[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE INSTITUTE OF TECHNOLOGY OF THE UNIVERSITY OF MINNESOTA]

Ionization Constants of Isomeric Hydroxynaphthaldehydes. Structure of Naphthalene Nuclei

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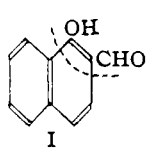
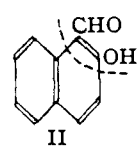
The problem concerning the stability of the double bonds in naphthalene derivatives gained renewed attention after the publication by Mills and Nixon[1] on hydrindene. Chemical investigations show a preference for the position of the double bond at C_{1-2},[2] but all of the physical evidence points to the existene of valence isomers which contain a double bond at C_{2-3}.

The ease with which polar effects are transmitted across a double bond has been treated theoretically by Sutton[3] and has been employed in a general form to explain the properties of apparently anomalous molecules with much success.[4]

Due to the pronounced increase in acidity of a hydroxyl group caused by a carbonyl group when the two are separated by a double bond, *i. e.* $\left(\begin{matrix}O\\ \|\\ -C-C=C-OH\end{matrix}\right)$, we chose a comparative study of the ionization constants of isomeric hydroxynaphthaldehydes. The compounds studied were



I



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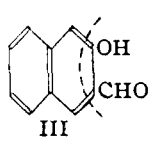
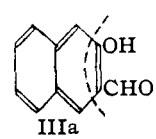


III



IIIa

Because of the vinylogous relation of structures I and II with formic acid, these compounds should be more acidic than that shown by III. The presence of a valence isomer IIIa would be indicated by an increase in the acidity of III over that of unsubstituted β-naphthol. This increase in acidity may be due in part to a dipole effect as observed with α-halogen acids. That the mutual effect of the groups due to their external distance from one another is not important was shown in the work of Bergmann and Hirshberg.[5] Any difference in acidity between I and II is dependent on the relative positions of these groups to the remainder of the molecule and not upon any difference in the type of bonding involved. The values found for these compounds are given in Table I.

TABLE I

Compound	Potential Satd. KCl – H_2(Pt)	P_K	(Temp. 25°) K
α-Naphthol	0.8960	11.00	0.1×10^{-10}
β-Naphthol	.8960	11.00	0.1×10^{-10}
2-Hydroxy-1-naphthaldehyde	.7344	8.27	53.7×10^{-10}
1-Hydroxy-2-naphthaldehyde	.7102	7.86	138.0×10^{-10}
3-Hydroxy-2-naphthaldehyde	.8325	9.93	1.175×10^{-10}

Discussion of Results

In order to have a basis for comparison, the K values for α-naphthol and β-naphthol were determined in the solvent used for the other measurements. It seems evident from the data given above that the large differences in acidity observed with C_{1-2} disubstituted derivatives as contrasted to C_{2-3} derivatives cannot be accounted for by a slight variation in the absolute distance between the groups and must depend largely on the type of linkage involved. That the ionization constants for the C_{1-2} and C_{2-1} compounds would not be identical was expected because of the small but definite difference which exists between the values for unsubstituted α- and β-naphthoic acids.[5] This difference points to the magnitude of the effect caused by the remainder of the molecule. That this factor is small as compared with that caused by the type of linkage between the two substituents is obvious from the following ratios

$$K_I/K_{II} = 2.56, \quad K_I/K_{III} = 117$$

The fact that we found no noticeable difference between α- and β-naphthols may be attributed to the difficulty of measuring pH values in this region.

Procedure

The pK values were determined by measuring the pH value of a solution of the aldehyde which

(1) Mills and Nixon, *J. Chem. Soc.*, 2510 (1930).

(2) Fieser and Lothrop, THIS JOURNAL, **57**, 1459 (1935); McLeish and Campbell, *J. Chem. Soc.*, 1103–1108 (1937).

(3) Sutton, *Proc. Roy. Soc.* (London), **A133**, 668 (1931).

(4) Fuson, *Chem. Rev.*, **16**, 1 (1935).

(5) Bergmann and Hirshberg, *J. Chem. Soc.*, 331 (1936).

had been half neutralized with standard sodium hydroxide and by making use of the following expressions

$$[H^+] = K[HA/A^-] = K$$
$$pH = -\log K$$

All of the samples were compared at a concentration of 0.05 M in ethanol–water mixtures (50% by weight). A standard arrangement of a saturated calomel cell and hydrogen electrode was used.[6] The pH values of the hydroxyaldehydes were checked repeatedly by a calibrated glass electrode to within 0.05 unit on freshly prepared solutions.

Experimental

2-Hydroxy-1-naphthaldehyde was prepared by the action of chloroform and sodium hydroxide on β-naphthol.[7] The material was purified by formation of the bisulfite addition compound followed by decomposition and recrystallization from ethyl alcohol; yield 70%, m. p. 81–82°.

3-Hydroxy-2-naphthaldehyde was obtained from purified 2-hydroxy-3-naphthoic acid[8] by conversion to the acetyl derivative, formation of the acid chloride, reduction with hydrogen and palladium followed by saponification with dilute sodium hydroxide. The aldehyde after decomposition of the bisulfite addition product was recrystallized several times from ethanol and melted at 98–98.5°.

1-Hydroxy-2-naphthoic acid was prepared by a modification of Eller's method.[9] Sixty grams of α-naphthol was treated with the calculated quantity of sodium hydroxide and evaporated to complete dryness. The sodium salt was pulverized and immediately placed in a chilled bomb of one-liter capacity with a large excess of dry ice. The pressure of the closed bomb on standing rose to 450–500 lb./sq. in. (30–36 atm.). The temperature was raised slowly and at 130–135° the absorption of carbon dioxide was extremely rapid. Within an hour the pressure fell almost to zero. The contents of the bomb after cooling was added to a liter of water containing 75 g. of sodium carbonate and finally filtered. Careful acidification with hydrochloric acid yielded 72 g. or 92% of the desired acid which melted at 189–190°. Recrystallization raised the melting point to 190–191°.

1-Hydroxy-2-naphthaldehyde was prepared by the reduction of the corresponding acid with 3% sodium amalgam[10] in the presence of boric acid and sodium bisulfite. After decomposition of the solution with sulfuric acid the material was steam distilled and recrystallized from ethanol, m. p. 55°.[11]

Summary

The ionization constants of three isomeric hydroxynaphthaldehydes have been compared. These values indicate that the double bond in these naphthalene derivatives is largely between C_1 and C_2.

The acidity of the C_{2-3} disubstituted compound is attributed to valence isomers which contain a double bond between C_2 and C_3 thus giving rise to a vinylogous relation with formic acid.

These results are in full agreement with other physical measurements and quantum mechanical considerations.[12]

(6) Davies, "Fundamentals of Physical Chemistry," P. Blakiston Sons and Co., 1932, p. 229.
(7) Fosse, *Bull. soc. chim.*, [3] **25**, 371 (1901).
(8) Boehm and Profft, *Arch. Pharm.*, **269**, 25 (1931).
(9) Eller, *Ann.*, **152**, 277 (1868).
(10) Weil and Ostermeier, *Ber.*, **54**, 3217 (1921).
(11) Boedecker and Volk, *Chem. Zentr.*, **107**, I, 883 (1936).
(12) Robertson, *J. Chem. Soc.*, 131 (1938).

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The Alkylation of Oxymethylene Desoxybenzoin

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Oxymethylene ketones on treatment with an alcohol and hydrochloric acid have been reported either to yield an enol ether or to undergo hydrolysis with regeneration of the parent ketone from which the oxymethylene compound was prepared. Ether formation has been reported for oxymethylene camphor[1] and oxymethylene desoxybenzoin,[2] while oxymethylene acetone, acetophenone and menthone undergo hydrolysis[1] (pp. 385, 386). Quite recently, in the acid cleavage of a heterocyclic compound whose structure is not pertinent to the present discussion, we obtained a product which could only be formulated as the dimethylacetal of phenylbenzoylacetaldehyde (I, R = CH_3)—the acetal, that is, of the ketonic tautomer of oxymethylene desoxybenzoin. We were able to establish the structure of the acetal by synthesizing it, using the general method of acetal synthesis, from oxymethylene desoxybenzoin and methyl alcohol in the presence of hydrochloric acid. Similarly the ethyl and benzyl acetals (I, R = C_2H_5 and $CH_2C_6H_5$) were prepared from the corresponding alcohols. This selective acetal synthesis was in such striking contrast to all pre-

(1) Bishop, Claisen and Sinclair, *Ann.*, **281**, 366, 383 (1894).
(2) (a) Jörissen, Dissertation, Basel, 1893; (b) Wislicenus and Ruthing, *Ann.*, **379**, 253 (1911).