Cycloalkylidene-diphenols and a cycloalkylene-phenol were obtained and suitable derivatives thereof prepared. The results obtained further support the previously suggested steric hindrance hypothesis governing the condensation of cyclic ketones with ortho alkylated phenols.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW YORK UNIVERSITY]

Steric Hindrance in Ketone–Naphthol Condensations. The Condensations of the Naphthols with Cyclohexanone

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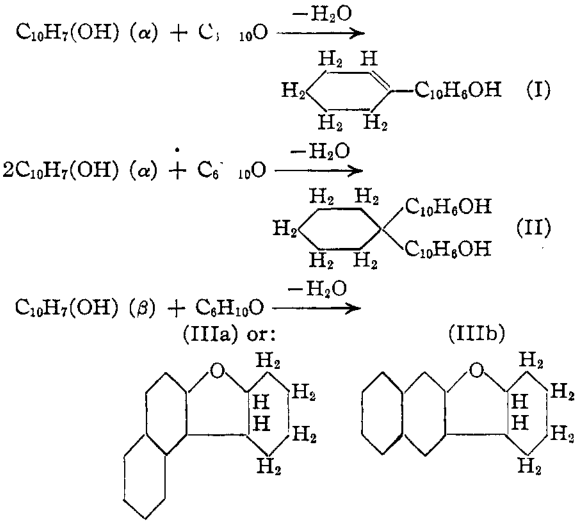
In a previous publication[1] it was asserted that in the condensation of ketones with phenols "the nature of the end product is influenced not only by the type of carbonyl compound employed, but also by the type of phenol used" and that "this influence exerts itself particularly through the position of the second substituent in the benzene ring, *i. e.*, whether it is *ortho*, *meta* or *para* to the hydroxyl group." This hypothesis was fully substantiated in a subsequent communication[2] in which condensations of various phenols with cyclohexanone derivatives were reported. In this it was shown that in cases where the alkyl radical in the final condensation product is adjacent to the carbon carrying the cyclohexenyl radical, steric hindrance effects inhibit the introduction of a second phenolic radical. Thus, instead of the normal di-phenols, unsaturated phenolic products are obtained. Further, it was indicated that when steric hindrance becomes too great, ortho alkylation takes place, leading to the formation of coumarans.

In continuation of these studies of steric hindrance in ketone–phenol condensations and in order to prove the generality of the above conclusion, these investigations were extended to the naphthols.

The results obtained were entirely in accordance with the foregoing postulation. Thus, when α-naphthol was condensed with cyclohexanone, not only was the normal di-naphthol, the 2,2-di-((4′-hydroxy)-naphthyl)-cyclohexane (II) obtained, but the cyclo-alkylene-naphthol, the 1-(4′-hydroxy)-naphthyl-cyclohexene-1 (I) was secured as well. To prove the unsaturated character of the latter, the acetate (Ia) was prepared and brominated, and the resulting crystalline dibromide (Ib) isolated. Titration of this dibromide (Ib) with 0.01 N sodium hydroxide solution gave a neutralization equivalent equal to one half the molecular weight of the compound, indicating the hydrolysis of at least one bromine atom and thus confirming the presence of bromine in the isocyclic side chain.

The condensation of β-naphthol with cyclohexanone was also studied. The condensation was slow, but positive, yielding no phenolic products, but, instead, the 2,3-tetramethylene-4,5[or 5,6]-benzocoumaran (IIIa or IIIb).

The formation of all three types of condensation product may be represented as


$C_{10}H_7(OH)$ (α) + $C_6H_{10}O \xrightarrow{-H_2O}$ (I)

$2C_{10}H_7(OH)$ (α) + $C_6H_{10}O \xrightarrow{-H_2O}$ (II)

$C_{10}H_7(OH)$ (β) + $C_6H_{10}O \xrightarrow{-H_2O}$ (IIIa) or: (IIIb)

Experimental

1-(4′-Hydroxy)-naphthyl-cyclohexene-1 (I).—Half molar quantities of α-naphthol and cyclohexanone were placed in a 1-liter, triple-necked, round-bottomed flask which was provided with a reflux condenser, a thermometer and a gas inlet tube extending to the bottom of the vessel. The mixture was warmed until complete solution took place and then was cooled to below 30°. A vigorous stream of dry hydrogen chloride gas was passed into the system for six hours at room temperature, then the flask was stoppered and left standing for twelve hours, when com-

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[1] J. B. Niederl and co-workers, THIS JOURNAL, **61**, 348 (1939).

[2] J. B. Niederl and co-workers, *ibid.*, **61**, 1785 (1939).

plete solidification had taken place. The mass was then crushed, washed with water and twice leached with 5% sodium hydroxide, after which it was again washed thoroughly with water. The residue was chilled until it was solid and recrystallized from a minimum quantity of 95% ethyl alcohol, separating thus any alcohol-insoluble products. The compound is no longer soluble in Claisen solution, but couples with diazotized *p*-nitroaniline; yield after recrystallization, 80%; m. p. 80°.

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.71; H, 7.14. Found: C, 85.42; H, 7.22.

Acetate (Ia).—Ten grams of (I) was dissolved in 50 ml. of acetic anhydride, the solution placed in a ground-glass joint apparatus and refluxed for four hours. Then the mixture was poured into 500 ml. of water and the whole vigorously stirred. After a time the residue solidified and was separated by filtration. The crude acetate was recrystallized from 95% ethyl alcohol. The conversion to the acetate was quantitative, m. p. 94°.

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.20; H, 6.77; mol. wt., 266. Found: C, 81.09; H, 6.97; mol. wt., 265.

Di-bromide (Ib).—Ten grams of (Ib) was dissolved in 50 ml. of carbon tetrachloride and placed in a round-bottomed flask, the solution then being cooled to 5° in an ice-water-bath. The solution was stirred vigorously with the aid of a mechanical stirrer while one mole equivalent of bromine dissolved in carbon tetrachloride (1 g. of bromine per 5 ml. of solution) was added at the rate of 1 ml. per minute. When the addition of bromine was completed, the reaction mixture was poured into an evaporating dish and permitted to stand at room temperature until half the solvent had evaporated. By this time most of the dibromide had precipitated out while any substitution by-products remained dissolved. The mixture was then filtered and the crude dibromide was dissolved in the minimum quantity of acetone. A volume of water equal to one-fourth the volume of the acetone solution was added at once and stirred. In a few moments the purified dibromide crystallized from the solution and was separated by filtration; yield, 20%; m. p. 147°.

Anal. Calcd. for $C_{18}H_{18}O_2Br_2$: C, 50.70; H, 4.22; mol. wt., 426. Found: C, 50.73; H, 4.24; neut. equiv., 210.

1,1-Di-((4′-hydroxy)-naphthyl)-cyclohexane (II).—Half molar quantities of α-naphthol and cyclohexanone were condensed exactly as described for (I) with the single difference that the condensation was carried out at 100°. After standing for twelve hours in a tightly stoppered flask, the product was treated with 300 ml. of acetone and filtered. The residue was washed with 50 ml. of acetone and dried at room temperature. The compound was insoluble in Claisen solution but coupled with diazotized *p*-nitroaniline; yield, after treatment with acetone, 50%; m. p. 233°.

Anal. Calcd. for $C_{26}H_{24}O_2$: C, 84.78; H, 6.44; mol. wt., 368. Found: C, 84.62; H, 6.72; mol. wt., 381, 377. The molecular weight determination was performed cryoscopically according to K. Rast.[3]

Di-benzoate (IIa).—One gram of (II) was dissolved in 5 ml. of pyridine and 2 ml. of benzoyl chloride was added. The mixture was refluxed very gently for one-half hour and poured into 50 ml. of 5% sodium carbonate solution and vigorously stirred. When the product had hardened, the supernatant liquid was poured off and the residue was washed with water by decantation. A minimum amount of boiling alcohol was added to dissolve most of the residue. The alcoholic solution was then filtered and the filtrate cooled. The benzoate crystallized out and was filtered off. It was then purified by further crystallization from alcohol; m. p. 223°; mixed m. p. with (II), 207°.

Anal. Calcd. for $C_{40}H_{32}O_4$: C, 83.33; H, 5.55. Found: C, 83.48; H, 5.43.

2,3-Tetramethylene-4,5[or 5,6]-benzo-coumaran (IIIa or IIIb).—Half molar quantities of β-naphthol and cyclohexanone were dissolved in 80 ml. of acetic acid and condensed as described for (I). After standing for two weeks the flask was opened and the contents poured into a liter of water. The supernatant liquid was decanted and the residue twice leached with 5% sodium hydroxide solution, after which it was washed thoroughly with water. It was then chilled until semi-solid and dissolved in a very large volume of boiling alcohol. The alcoholic solution was chilled in ice. Water was added to cause the separation of the product and the resulting precipitate filtered off. After this treatment was twice repeated, the product was obtained as a nearly-white, amorphous solid; yield, 20%; m. p. 66–68°. The compound was insoluble in Claisen solution and did not undergo diazotization coupling reactions. Acetylation with acetic acid anhydride also was negative.

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.71; H, 7.14; mol. wt., 224. Found: C, 85.50; H, 7.45; mol. wt., 249.

Summary

Steric hindrance phenomena encountered in certain types of ketone–phenol condensations were extended to include the condensation systems of the naphthols with cyclohexanone. From such systems and in accordance with previous postulations a cyclo-alkylidene-di-naphthol, a cyclo-alkylene-naphthol and a naphthyl-cyclohexyl-coumaran were isolated and derivatives thereof prepared.

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[3] K. Rast, as described in J. B. Niederl and V. Niederl, "Micromethods of Quantitative Organic Analysis," J. Wiley and Sons, Inc., New York, N. Y., 1938, p. 175.