

the solution decanted, cooled, filtered, and the filtrate used for re-extraction of the tar. Several repetitions of this procedure gave 25.7 g. (32%) of fine colorless crystals, m. p. 72°. 4-Methyl-6-hydroxycoumarin was prepared by the method of Borsche.¹⁸ Yields were raised slightly by the use of stirring during the slow addition of sulfuric acid. A 40% yield of crude material was thus obtained, which, after recrystallization from alcohol, amounted to 27%, m. p. 250–254°. 7,8-Benzocoumarin was prepared by the method of Bartsch.¹⁹

Hydrogenations.—The apparatus and general procedure have been described in a previous paper.² Isolations were carried out in the same way except as otherwise noted. The hydrogenation data are listed in Table III. Identification rested to a large extent on analysis and physical constants, which are listed in Table IV.

Substituted Chromans.—6-Methylchroman, 7-methylchroman and 4,7-dimethylchroman were prepared in yields of 85–88% from the corresponding phenolic alcohols by the method previously described for chroman.² The colorless products were allowed to stand over sodium and redistilled prior to analysis and hydrogenation. 7,8-Benzochroman was prepared from 2-(γ -hydroxypropyl)-naphthol-1 (0.06 mole) in the same manner, except that relatively more phosphorus tribromide (0.06 mole) was used. The product (53%) was a lemon-colored liquid, which was not decolorized by redistillation from Raney nickel.

Isolation of 2-(γ -Hydroxypropyl)-naphthol-1 (Va).—The product from the hydrogenation of 7,8-benzocoumarin over copper chromate (Table III) was removed from the bomb with ether, and the catalyst removed by filtration.

(18) Borsche, *Ber.*, **40**, 2732 (1907).

(19) Bartsch, *Ber.*, **36**, 1966 (1903).

The ether solution was then shaken with 10% sodium hydroxide solution and separated. The ether extract was dried with magnesium sulfate. Distillation through the Widmer column gave 2.4 g. (5%) of 7,8-benzotetrahydrochroman (IX), and a large non-phenolic residue which could neither be crystallized nor distilled. The alkaline solution was acidified and extracted with ether. This ether extract was then washed with sodium bicarbonate and dried over anhydrous magnesium sulfate. After removal of the ether under vacuum, there remained a slightly yellow, gummy solid, 28 g., m. p. 69–74°. On recrystallization from benzene and ligroin (b. p. 70–90°), 14.1 g. of Va (m. p. 84–86°) was obtained. From the filtrate, 0.9 g. more material was isolated. The purified product gave a characteristic strong pink color with ferric chloride. The residue after removal of solvents, while phenolic in character, could not be crystallized, and presumably contained a large proportion of material hydrogenated in the non-oxygenated ring.⁶

Summary

The data now available indicate that both phenolic alcohols and saturated lactones are intermediate in the conversion of coumarins to hexahydrochromans over Raney nickel. These lactones are apparently converted, by the type of reaction generally observed over copper chromite, to dihydroxy compounds, which then undergo ring closure. The conversion of some substituted coumarins to phenolic alcohols, chromans and hydrogenated chromans has been described.

PHILADELPHIA, PENNA.

RECEIVED AUGUST 8, 1940

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW YORK UNIVERSITY]

Indano-indanes¹

BY JOSEPH B. NIEDERL AND RICHARD H. NAGEL²

In the condensation of acetone with pyrocatechol and pyrogallol "indane"-type crystalline condensation products, 5,5',6,6'-tetrahydroxy- and 5,5',6,6',7,7'-hexahydroxy-, 3,3,3',3'-tetramethyl-*bis*-1,1'-spirohydrindene, respectively, were encountered.^{3,4,5} It is the purpose of this communication to show that "indane"-types of compounds are also obtainable when α - and γ -di-ketones and

catechol, or pyrogallol, are subjected to condensation in the presence of an acidic catalyst. In all these cases crystalline indanoindane types of compounds were produced. Since these types of compounds show a similar structural relationship as "indole" to "dindole,"⁶ the name "dindane" has been suggested provisionally for these compounds.

Thus di-acetone and catechol yielded the 1,1'-dimethyl-5,5',6,6'-tetrahydroxy-dindane (I); the same diketone and pyrogallol, the analogous 1,1'-dimethyl-5,5',6,6',7,7'-hexahydroxy-dindane (II) and di-acetyl the unsubstituted, 5,5',6,6'-tetrahydroxydindane (III). All these compounds, as well as the previously prepared "spirohydrin-

(1) Presented in part before the Division of Organic Chemistry at the recent Cincinnati and Detroit meetings of the American Chemical Society.

(2) Abstracted from a portion of the thesis submitted by Richard H. Nagel to the faculty of the Graduate School of New York University in partial fulfillment of the requirements for the degree of doctor of philosophy.

(3) C. H. Fisher, R. W. Furlong and M. Grant, *THIS JOURNAL*, **58**, 820 (1936).

(4) W. Baker, *J. Chem. Soc.*, 1678 (1934).

(5) W. Baker and J. C. McGowan, *ibid.*, 347 (1938).

(6) "Beilstein's Handbuch der organischen Chemie," 4th ed., Vol. XXIII, p. 253.

denes," have certain reactions in common. Thus all these compounds give an intense coloration with alkalis and form the respective esters (acetates Ia, IIa, IIIa), propionate (Ib) and quinones (Ic) possessing a metallic luster. The formation of these new types of carbocyclic compounds may have proceeded either by interaction

an identical reaction mechanism as postulated for numerous other ketone-phenol condensations, namely, the intermediate formation of "phenol-hydrin" types of compounds,⁷ *i. e.*, "double-catechol-hydrins," which then through intramolecular dehydration, followed by cyclization, underwent "dindane" formation as illustrated

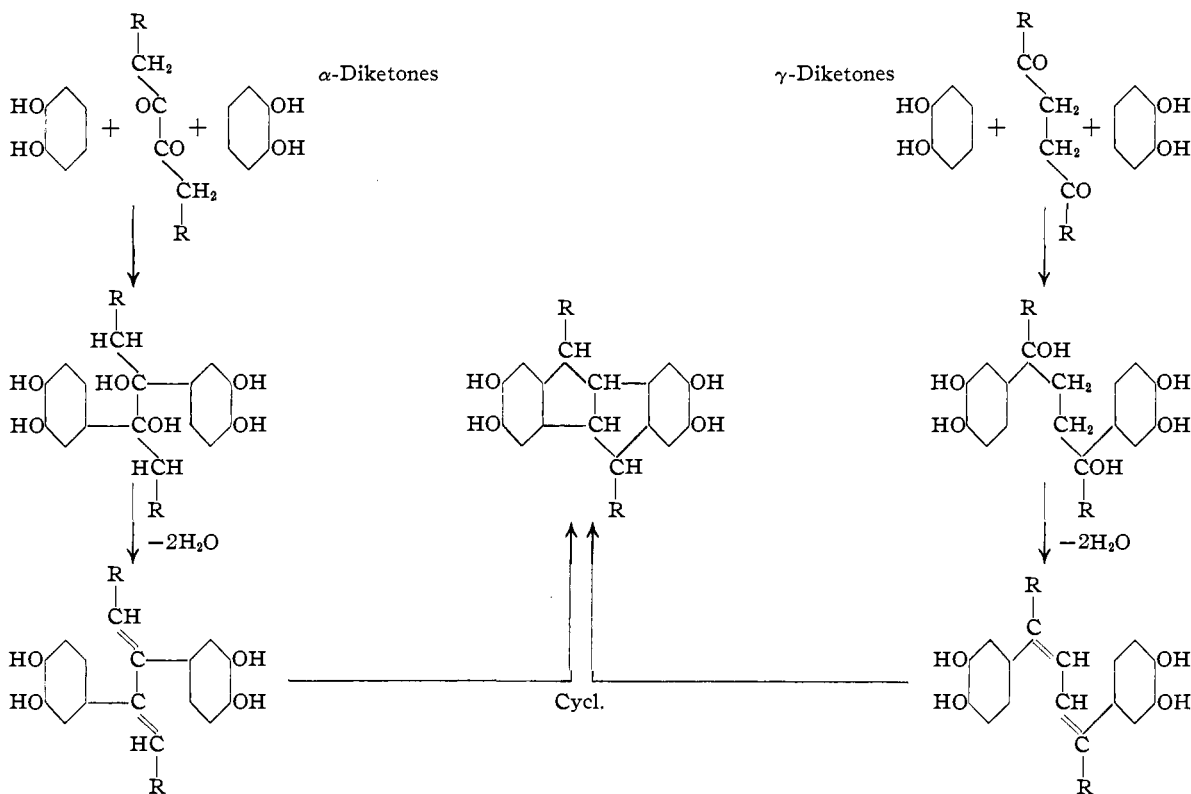


TABLE I
CHEMICAL CONSTANTS AND ANALYSES OF DINDANE COMPOUNDS

Compound	M. p., °C. (uncorr.)	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Diacetone-Catechol Condensation Product						
I 1,1'-Dimethyl-5,5',6,6'-tetrahydroxydindane	300	C ₁₈ H ₁₈ O ₄	72.48	72.60	6.04	6.31
(a) acetate	238-240	C ₂₆ H ₂₆ O ₈	66.95	66.71	5.58	5.30
(b) propionate	182	C ₃₀ H ₃₄ O ₈	68.96	69.19	6.51	6.69
(c) quinone	310	C ₁₈ H ₁₆ O ₄	72.90	72.60	5.40	5.73
Diacetone-Pyrogallol Condensation Product						
II 1,1'-Dimethyl-5,5',6,6',7,7'-hexahydroxydindane	310	C ₁₈ H ₁₈ O ₆	65.45	65.40	5.45	5.01
(a) acetate	244	C ₃₀ H ₃₀ O ₁₂	61.64	61.83	5.13	5.37
Diacetyl-Catechol Condensation Product						
III 5,5',6,6'-Tetrahydroxydindane	300	C ₁₆ H ₁₄ O ₄	71.11	70.77	5.18	5.31
(a) acetate	225	C ₂₄ H ₂₂ O ₈	65.75	65.46	5.02	5.12

through intermolecular dehydration and subsequent addition of two molecules of pyrocatechol, or pyrogallol with the "di-enols" of di-acetyl or diacetone. Still more probable is that the formation also of these carbocyclic compounds involves

The authors are indebted to Prof. Wm. C. West of the department of physical chemistry of this University for taking and examining the absorp-

(7) M. E. McGreal and J. B. Niederl, "Abstracts of Papers, 97th Meeting, Am. Chem. Soc.," Baltimore, Md., 1939, M. pp. 5-7.

tion spectra of some of the compounds given in this communication. The absorption spectra definitely were not of the "anthracene"-type, the only other structural possibility.

Experimental

1,1'-Dimethyl-5,5',6,6'-tetrahydroxy-dindane (I).—One mole (110 g.) of pyrocatechol was dissolved with 0.25 mole (28.5 g.) of diacetone (b. p. 190–193°) in an excess of 70% sulfuric acid. Crystallization took place in less than a week. The crystals were drained off on a porous tile and when recrystallized by dissolving them in alcohol at room temperature and allowing the solvent partially to volatilize, white needles, giving an intense blue coloration in alkalies, both hydroxide and carbonate, were obtained.

Acetate (Ia).—Ten grams of the pyrocatechol condensate was refluxed with 50 cc. of acetic anhydride for six hours. On standing overnight, the acetate crystallized out and was recrystallized from hot ethyl alcohol. The crystals were insoluble in alkali and gave no coloration with these reagents.

Propionate (Ib).—Five grams of the pyrocatechol condensate and 50 cc. of propionic anhydride were refluxed for six hours. Since no crystals appeared on standing, the solution was thrown into cold water and allowed to stand for twelve hours. The crystals formed were filtered off and recrystallized. The compound is also insoluble in alkalies and does not give the characteristic color reaction with these reagents.

Quinone (Ic).—Upon prolonged boiling of the diacetone-pyrocatechol condensation product (I) in water or dilute aqueous alcohol, brown metallic plates of the quinone (Ic) are obtained. The product is recrystallized from 95% alcohol.

1,1'-Dimethyl-5,5',6,6',7,7'-hexahydroxydindane (II).—One mole (126 g.) of pyrogallol, 0.25 mole (28.5 g.) of diacetone, and an excess of 70% sulfuric acid were warmed on the steam-bath until solution was obtained, and then allowed to stand. At the end of twenty-four hours the entire mass had solidified; it was drained free of adhering oil on a porous tile, and when dry was triturated with an equal weight of water in a mortar to remove unreacted pyrogallol. The residue was then boiled with a large excess of water and allowed to stand. Upon cooling and slight evaporation, deep-red crystals appeared, which proved to be the quinone. When the water extract was

then allowed to evaporate to about one-quarter of its volume, a second crop of crystals, having a slight pinkish tinge, was obtained. These crystals are soluble in Claisen solution.

Acetate (IIa).—Ten grams of the pyrogallol-di-acetone condensation product was refluxed with 50 cc. of acetic anhydride in an all-glass apparatus, for eight hours. The excess reagent was distilled off and the residue was dissolved in a minimum quantity of boiling 95% alcohol. Upon cooling the acetate crystallized out. The compound was recrystallized from the same solvent.

5,5',6,6'-Tetrahydroxy-dindane (III).—A solution of one mole (110 g.) of catechol and 0.25 mole (21.5 g.) of diacetyl (b. p. 88.5–90°) in an excess of 70% aqueous sulfuric acid was allowed to stand at room temperature for one week. By this time the dindane compound had crystallized out of the reaction mixture. The crystals were filtered off and were then recrystallized from 95% ethyl alcohol. The compound gives an intense green coloration with alkalies.

Acetate (IIIa).—Ten grams of the above condensation product was refluxed with 50 cc. of acetic anhydride in an all-glass reflux apparatus for six hours. The acetate crystallized out upon standing overnight, and they were then separated and recrystallized from 95% ethyl alcohol. The crystals were insoluble in alkali and did not give the brilliant green coloration with alkalies.

Summary

It was found that when diketones are substituted for monoketones in carbonyl compound-phenol condensations, the previously established generalities are followed and comparable types of condensation products result. Thus α - and γ -diketones, when condensed with catechol and with pyrogallol, yield types of condensation products, possessing an "indane" or "hydrindene" type of structural pattern, similar to the condensation products of monoketones and these phenols. In the present case these crystalline condensation products, furthermore, constitute a new type of poly-carbocyclic compounds for which the name "dindane" has been suggested provisionally.

WASHINGTON SQUARE COLLEGE
NEW YORK, N. Y.

RECEIVED AUGUST 12, 1940