

those found for other free radicals and interpreted in terms of resonance energy.

3. A complete description of the method used for preparing pentaphenylethyl, together with

the technique developed in this Laboratory for preparing and handling materials out of contact with air, is given.

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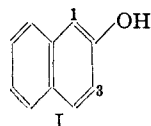
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Structure of Naphthalene

BY LOUIS F. FIESER AND WARREN C. LOTHROP

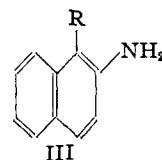
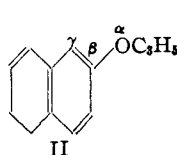
In 1893 Marckwald¹ called attention to the remarkable difference between the two positions ortho to the functional group of β -naphthol or β -naphthylamine, and he interpreted the difference in terms of Erlenmeyer's symmetrical formula for naphthalene. According to this formula (I)



the ortho carbon atom at C_1 is joined to the atom carrying the functional group by a double linkage while the connection to C_3 is by means of a single bond. If these positions represent a fixed condition of the bonds, Marckwald argued, the differences between C_1 and C_3 are easily understandable. As applied to the bond structure of the substituted ring of β -naphthol, this argument has never been contested, and indeed many facts have accumulated in support of the view that there is a double bond at C_1-C_2 and a single bond at C_2-C_3 .

One line of evidence is from the coupling reaction, or rather from its failure in certain specific cases. β -Naphthol couples at C_1 , but if this position is blocked by a stable group (alkyl) no coupling with diazotized amines occurs, while a less stable group (carboxyl, halogen) is displaced by the reagent. In no case is the other ortho position attacked. The failure to react cannot be ascribed to the lower degree of reactivity of the β -position of naphthalene as compared with the α -position, for a 1-naphthol substituted at C_4 couples easily in the β -position, C_2 . It is not merely a difference in the degree of reactivity which is involved, but a difference in kind. The exact interpretation depends upon the mechanism assumed for the coupling reaction, but the same conclusion is reached in any case. Whether a diazotized amine adds to the enol double bond of β -naphthol or to the conjugated system of which the unsaturated oxygen atom forms a part, or whether a diazo ether or an ox-

onium salt forms and rearranges, a double bond is involved in one way or another and the course of the reaction in one case and its failure in the other serves to locate the position of unsaturation at C_1-C_2 . The conversion of β -naphthol allyl ether (II) into 1-allyl-2-naphthol by heating



clearly is a true molecular rearrangement, and it conforms to the same rules, a substituent at C_1 effectively preventing the rearrangement.² Considering the reaction as a simple α, γ -shift, it may be said that the failure of the 1-substituted ether to rearrange shows that the carbon atom at C_3 does not and cannot form the end of an α, γ -system and hence that there is no double bond between C_2 and C_3 . The Skraup reaction may involve still another kind of substitution, but it shows the same peculiarity. While β -naphthylamine forms a hetero ring extending to the 1-position, substances of the type of III are reluctant to form naphthoquinolines.^{1,2a}

Further evidence of a fixed bond structure in at least a part of the naphthalene molecule is furnished by reactions involving the replacement or modification of a functional group rather than a nuclear substitution. According to the theory suggested by Henry³ and extended by Wegscheider,⁴ the etherification of β -naphthol with alcohol and a mineral acid probably involves an addition

product which loses water. The

(2) Claisen, *Ber.*, **45**, 3157 (1912).

(2a) Fries, *Ann.*, **516**, 285, footnote (1935).

(3) Henry, *Ber.*, **10**, 2041 (1877).

(4) Wegscheider, *Monatsh.*, **16**, 140 (1895).

(1) Marckwald, *Ann.*, **274**, 331 (1893); **279**, 1 (1894).

work of Woroshtzow⁵ points to this type of structure for the bisulfite addition product isolated by Bucherer.⁶ Whether or not the formulation represents the precise mechanism, some such participation of the double bond hardly can be questioned. Davis'⁷ observation that the etherification is almost completely stopped by the introduction of a halogen atom or a nitro group at C₁ is in good agreement with this view, for it is understandable that the blocking group should hinder an addition to the double bond to which it is attached. It might be argued that an ortho group at C₁ retards the reaction simply because of its proximity in space to the hydroxyl, but the following extension of Davis' observations shows that this objection cannot be sustained. It will be seen from the results given in Table I that alkyl groups, like halogen and nitro groups, block the etherification when located at C₁. If this were an ordinary ortho effect depending upon the steric factor, an ortho alkyl group at C₃ would act in the same way, but instead of hindering the etherification a methyl group at C₃ actually promotes the reaction. Since a methyl group has a similar influence even when it is located in the adjoining nucleus at C₆,

TABLE I
METHYLATION OF DERIVATIVES OF β -NAPHTHOL AT 100°
(SEVENTEEN HOURS)

Proportions: 2 g. of the naphthol, 10 cc. of a solution of 3 g. of *p*-toluenesulfonic acid (m. p. 104°) in 180 cc. of methyl alcohol.

Substituents	Total recovery, %	% of total etherified
None	100	51
1-Ethyl	100	0
1-Benzyl	96	0
6-Methyl	95	74
3,7-Dimethyl	96	94
1-Chloro	91	2
6-Bromo	99	26
1,6-Dibromo	93	2
3,6-Dibromo	95	11

it may be concluded that this type of ortho-para directing group, except when it is at C₁, renders the nucleus more susceptible to the formation of the intermediate adduct. A halogen atom at C₃ impedes the etherification, but the effect is largely a chemical, rather than a stereochemical, one, since halogen at C₆ exerts a similar influence. The effect of this type of group is consistent with the fact that halogen atoms retard rather than promote ordinary aromatic substitutions. It

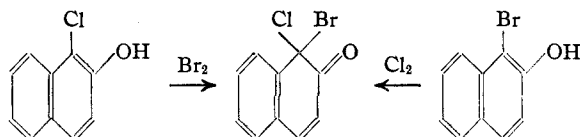
(5) Woroshtzow, *Bull. soc. chim.*, [4] **35**, 996 (1924).

(6) Bucherer, *J. prakt. Chem.*, **69**, 49 (1904).

(7) Davis, *J. Chem. Soc.*, **77**, 33 (1900).

may be concluded that the blocking of the etherification is not a case of ordinary steric hindrance, for it occurs only when the group in question is situated at one of the two ortho positions. This set of facts again points to the presence of a double linkage at C₁-C₂ and to the absence of such a seat of unsaturation at C₂-C₃.

In all these cases the naphthalene compounds stand in marked contrast to the corresponding derivatives of benzene. A para alkyl phenol with two free ortho positions is substituted first at one of these positions and then at the other. If the first reaction in some way involves an enol double bond, then it is evident that the second substitution is preceded by the migration of the double bonds in such a way as to provide an enol grouping suitable for this reaction. Positive evidence that the double bonds of naphthalene are not free to migrate in this manner is furnished by the extensive series of observations initiated by Zincke and extended by Fries⁸ on the halogenation of naphthols and naphthylamines. 1-Chloro (or bromo)-2-naphthol on halogenation does not form the 1,3-dihalo compound, as would be expected if the naphthol behaved like a phenol, but reacts to form a keto halogenide, for example



The halogen, finding no double bond extending to the free position ortho to the directing group, reacts with the —CX=C(OH)— system even though this is less amenable to reaction than the system —C(OH)=CH— would be if it were available.⁹

An entirely different method of probing for unsaturated centers has been developed by Mills and Smith.¹⁰ The location of the —CH=N— bond of the isoquinoline nucleus was established by noting its activating influence on a methyl group at C₁, and the absence of such an influence on a methyl group at C₃.

The extensive and varied evidence leaves little ground for questioning the statement that the two ortho positions of β -naphthol differ in kind. The only rational interpretation that has been given of this striking fact is in terms of a

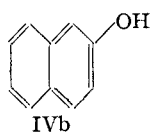
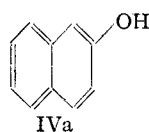
(8) See, for example: Zincke, *Ber.*, **21**, 3378, 3540 (1888); Fries and co-workers, *ibid.*, **39**, 435 (1906); **41**, 2614 (1908); *Ann.*, **484**, 245 (1930).

(9) Fries, *ibid.*, **454**, 121 (1927).

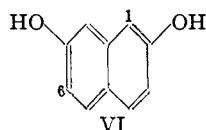
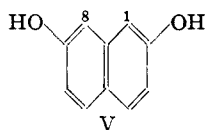
(10) Mills and Smith, *J. Chem. Soc.*, **121**, 2724 (1922).

Kekulé bond-structure for naphthalene in which double and single bonds are fixed in the α,β - and the β,β -positions, respectively. This is a convincing argument in favor of the Kekulé theory of aromatic structure, for the reactions and properties just discussed would be meaningless from the point of view of those other formulas which indicate that the β -carbon atoms of naphthalene are joined to both ortho positions by the same kind of linkages. The Baeyer-Armstrong formula for benzene, Thiele's second formula, the centric electron formula, and the electron-triplet formula all appear incapable of application to naphthalene and hence inadequate.

The establishment of the positions of the unsaturated centers in one part of the naphthalene molecule of course does not settle the problem of the complete bond structure. The facts cited may be explained on the basis of either the symmetrical (I) or the unsymmetrical structure (IVa), although in the latter case some additional assumption must be made regarding the failure of the substance to exist in the other possible form IVb. An indication of the bond structure of both



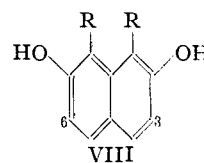
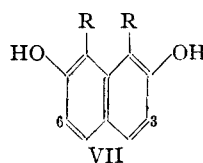
rings should be furnished by the behavior of 2,6- or 2,7-dihydroxynaphthalene. If the latter compound has the symmetrical structure V, it should



be attacked by substituting agents at the two enolic ortho positions C_1 and C_8 , but if the structure is unsymmetrical, as in VI, the disubstitution might be expected to occur at C_1 and C_6 . Actually, coupling occurs at the 1 and 8 positions,¹¹ but this provides no proof of the structure V for it is possible to reconcile formula VI with the observation. It may be supposed that the first substituent enters at C_1 and that the bonds shift to the alternate unsymmetrical arrangement and provide an enol group at C_8 for the entrance of the next azo group.

There is, however, an unequivocal method of settling the matter. If the 1,8-dialkyl derivative

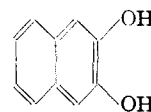
of 2,7-dihydroxynaphthalene has the structure of VII, it should be incapable of ortho substitution, whether direct or indirect, in the free positions 3 and 6. If the substance exists in the form of VIII, or if it can tautomerize to this form with



an available enolic ortho position at C_6 , such substitution should be possible. Compounds of this type, as well as various 1,5-dialkyl-2,6-dihydroxynaphthalenes, have been prepared and their reactions investigated and in every case the tests were negative. These naphthols do not couple, even with particularly active diazo components, and their allyl ethers do not rearrange. According to this evidence the unsymmetrical structure is eliminated as a basis for accounting for the reactions of the naphthols, and hence, by entirely reasonable inference, for naphthalene itself. Naphthalene must have the symmetrical structure first suggested by Erlenmeyer; the bonds occupy fixed positions and are not free to migrate.

There is one other piece of chemical evidence which has reference to the bond structure as a whole, namely, the failure of 2,3-dihydroxynaphthalene to yield a quinone on oxidation. The observation was cited first by Marckwald,¹ and it has been demonstrated in recent years both by chemical¹² and by electrochemical¹³ evidence that this is not due to the lack of stability of the hypothetical 2,3-quinone, for it is never produced, but rather to the formation as a primary oxidation product of a univalent-oxygen free radical. The two hydroxyls function independently and not, as when the carbon atoms holding such groups are connected by means of a double bond, as a unit. The compound does not appear capable of existing in the unsymmetrical form:

Finally Kohlrausch¹⁴ has reported that the unsymmetrical formula for naphthalene is inconsistent with the Raman and infra-red spectra of the hydrocarbon. The data do not, like the chemical evidence, distinguish between the various symmetrical formulas, but the results are entirely consistent with the particular form of symmetri-



(11) Ruggli and Courtin, *Helv. Chim. Acta*, **15**, 110 (1932).

(12) Fries and Schimmelschmidt, *Ber.*, **65**, 1502 (1932).

(13) Fieser, *This Journal*, **52**, 5219 (1930).

(14) Kohlrausch, *Ber.*, **68**, 893 (1935).

cal formula which is indicated by the chemical observations.

The conclusion reached in this review and extension of earlier work is that naphthalene differs from benzene only in the matter of the mobility of the bonds and in the degree of reactivity or unsaturation. The first difference is an important one, and one which in the past has received too little attention. Thus Pauling and Wheland's¹⁵ calculation of the resonance energy of naphthalene appears to assume a mobility of the bond structure comparable with that of benzene. As for the reason for the fixed condition of the double bonds, Fries has made the plausible suggestion that naphthalene has little tendency to exist in the unsymmetrical form because one of the rings would have to depart from the aromatic condition and become dihydride, or quinonoid, in character. In the Erlenmeyer formula neither ring is an entirely true benzenoid nucleus because the central bond is shared between the two rings and conjugated in two different directions, but each approaches as nearly as possible the stable condition of an isolated benzene ring. The tendency to approach this stable condition, which is perhaps the most important feature characteristic of all aromatic rings, results in naphthalene in the suppression of oscillation.¹⁶ Because of this restriction, possibly because of the valence claim from two directions made on the double bond shared between the rings,¹⁶ the two nuclei are less aromatic and more unsaturated than true benzene rings.

As for the enhanced reactivity of the α -positions of naphthalene, attention may be called to an interesting comparison with the diphenyl polyenes.¹⁷ With these substances the reactive positions are at the two ends of the conjugated aliphatic system terminating in benzene rings.



In naphthalene the 1,4 conjugated system of ring B is similarly anchored at the two ends, in this case into the same benzene nucleus (A). The 1,4-reduction of naphthalene and of diphenylbutadiene by similar agents appear to be entirely

comparable reactions and possibly the same factors determine the reactivity in each case.

Experimental Part

For purposes of the tests it was necessary to prepare and to establish the structures of certain dialkyl derivatives of 2,6- or 2,7-dihydroxynaphthalene, for such substances have not been reported previously. Various methods were found for the introduction of alkyl groups, but difficulties were encountered in attempting to prove the structures by degradative methods. The problem was solved, at least in the case of one compound of the 2,7-series, by the synthesis of a substance of the desired structure. In the case of the other compounds the structures can be inferred with a reasonable degree of confidence from the preparative methods, and, since their behavior in the test reactions was identical with that of the 1,8-dialkyl-2,7-dihydroxynaphthalene of proven structure, the formulas assigned can be regarded as completely established. The methods of preparation require only brief comment and the properties of the compounds are summarized in Table II.

For the preparation of 1,5-diaceto-2,6-dihydroxynaphthalene, a suspension of 12 g. of 2,6-diacetoxynaphthalene¹⁸ and 15.8 g. of aluminum chloride in 100 cc. of carbon bisulfide was refluxed for two hours, the solvent was distilled, and the residue was heated in a bath at 150° for four hours. After decomposition with ice, the yellow product was precipitated from a clarified, alkaline solution, distilled *in vacuo*, and crystallized from benzene-ligroin: yield, 7 g. (58%). The ether was best obtained from the crude material with dimethyl sulfate, for the product was easily purified by vacuum distillation with little loss of material (70% yield from the diacetoxynaphthalene). Although 1-aceto-2-naphthol (m. p. 65°) can be reduced with fair success to 1-ethyl-2-naphthol by the Clemmensen method,¹⁹ this method failed completely in the case of 1,5-diaceto-2,6-dihydroxynaphthalene, probably because of the high melting point and lack of solubility of this compound. The Wolf-Kishner method and high pressure hydrogenation likewise proceeded poorly. The reduction of the dimethyl ether was then investigated. The Wolf-Kishner method failed in this case apparently for the reason that before reduction occurs the compound is cleaved by sodium ethylate with the elimination of the aceto groups. When 1,5-diaceto-2,6-dihydroxynaphthalene was heated with alcoholic sodium ethylate at 170° there was obtained a compound, m. p. 155°, having the composition and properties of the methyl ethyl ether of 2,6-dihydroxynaphthalene (calcd.: C, 77.18; H, 6.99. Found: C, 76.94; H, 7.05). The hydrogenation of the diaceto dimethyl ether in alcohol in the presence of copper chromite

(15) Pauling and Wheland, *J. Chem. Phys.*, **1**, 362 (1933).

(16) Fries, Walter and Schilling, *Ann.*, **516**, 248 (1935).

(17) Kuhn and Winterstein, *Helv. Chim. Acta*, **11**, 87 (1928).

(18) Emmert, *Ann.*, **241**, 370 (1887).

(19) Fries and Engel, *ibid.*, **439**, 243 (1924).

TABLE II
 NAPHTHALENE DERIVATIVES

Compound	Recryst. solvents	Description	M. P., °C.	Formula	Analyses, %			
					Calcd.		Found	
					C	H	C	H
1 1,5-Diaceto-2,6-dihydroxynaphthalene	Bz + lig.	Fine, pale yellow plates	263	C ₁₄ H ₁₀ O ₄	68.82	4.96	69.18	4.98
2 Diacetate	Bz + lig.	Colorless plates	189	C ₁₈ H ₁₄ O ₆	65.83	4.91	66.03	4.96
3 Dimethyl ether	MeOH	Small, colorless plates	216	C ₁₆ H ₁₄ O ₄	70.55	5.92	70.64	6.08
4 1,5-Diethyl-2,6-dihydroxynaphthalene	CHCl ₂ :CHCl ₂	Faintly yellow needles, blue-green in alk.	262	C ₁₄ H ₁₆ O ₂	77.78	7.41	77.48	7.59
5 Dimethyl ether	Ether, alc.	Fine needles	186	C ₁₈ H ₁₆ O ₂	78.62	8.27	78.32	7.97
6 2,6-Dialloxynaphthalene	Alc.	Plates containing solvent	112	C ₁₆ H ₁₆ O ₂	79.98	6.71	80.02	6.71
7 1,5-Diallyl-2,6-dihydroxynaphthalene	Dil. alc.	Long needles, green-blue in alk.	168	C ₁₈ H ₁₈ O ₂	79.98	6.71	79.92	6.78
8 Dicomarone derivative	Ether, alc.	Plates	172	C ₁₇ H ₁₆ O ₂	79.98	6.71	80.30	6.91
9 Dimethyl ether	Dil. alc.	Plates	113	C ₁₈ H ₂₀ O ₂	80.56	7.53	80.56	7.58
10 Diallyl ether	Acetone	Plates	100	C ₂₂ H ₂₄ O ₂	82.49	7.56	82.60	7.76
11 1,5-Dibenzyl-2,6-dihydroxynaphthalene	Alc.	Stout needles containing solvent	191	C ₂₄ H ₂₀ O ₂	84.64	5.94	84.50	6.14
12 Diacetate	Dil. alc.	Small, colorless plates	183	C ₂₂ H ₁₈ O ₄	79.20	5.70	78.99	5.99
13 1,5-Dibenzoyl-2,6-dihydroxynaphthalene	Dil. alc.	Bright yellow needles	282	C ₂₄ H ₁₆ O ₄	78.26	4.37	78.44	4.59
14 Diacetate	Alc., acetone	Colorless plates	226	C ₂₈ H ₂₀ O ₂	74.30	4.47	74.37	4.70
15 1,6-Dihydroxydihydropleiadene	Dil. AcOH	Pale yellow needles	217	C ₁₈ H ₁₆ O ₂	82.42	5.38	82.58	5.14
16 Dimethyl ether	Alc.	Pale yellow needles	163	C ₂₀ H ₁₈ O ₂	82.70	6.27	82.78	6.43
17 Diallyl ether	Dil. alc.	Long, yellow needles	93	C ₂₄ H ₂₂ O ₂	84.16	6.49	84.00	6.62

catalyst at 140° and 2000 lb. pressure proceeded smoothly (69% yield), and the desired 1,5-diethyl-2,6-dihydroxynaphthalene was obtained by demethylation with hydrobromic acid and glacial acetic acid in an atmosphere of nitrogen.

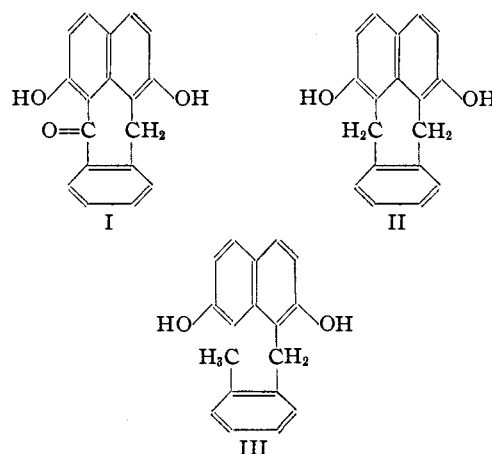
The diallyl ether of 2,6-dihydroxynaphthalene was obtained by allylation in the presence of acetone and potassium carbonate (90% yield), and for the rearrangement it was heated slowly to 190° in an atmosphere of nitrogen. The exothermic reaction was complete in a few minutes and further heating was found undesirable (85% yield). For characterization this compound was allylated, methylated and converted into the dicoumarone (with acetic acid-hydrobromic acid).

1,5-Dibenzyl-2,6-dihydroxynaphthalene was prepared by boiling a suspension of dihydroxynaphthalene (5 g.) and sodium (1.5 g.) in toluene (20 cc.) for twelve hours, adding benzyl chloride and boiling for twelve hours; yield, 7.4 g. (70%). Benzylation in soda solution²⁰ gave a 10% yield of the same compound. It was hoped that the structure of the compound might be established by conversion to 1,5-dibenzyl-2,6-dihydroxynaphthalene, but on distillation with zinc dust the benzyl groups were eliminated as well as the hydroxyls and the only hydrocarbon found in the distillate was naphthalene. This affords some indication that the benzyl groups are located in α -positions.

1,5-Dibenzyl-2,6-dihydroxynaphthalene was also obtained by the high pressure hydrogenation of the dibenzoyl compound, but in the one experiment conducted the yield was very poor. It appears essential in such a case to protect the hydroxyl groups by methylation. The dibenzoyl compound was obtained in 86% yield by adding in the cold a solution of 2,6-dimethoxynaphthalene (22.1 g.) in tetrachloroethane (400 cc.) to a cooled melt from benzoyl chloride (33 g.) and aluminum chloride (63.5 g.). After stirring for seventeen hours at room temperature the mixture was worked up. The methoxyl groups had been completely hydrolyzed in the course of the reaction. A sample of the material for analysis (m. p. 282°) was purified through the diacetate. Fierz-David and Jac-

card,²¹ who employed a different method, report a melting point of 275°. All attempts to verify the claim made in the patent literature²² that the compound can be converted into a vat dye by the action of sodium aluminum chloride were unsuccessful.

In order to obtain a dialkyl compound of certain structure it was decided to start with 1,6-dihydroxy-12-pleiadene, I, for the method of synthesis²³ leaves no doubt as to the structure of the compound. Before the mobility of



a carbonyl group in an α -position adjacent to a hydroxyl group was fully appreciated, an attempt was made to reduce I by high pressure hydrogenation. The product, obtained as pale yellow needles, m. p. 235–236° from alcohol, in 65% yield, contains two hydrogen atoms more than the expected product II and it couples with diazotized sulfanilic acid. It probably has the structure of 1-(*o*-methylbenzyl)-2,7-dihydroxynaphthalene, III. (Calcd. for C₁₈H₁₈O₂: C, 81.79; H, 6.10. Found: C, 82.14, 82.18; H, 6.17, 6.27.)

The dimethyl ether of II (1,6-dimethoxydihydropleiadene) was obtained without difficulty by the hydrogenation

(21) Fierz-David and Jaccard, *Helv. Chim. Acta*, **11**, 1047 (1928).

(22) *Chem. Zentr.*, **II**, 336, 1087 (1927).

(23) Fieser, *THIS JOURNAL*, **55**, 4977 (1933).

(20) German patent 422,948 (*Chem. Zentr.*, **I**, 2841 (1926)).

tion of the dimethoxypleiadone, and demethylation with hydrobromic and acetic acids gave II.

Coupling and Rearrangement Tests.—The 1,5-diethyl, 1,5-dibenzyl and 1,5-diallyl derivatives of 2,6-dihydroxynaphthalene, as well as 1,6-dihydroxydihydropleiadene, are all sensitive to oxidation in alkaline solution by air or by nitrous acid, and in carrying out coupling tests some precautions had to be taken to avoid some discoloration arising from these sources. The naphthols were dissolved in alkali in an inert atmosphere, and the diazotized sulfanilic acid used was precipitated as the inner salt, washed with water and suspended in water containing a trace of urea. *p*-Nitrobenzene diazonium chloride was prepared in glacial acetic acid solution, precipitated and washed with ether. There was in no case any appreciable color change on bringing the components together in alkaline solution under these conditions, and the naphthols could be recovered on acidification. The behavior of 1-ethyl-2-naphthol (which does not couple) was noted for comparison, and β -naphthol was always used for a control.

In three cases (see table) the diallyl ethers were prepared and the possibility of their rearrangement investigated. It was found that the substances decompose somewhat when heated for a prolonged period, even in the absence of air, but no alkali-soluble products were found. When heated for five minutes at 210°, that is, under conditions more than sufficient for the complete rearrangement of the diallyl ether of 2,6-dihydroxynaphthalene, the substances could be recovered essentially unchanged.

Etherification Experiments.—The methylations summarized in Table I were carried out in sealed tubes heated in a steam bomb, and care was taken to maintain identical conditions. After cooling, the contents of a tube was transferred to a flask, diluted with water and the product

extracted with ether. The ethereal solution was extracted thoroughly with 5% alkali, and this was then acidified and extracted with ether. The ethereal solutions were dried, the solvent removed and both the naphthol fraction and the naphthol ether fraction were weighed. The identity and purity of the products were checked by melting point determinations. In Table I is given the total amount of material accounted for and the percentage of the total found as the ether. Duplicate runs agreed within 2% or better.

Summary

Methods which have served to locate the enol double bond of β -naphthol have been applied to a study of the bond structure of 2,6- and 2,7-dihydroxynaphthalene. The results indicate the presence in these compounds of enol groupings between the α - and β -positions in both rings and the absence of double bonds at the β,β -positions. It is clear that naphthalene contains two Kekulé rings, that these have the symmetrical arrangement of the Erlenmeyer formula, that the bond structure is immobile, and that the hydrocarbon cannot exist to any appreciable extent in the unsymmetrical form. The special structure very probably arises from the general tendency of unsaturated rings to assume and to preserve the aromatic type.

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CAMBRIDGE, MASSACHUSETTS RECEIVED JUNE 5, 1935

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

Quantitative Studies of the Infra-red Absorption of Organic Compounds Containing NH and OH Groups¹

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This paper constitutes a second report³ in a program of study of the quantitative infra-red absorption of organic compounds, being carried out in this Laboratory with the purpose of applying the data thus obtained to the chemistry and structure of these molecules. The absorption coefficients of a considerable number of compounds containing the NH group involving several different types have now been measured as well as

those for a number of typical OH compounds, and this material has been applied to the analysis and structural study of a number of unknowns, working in conjunction with the organic section of this Laboratory. These first steps in the application of our results have given sufficient promise to justify their extension to other problems, which involve more interest to the organic chemist⁴ and such studies are now in progress.

Experimental

The procedure used in carrying out these measurements has been described in the papers referred to above,^{1,3} though some improvements in

(1) For the first paper of this series see *THIS JOURNAL*, **55**, 3574 (1933).

(2) Fellow of the John Simon Guggenheim Memorial Foundation during part of this work.

(3) Since our first paper, Liddel and Kasper, at the suggestion of the late Dr. E. W. Washburn, have also measured the absorption of a large number of pure hydrocarbons using the apparatus and technique described in our first paper: see *Bureau of Standards Journal of Research*, **11**, 599 (1933).

(4) Hilbert, Wulf, Hendricks and Liddel, *Nature*, **135**, 147 (1935), a method for detecting some forms of chelation.