INTRODUCTION

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Naphthalene and its derivatives are of interest as they are important intermediates for the manufacture of industrially useful products. Naphthalene derivatives are also found in nature especially in the form of naphthoquinone derivatives such as vitamin K_1 and K_2. The chemistry and technology of naphthalene compounds has been discussed by Donaldson[1] and naphthalene and its derivatives have been reviewed in detail in Elsevier's Encyclopaedia[2].

As the positions 1,4,5 and 8 (α-position) and 2,3,6 and 7 (β-position) are identical two sets of isomeric monosubstitution products of naphthalene are possible such as α-and β-naphthol and α-and β-naphthylamine. Numerous studies have been made on the mono substituted derivatives. There are however ten isomeric disubstituted naphthalenes possible. All the ten dihydroxynaphthalenes are known. The studies on substitution in the dihydroxy naphthalenes are more complex because of the possibility of formation of various isomeric products.

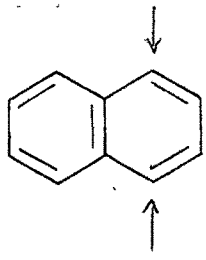
A good deal of work has been carried out on different dihydroxynaphthalenes with a view to establish the bond structure of naphthalene. Fieser and Lothrop[3] studied this question in detail. They examined the coupling behaviour of dihydroxynaphthalenes and found that 2,7-dihydroxy-naphthalene couples only at position 1 and 8 and not at 1 and 6. Coupling behaviour of 1,8-dialkyl-2,7-dihydroxy-naphthalene was also examined but the results were negative

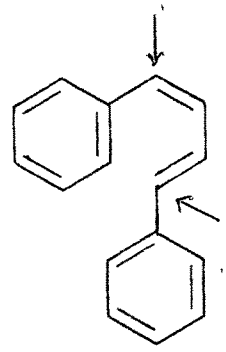
even with reactive diazonium compounds. 1,5-Dialkyl-2,6-dihydroxynaphthalene also failed to couple. The striking difference in reactivity between carbon 1 and 3 in naphthols was attributed to a double bond between carbon atoms 1 and 2 and a single bond between carbon atoms 2 and 3. Thus β-naphthol couples at position 1 but if this is blocked by a stable group,no coupling occurs with diazotised amines. The other ortho position is never found to react in this case. The conversion of β-naphthol allyl ether into 1-allyl-2-naphthol by heating, also conforms to the same rules, a substituent at C_1 effectively preventing the rearrangement[4]. Thus it is evident that it cannot be considered merely as a difference in the degree of reactivity, but a difference in kind.

Further, the application of the Skraup quinoline synthesis to β-naphthylamine has been adjudged to afford evidence to bond fixation in the 1,2-positions. The heterocyclic ring formed extends to position 1 and not to position 3. The fact that an alkyl group at position 1 prevents the reaction while a 1-bromo group may be displaced demonstrates the marked difference in reactivity between positions 1 and 3 . Reactions involving the replacement or modification of a functional group also point to the above conclusion. It can also be seen that in all these reactions naphthalene compounds stand in marked contrast to the corresponding benzene derivatives. For example, a para alkyl phenol is substituted at one of the two free ortho positions first and then at the other

If the first reaction 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. But observations by Zincke[5] and by Fries[6] on the halogenation of naphthols and naphthylamines indicate that the double bonds of naphthalene are not free to migrate. The study of Raman and infra red spectra of naphthalene by Kohlrausch[7] also indicates a symmetrical structure for the hydrocarbon.

Fieser also suggests that the proximity of the other ring may be a factor in the relative reactivity of the α-position. He compares the hydrogenation of naphthalene (1,4-reduction) by similar agents, with that of 1,4-diphenyl butadiene, the relative bond fixation of the former giving the two systems considerable similarity.



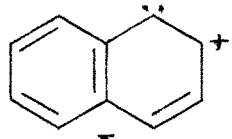


Some of the chemical reactions, evidence derived from quantum mechanics, and other physical evidence do not however reconcile with the above conclusions.

Pauling and Wheland's [8] calculation of the resonance energy of naphthalene appears to assume a mobility of the bond structure comparable with that of benzene.

Studies in ozonolysis of different naphthalene derivatives have also furnished enough evidence to show the existence of alternative unsymmetrical formula[9]. A few chemical reactions in which the 3-position of naphthalene is found to be reactive may also be mentioned here. Schmitt and Burkhard[10] found that 2-hydroxy-3-naphthoic acid is formed by the action of carbon dioxide on sodium β-naphthoxide at high temperatures. Bell[11] brominated the p-tolylsulphonyl derivative of 1-bromo-2-naphthylamine in pyridine solution to get the 1,3-dibromo derivative. Hodgson and Elliot[12] obtained the 3-acetoxy mercuri-1-nitro-2-naphthylamine by the mercuration of 1-nitro-2-naphthylamine.

Pauling considered the number of stable ionic structures such as (I) that can be formulated in which electrons become available in the α or β position under the influence of the attacking group. For the α-position



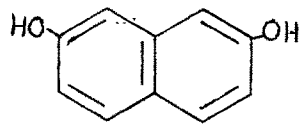
I

there are 7 possibilities but the β-position has only 6 and he concluded that the polarising effect would be greater for the α-position and that substitution should occur there but the orienting effect would be weak.

Syrkin and Dyatkina[13] pointed out that in the singly excited canonical forms of naphthalene the long range bonds are so weak that the carbon atoms involved may be considered to be almost trivalent ; α-carbon atoms are affected in 16 cases, β-carbon atoms in only 12.

A more accurate calculation for all 42 canonical forms shows the quantum weights of the unsaturated α and β position to be in the ratio 2:1

The stability of naphthalene is thus attributed to its resonance among 42 canonical structures, the three unexcited structures contributing about 65 % . In the case of 2,7-dihydroxynaphthalene, these may be represented as II,III and IV.



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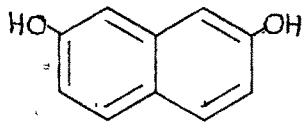

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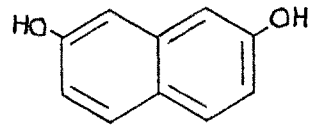

IV

Studies on substitution and synthesis of oxygen heterocycles from dihydroxy naphthalenes and from the dihydroxy derivatives of diphenyl, diphenyl methane, benzophenone and diphenyl sulphone has been going on in our laboratories and the present studies are a part of that work.

Chapter I deals with the synthesis of α- and γ pyrones from 1,4, 1,5 and 2,7-dihydroxynaphthalenes by the application of known reactions such as Pechmann, Perkin, Knoevenagel and Kostanecki-Robinson reaction and the establishment of their structures.

Chapter II deals with the synthesis of γ-pyrones from hydroxy naphtho α- and γ-pyrones.

Chapter III deals with the synthesis of various substituted and unsubstituted furo naphtho α- and γ-pyrones

from several hydroxy naphtho α- and γ-pyrones.

Chapter IV deals with the synthesis of various simple and substituted bichromonyl, bibenzofuranyl and bicoumarinyl ether from 4,4'-dihydroxy diphenyl ether.

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