made for any potential which may be present before the capsule of the free radical is broken, and finally the free radical is introduced. A Wolf potentiometer reading directly to 10^{-5} v. was used with a L and N type HS galvanometer sensitive to 10^{-11} amp. The resistance of the cells was of the order of 10^6 ohms although in some of the earlier cells it was as high as 10^{12} ohms, thus making measurement difficult.

An unexpected difficulty was encountered in determining the potentials of the cells. The cells were found to possess a potential of the order of magnitude of 0.1 v. before the free radical had been introduced. This potential could not be eliminated and was difficult to explain. A great many experiments were performed to discover the cause of the potential but no theory was formulated which could account for all of the experiments. Assuming that the solution was not at equilibrium with the amalgam, cells were constructed which would allow further shaking of the solution and amalgam in the cell. This procedure altered the magnitude of the potential but did not eliminate it. A cell was constructed with gold, platinum and amalgam electrodes all in the same cell. No potential was obtained between two amalgam electrodes, and none between two platinum or between a gold and a platinum electrode. However, a very persistent potential was present between the gold or platinum and the amalgam electrode. This experiment seems to eliminate surface effects in the platinum as the sole cause of the potential as it would be improbable that the gold would behave in exactly the same manner. It seems very likely that the potential is due at least in part to the electrolyte as in some cells which had stood so long as to give very low potentials an addition of more electrolyte would give a larger voltage. This is rather hard to understand in the light of the fact that the reaction of amalgam with triphenylchloromethane is so rapid as to appear to be complete in ten or fifteen minutes. The cells had often been shaken for several days. The potential would persist for weeks in spite of all attempts to destroy it by short-circuiting the cell or even applying an external potential to the cell. After several weeks the value was usually reduced to a few millivolts. Under the circumstances the difficulty could be handled in two ways. In the first place it would be possible to wait until this initial e. m. f. had disappeared or become too small to be of importance. This would have involved a great delay in making measurements and introduced an additional uncertainty due to possible decomposition of the free radical. Furthermore it would seem entirely possible that the addition of the free radical might be a disturbing factor which would again give rise to the mysterious e. m. f. A better method seemed to be to assume that the mechanism giving rise to the initial e. m. f. involves such small amounts of material as to have but a very small capacity factor and that the addition of the large amount of free radical would mask completely any potential due to a side reaction. To test this assumption cells were constructed and measurements taken without delay when the initial e. m. f. was near its highest value. These cells seem to justify the assumption that the e. m. f. may be neglected.

Discussion of Results

The e. m. f. of a cell in which the over-all cell reaction is the addition of sodium to an ethane ($2Na + R_2 \longrightarrow 2NaR$) may be most conveniently considered in terms of the addition of sodium to the free radical ($Na + R \longrightarrow NaR$). The e. m. f. of the cell is then given by the equation

$$E = E_0 - \frac{RT}{nF} \ln \frac{(NaR)}{(Na)(R)} \qquad (1)$$

in which E_0 equals $(RT/nF) \ln K$ and "K" is the equilibrium constant for the reaction. The reason for treating the cell reaction in this fashion is that in earlier papers we have determined the free energy change accompanying the addition of sodium to various free radicals and from these

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[3] Bent, Gresham and Keevil, This Journal, **58**, 1307 (1936).

[4] Bruce and Bent, *ibid.*, **53**, 990 (1931).

TABLE I

EXPERIMENTAL CONCENTRATIONS AND VALUES OF E_0

Calculated from the equation $E = E_0 - \frac{RT}{nF} \ln \frac{(\text{NaR})}{(\text{Na})(\text{R})}$

Free radical	N of NaR in ether $\times 10^3$	N of R in satd. soln. in ether $\times 10^3$	N of Na in Hg $\times 10^2$	E_0, calcd. from E	E_0 calcd. from previous analyt. data	Spurious e. m. f.	
						Max.	Last values before run
Triphenylmethyl	1.11	0.519	0.903	0.999	1.01		
	1.11	.519	.903	.989			
	4.90	.519	.903	1.018		0.09	0.0078
	3.14	.519	.903	1.016		.065	.0070
	6.906	.519	5.04	1.015		.093	.0071
	5.71	.519	5.04	1.008		.064	.0011
	3.01	.519	5.04	1.011		.143	.01
	3.01	.519	5.04	1.001		.104	.079
Diphenyl-α-naphthyl	3.51	3.62	5.04	1.10	1.04	.070	− .014
	2.96	3.62	4.91	1.02		.085	− .012
Phenylbiphenyl-α-naphthyl	2.48	1.41	5.04	1.211	1.08	.195	.122
	1.04	1.41	5.04	1.038		.194	.145
		N of R_2 in satd. soln. in ether $\times 10^3$		E, exptl.			
Dibiphenylene diphenylethane	2.58	0.106	5.13	0.599		0.565	0.515
	2.57	.106	5.04	.602		.639	.524

data can calculate the value of E_0. The values of E_0 so calculated have been found to be remarkably constant. We may summarize the results by saying that in twenty cases in which a group attached to the central carbon has been changed the average of the effects on the free energy change for the reaction is about one kilogram calorie and the maximum effect is three. These substitutions involve groups which are aliphatic, aromatic, polynuclear and heterocyclic. The small differences observed in passing from one free radical to another may be predicted roughly from the series to which the compound belongs and the number of benzene rings in the compound. The average value for E_0 is 1.08 v.

We have determined the value of E_0 of equation (1) for triphenylmethyl, diphenyl-α-naphthylmethyl and phenyl-diphenyl-α-naphthylmethyl by the potentiometric method. The purpose of these experiments was to test the method and in particular to discover whether or not we are justified in ignoring the initial potential which was observed before the introduction of the free radical. The results of these experiments are reported in Table I.

The concentration of NaR is determined at both the beginning and the end of the experiment. The activity of the sodium referred to pure metal as the standard state is calculated from the concentration of the amalgam with the aid of the equation of Bent and Hildebrand.[5] The first two runs reported on hexaphenylethane are not considered as good as the latter runs due to the unusually high resistance of the cell. Some of the cells could be measured to hundredths of a millivolt but it is doubtful if the results are significant to more than a few millivolts. The average of the last four cells on hexaphenylethane is in very good agreement with the average of the analytical measurements previously reported and recorded in the third from the last column of the table.

The results for the next two compounds are much less satisfactory. These compounds have not been studied as thoroughly by either the analytical or potentiometric method so that agreement as good as in the case of hexaphenylethane is hardly to be expected. We have no explanation, however, for such a large discrepancy as is shown by the next to the last value recorded in the table.

Table I leads to the conclusion that the potentiometric method measures the free energy of addition of sodium to the compound being studied. The evidence is particularly good in the case of hexaphenylethane. The variation in concentration of sodium in the amalgam and also of the product of the reaction in solution result in the expected effect on the potential of the cell. The results of the potentiometric method agree with

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[5] Bent and Hildebrand, THIS JOURNAL, **49**, 3011 (1927).

the analytical results at least as well as the results by the first method agree with each other.

We hoped to study by the method just described compounds which react too slowly to be measured by a direct analytical method. In particular we wished to study ethanes which dissociate into free radicals to such a slight extent that the reaction cannot be detected by ordinary means. If one knows E_0 in equation (1), the activity of the sodium in the amalgam used as an electrode and the concentration of the product of the reaction, then one has a method of calculating the concentration of free radical from the observed e. m. f. This concentration would then allow one to calculate the equilibrium constant for the dissociation of the ethane into the free radical and hence the strength of the C–C bond, providing certain assumptions are made regarding ΔS for the reaction.

The compound chosen was dibiphenylene-diphenylethane. This compound was prepared and studied in exactly the same kind of cell discussed above. The extent to which the ethane is dissociated is not definitely known but it has been estimated that ΔF for the process is greater than 7 kcal. This would mean that the observed e. m. f. should be small on account of the small concentration of free radical present. To our surprise we obtained a much larger value. This can only mean that our original assumption that E_0 is the same for all free radicals breaks down in the case of the first compound to which we attempt to apply it. If we reverse our procedure and attempt to calculate E_0 by assuming ΔF for the dissociation of the free radical to be at least 7 kcal. we obtain a value of at least 1.5 v. This result makes it seem very unlikely that the extension of the potentiometric method to the calculating of the strength of C–C bonds in this manner can be justified. It also indicates that one must be very cautious in drawing conclusions from experiments using sodium amalgam or sodium potassium alloy to cleave organic compounds. Since the stability of the sodium compound can vary by as much as 0.4 v. (9 kcal.) the reaction cannot be considered solely in the light of the breaking of a C–C bond.

It is interesting to discover that the large difference between the value of E_0 for triphenylmethyl and dibiphenylene-diphenylethane is quite in harmony with the relative strength of the corresponding hydrogen compounds as acids.[6] The following equations indicate the close connection between these two reactions.

$$\begin{array}{rcll}
\mathrm{NaR} + \mathrm{HR'} & = & \mathrm{NaR'} + \mathrm{HR} & (1)\\
\mathrm{Na^+} + \mathrm{R^-} & = & \mathrm{NaR} & (2)\\
\mathrm{NaR'} & = & \mathrm{Na^+} + \mathrm{R'^-} & (3)\\
\mathrm{H} + \mathrm{R'^*} & = & \mathrm{HR'} & (4)\\
\mathrm{HR} & = & \mathrm{H} + \mathrm{R^*} & (5)\\
\hline
\mathrm{R^-} + \mathrm{R'^*} & = & \mathrm{R'^-} + \mathrm{R^*} & (6)\\
2\mathrm{Na} + \mathrm{R_2} & = & 2\mathrm{NaR} & (7)
\end{array}$$

In these equations R and R′ are taken to represent triphenylmethyl and biphenylenephenylmethyl. Reaction (1) represents the action of a weak acid on the salt of a still weaker acid. The fact that the reaction takes place indicates that HR′ is a stronger acid than HR. In order to discover the fundamental property of the molecule which determines its acid strength we have written equations (2) to (5). According to Kraus and Fuoss the dissociation constant of a salt in a given solvent of low dielectric constant is determined primarily by the size of the ion. Since the two anions under consideration each contain just three benzene rings it seems very probable that the value of ΔF for reactions (2) and (3) will cancel as they are written. We next make the very plausible assumption that the strength of the hydrogen–carbon bond is the same in these two molecules. This is implied when we write reactions (4) and (5) and assume that ΔF for these two reactions will cancel. The asterisk on the free radical implies that only the hydrogen bond has been broken and that the free radical so formed is not stabilized by resonance energy. The free radical under discussion is therefore purely hypothetical and is introduced for convenience in discussing the significance of the resonance energy. The sum of reactions (1) to (5) is given in equation (6). This equation shows that two factors are involved in determining the strength of an acid. The first of these is the destruction of the charge on one ion and the creation of a charge on the other, that is, the transfer of an electron. The second is the destruction of the resonance energy present in one ion and the creation of resonance energy in the other anion. These two factors are also involved in the addition of sodium to an ethane as illustrated by equation (7). If we consider NaR to be an ion pair[7] then the addition of sodium to an ethane involves the creation of a negative ion with its accompanying resonance energy. We therefore come to the conclusion that the ease with which

(6) Conant and Wheland, This Journal, **54**, 1212 (1932).

(7) Fuoss and Kraus, This Journal, **55**, 1019 (1933).

sodium will add to an ethane is determined not only by the strength of the carbon–carbon bond but also by those factors which determine the strength of the corresponding methane as an acid. According to McEwen[8] the difference in acid strength for these two methanes is about 16 kcal. The difference in the free energy of addition of sodium to the free radicals is found to be greater than 12 kcal. These results give a consistent explanation of the behavior of phenylfluorene as an acid and the stability of the sodium salt.

The results of the measurements on dibiphenylene-diphenylethane may be expressed in terms of the reaction $2Na + R_2 \longrightarrow 2NaR$ without any assumptions regarding the dissociation of the ethane into a free radical. ΔF so calculated is -61.9 kcal.

Summary

1. A potentiometric method is described for determining the free energy of addition of sodium to an organic compound.
2. An e. m. f. is reported which is not accounted for by accepted ideas of the nature of the compounds studied.
3. Dibiphenylene-diphenylethane is reported to have an abnormally large electron affinity which is directly related to the strength of phenylfluorene as an acid.

CAMBRIDGE, MASS. RECEIVED APRIL 29, 1936

[8] McEwen, THIS JOURNAL, 58, 1124 (1936).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Mesityl Phenyl Diketone

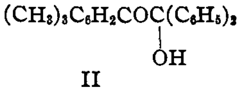
BY H. H. WEINSTOCK, JR., AND REYNOLD C. FUSON

Mesityl phenyl diketone (I) was selected for study because it appeared to afford an opportunity of determining the behavior of one of the carbonyl groups of an alpha diketone without interference from the other. It was supposed that the carbonyl group adjacent to the mesityl radical would be unaffected by most reagents, and that the diketone would, in fact, behave as a monoketone, in which, however, the carbonyl group would be unusually reactive. In general, this expectation has been supported by the experimental evidence; however, in certain reactions, both carbonyl groups seem to be directly involved.

The diketone behaves as a monoketone toward phenylmagnesium bromide, which converts it into the carbinol (II). Likewise the diketone gave a monoxime, a monosemicarbazone and a mono-2,4-dinitrophenylhydrazone. Also, it could not be induced to react with *o*-phenylenediamine. On the other hand, toward hydrogen peroxide the diketone behaves normally. Reduction with zinc and acetic acid gave a mixture of the two isomeric benzoins (III and IV).[1]

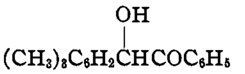
$(CH_3)_3C_6H_2COCOC_6H_5$

I



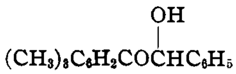
$(CH_3)_3C_6H_2CO\underset{\underset{OH}{|}}{C}(C_6H_5)_2$

II



$(CH_3)_3C_6H_2\overset{\overset{OH}{|}}{C}HCOC_6H_5$

III



$(CH_3)_3C_6H_2CO\overset{\overset{OH}{|}}{C}HC_6H_5$

IV

Vigorous reduction of the diketone yields the desoxybenzoin, V.

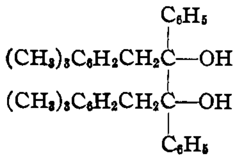
$(CH_3)_3C_6H_2CH_2COC_6H_5$

V

$(CH_3)_3C_6H_2COCH_2C_6H_5$

VI

This compound formed a phenylhydrazone and a dinitrophenylhydrazone, and with isopropylmagnesium bromide or ethylmagnesium bromide it was reduced to the pinacol (VII).



$$\begin{array}{l} \qquad\qquad\qquad\quad C_6H_5 \\ \qquad\qquad\qquad\quad | \\ (CH_3)_3C_6H_2CH_2C-OH \\ \qquad\qquad\qquad\quad | \\ (CH_3)_3C_6H_2CH_2C-OH \\ \qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\quad C_6H_5 \end{array}$$

VII

The structure of V was proved by synthesizing it from mesitylacetyl chloride and benzene. The isomeric desoxy compound (VI) is known. Both of these desoxybenzoins yield the benzil (I) when oxidized with selenium dioxide. Here it would appear that reduction had taken place preferentially at the hindered carbonyl group. However, the explanation is evidently not so simple as this, because when either of the benzoins (III and IV) is reduced the product is invariably V, no trace of VI being produced. This is especially

[1] Fuson, Weinstock and Ullyot, THIS JOURNAL, 57, 1803 (1935).