[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF PENNSYLVANIA]

The Hydrogenation of Some Substituted Coumarins[1]

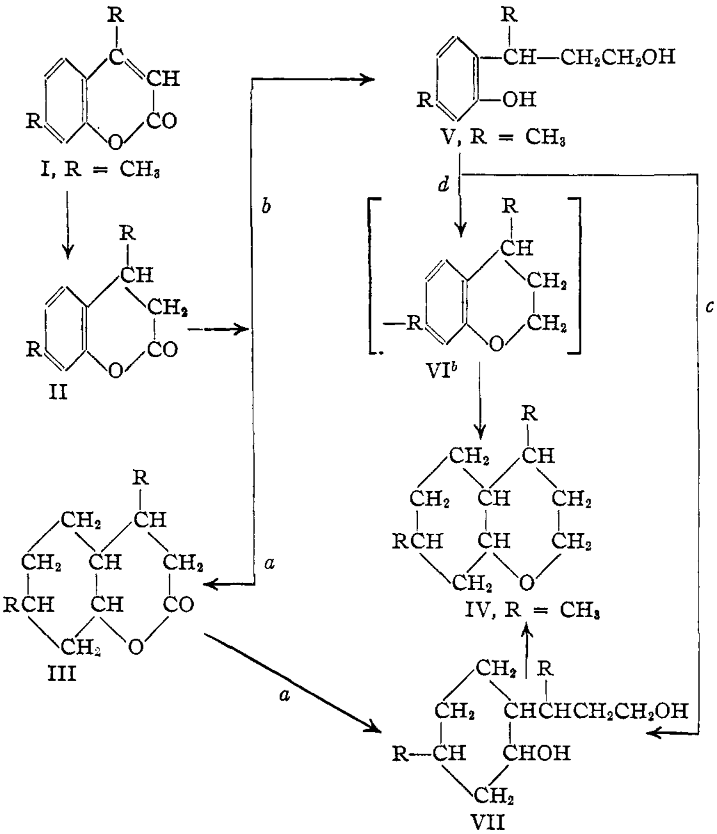
BY PETER L. DE BENNEVILLE AND RALPH CONNOR

This investigation was undertaken (1) to obtain further information concerning the mechanism of the formation of hexahydrochroman[2] by the hydrogenation of coumarin over Raney nickel, and (2) to investigate the preparation of chromans by the method previously described.[2]

The behavior of 4,7-dimethylcoumarin (I) over Raney nickel was of particular significance regarding the mechanism of hexahydrochroman formation. While coumarin gives octahydrocoumarin and hexahydrochroman, (I) did not give enough of the saturated lactone[3] to permit its isolation in the pure state. At 250°, 4,7-dimethylhexahydrochroman (IV) was the sole isolable product (75%); at 200°, IV was also formed (41–47%), and the other product (13–17%) was 2-(γ-hydroxy-*s*-butyl)-5-methylphenol (V). The isolation of V shows that Raney nickel may bring about hydrogenation of the ester group of coumarins in the same way as does copper chromite. Other examples of the conversion of esters to alcohols over nickel have been noted.[4]

TABLE I

PRODUCTS FROM THE HYDROGENATION OF COUMARINS[a]



[a] The numbers of the compounds given in Table I correspond to those used for similar products in the previous paper.[2] [b] Not obtained directly by hydrogenation.

It may be concluded from the data that the course of the reaction must follow both paths (*a* and *b*) shown in Table I. The isolation of the phenolic alcohol (V) seems to indicate that the formation of the cyclic ether from coumarin occurs by hydrogenation of the ester group in the normal manner, giving the dihydroxy compound, followed by dehydration of the latter.[5] There are, however, no data available to decide whether ring closure or hydrogenation of the benzene ring is the first step in the formation of IV from V (steps *c* and *d*). The isolation of octahydrocoumarin and its conversion to hexahydrochroman over Raney nickel were described previously,[2] and these data show that the saturated lactone (III) is also a precursor of the hexahydrochroman. The products isolated from the interrupted hydro-

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(1) This communication is constructed from a thesis submitted by Peter L. de Benneville in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Pennsylvania in June, 1940.

(2) De Benneville and Connor, THIS JOURNAL, **62**, 283 (1940).

(3) The dihydrocoumarin was in all cases formed prior to further reaction; this formation was shown by a pressure drop prior to the main reaction, and by isolation of dihydrocoumarin.[2]

(4) Folkers and Adkins, THIS JOURNAL, **53**, 1097 (1931); Palfray and Sabetay, *Chemie et Industrie, numéro spécial* (Congres de Bruxelles), 1935, p. 746; *Bull. Soc. Chim.*, **3**, 682 (1936); **5**, 1424 (1938); Rainey and Adkins, THIS JOURNAL, **61**, 1107 (1939); Ovakimian, Kuna and Levene, *ibid.*, **62**, 667 (1940).

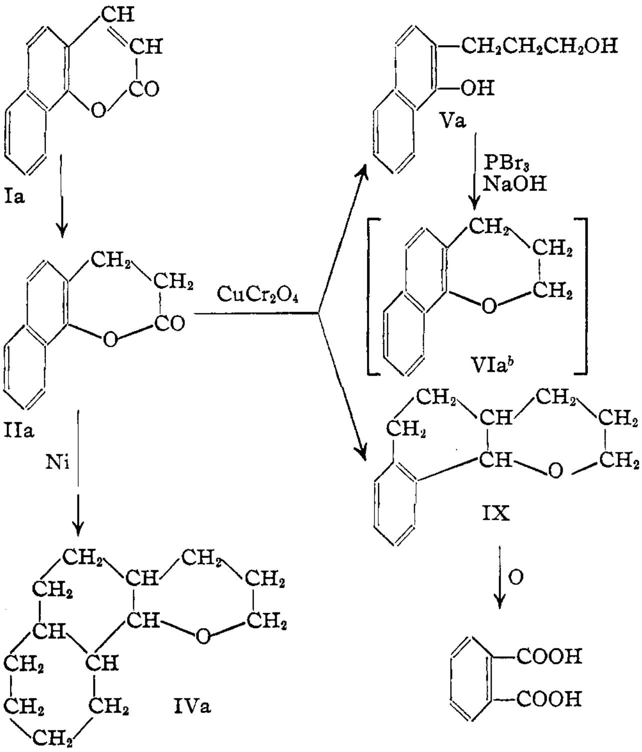
(5) This is in accord with other observations on the ease of ring closure in this series of compounds.[2] Such ring closure can also take place with copper chromite catalyst, as will be shown later in this paper.

genations therefore depend upon the relative rates of reaction of the octahydrocoumarin (III) and the dihydroxy compounds (V).

The hydrogenation of 4-methyl-6-hydroxycoumarin at 250° over nickel gave 4-methyl-6-hydroxyhexahydrochroman (45%) accompanied by a considerable amount of material which did not crystallize and which could not be distilled without decomposition. Under similar conditions, 7,8-benzocoumarin gave decahydro-7,8-benzochroman (47%) (Table II, IVa).

TABLE II

PRODUCTS FROM THE HYDROGENATION OF 7,8-BENZOCOUMARIN[a]



[a] The Roman numerals assigned to the products in Table II correspond to those used for analogous products in Table I and in the previous paper.[2] [b] Not obtained directly by hydrogenation.

The preparation of chromans by hydrogenation of the corresponding coumarins over copper chromite, followed by ring closure of the resulting phenolic alcohols with phosphorus tribromide and alkali, was further extended to several alkyl-substituted chromans, and to 7,8-benzochroman. Hydrogenation of 4,7-dimethylcoumarin, 7-methylcoumarin and 6-methylcoumarin gave 75–80% yields of the corresponding derivatives of 2-(γ-hydroxypropyl)-phenol. The chromans were prepared from these phenolic alcohols in 85–90% yield by the method previously described. Hydrogenation of 6-methylchroman and 7-methylchroman gave the corresponding hexahydrochromans (72%), thus completing a series of hexahydrochromans corresponding to all the coumarins studied.

Hydrogenation of 7,8-benzocoumarin (Ia) over copper chromite was complicated by side reactions, probably because the initial hydrogenation product was a derivative of α-naphthol.[6] Large amounts of both phenolic and non-phenolic residues indicated hydrogenation of one or the other of the two naphthalene rings. The products isolated were 2-(γ-hydroxypropyl)-naphthol-1 (Va) (35%), and 7,8-benzotetrahydrochroman (IX) (5–10%).[7] The latter was distinguished from the isomeric 7,8-tetramethylenechroman by oxidation to phthalic acid. Ring closure of the phenolic alcohol (Va) gave 7,8-benzochroman (VIa) (53%).

An attempt to prepare 4-methyl-6-hydroxychroman failed because of inability to isolate the corresponding phenolic alcohol from the hydrogenation of 4-methyl-6-hydroxycoumarin over copper chromite. The only compound isolated in this hydrogenation was 4-methyl-6-hydroxyhexahydrochroman[7] (31–35%). Ring hydrogenation in this case may be attributed to the presence of the hydroquinone nucleus. The presence of a phenolic group has been reported to labilize the benzene ring to attack over copper chromite.[8,9]

Experimental Part

4,7-Dimethylcoumarin was prepared by the method of Fries and Klostermann.[10] 7-Methylcoumarin was prepared in the manner described by Fries and Klostermann,[11] with one modification in the purification of the product. After one recrystallization from dilute alcohol, the colored 7-methylcoumarin was steam-distilled, yielding a colorless product (27%), m. p. 124–126°. 6-Methylcoumarin was prepared by the following modification[12] of the method of Thompson and Edee.[13] To a mixture of 54.0 g. of *p*-cresol

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(6) Musser and Adkins, THIS JOURNAL, **60**, 664 (1938).

(7) The formation of 7,8-benzotetrahydrochroman and 4-methyl-6-hydroxyhexahydrochroman offers in the case of copper chromite an example of ring closure of a dihydroxy compound similar to that with nickel catalyst previously discussed in this paper.

(8) Adkins, "Reactions of Hydrogen, etc.," University of Wisconsin Press, Madison, Wisconsin, 1937, p. 61.

(9) McClellan, Ph.D. thesis, University of Pennsylvania, Philadelphia, Pennsylvania, 1940.

(10) Fries and Klostermann, *Ber.*, **39**, 874 (1906).

(11) Fries and Klostermann, *Ber.*, **39**, 873 (1906).

(12) The authors are indebted to Mr. R. E. Houghton for working out the details of this procedure.

(13) Thompson and Edee, THIS JOURNAL, **47**, 2556 (1925).

TABLE III

HYDROGENATION DATA[a]

Compound	Moles	Time, hr.	Solvent	Catalyst, 5 g. of	Temp., °C.	Products
4,7-Dimethylcoumarin	0.2	0.5	.....	CuCr	250	80% 2-(γ-Hydroxy-*s*-butyl)-5-methylphenol
7-Methylcoumarin	.18	1	.....	CuCr	250	76% 2-(γ-Hydroxypropyl)-5-methylphenol
6-Methylcoumarin	.19	1.5	.....	CuCr	250	81% 2-(γ-Hydroxypropyl)-4-methylphenol
4-Methyl-6-hydroxycoumarin	.16	4	C_7H_{14}	CuCr	250	35% 4-Methyl-6-hydroxyhexahydrochroman[b]
7,8-Benzocoumarin	.24	3	.....	CuCr	250	31% 2-(γ-Hydroxypropyl)-naphthol-1[c] 5% 7,8-Benzotetrahydrochroman
4,7-Dimethylcoumarin	.2	3	C_7H_{14}	Ni	250	75% 4,7-Dimethylhexahydrochroman[d]
4,7-Dimethylcoumarin	.2	6	C_7H_{14}	Ni	205	44% 4,7-Dimethylhexahydrochroman[e] 13% 2-(γ-Hydroxy-*s*-butyl)-5-methylphenol[f]
4-Methyl-6-hydroxycoumarin	.15	3.5	C_7H_{14}	Ni	250	45% 4-Methyl-6-hydroxyhexahydrochroman[g]
7,8-Benzocoumarin	.13	3	C_7H_{14}	Ni	250	47% Decahydro-7,8-benzochroman
6-Methylchroman	.07	6	C_2H_5OH	Ni	230	72% 6-Methylhexahydrochroman
7-Methylchroman	.07	6	C_2H_5OH	Ni	230	72% 7-Methylhexahydrochroman

[a] The hydrogenations were carried out at hydrogen pressure of 100–200 atmospheres. [b] Small amounts of lower-boiling hydrogenolysis products were isolated. The residue (45%) after removal of the hexahydrochroman could not be distilled through a column, but was distilled without a column. It had a wide boiling range (150–200°, 3 mm.), and could not be crystallized, either before or after distillation. [c] The isolation of this material is described in the experimental part. [d] There was also isolated some higher-boiling material (5%), b. p. 148–150° (9 mm.), which appeared to be 4,7-dimethyloctahydrocoumarin. [e] An intermediate fraction (19%), b. p. 125–139° (4 mm.), appeared to be 4,7-dimethyloctahydrocoumarin, contaminated with the dihydrocoumarin. [f] After recrystallization, only 8% was isolated, but the remainder was soluble in alkali, indicating that it was also this product. [g] The residue (31%) could neither be distilled nor crystallized.

TABLE IV

PHYSICAL CONSTANTS AND ANALYSES OF PRODUCTS

Compound	B. p. obsd., °C.	Mm.	n^t_D	t, °C.	d^t_4	MR_D Calcd.	MR_D Found	Empirical formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
4,7-Dimethylhexahydrochroman	121–122	38	1.4672	25	0.928	50.23	50.25	$C_{11}H_{20}O$	78.5	78.2, 78.5	12.0	12.0, 12.1
6-Methylhexahydrochroman	100–101	25	1.4668	29	0.932	45.62	45.83	$C_{10}H_{18}O$	77.9	78.1, 78.2	11.8	11.9, 12.0
7-Methylhexahydrochroman	95–97	25	1.4649	29	0.931	45.62	45.68	$C_{10}H_{18}O$	77.9	77.7, 77.9	11.8	11.9, 12.0
4-Methyl-6-hydroxyhexahydrochroman	149–153	19	1.4982	25	1.063	47.14	46.90	$C_{10}H_{18}O_2$	70.6	70.9, 70.5	10.7	10.6, 11.0
7,8-Benzotetrahydrochroman	116–120	4	1.5525	29	1.056	55.87	56.94[a]	$C_{13}H_{16}O$	82.9	83.1, 83.2	8.57	8.79, 8.87
Decahydro-7,8-benzochroman	111–113	5	1.4982	29	0.988	57.30	57.61	$C_{13}H_{22}O$	80.3	80.2, 80.2	11.4	11.7, 11.6
4,7-Dimethylchroman	135–136	38	1.5300	28	1.010	48.83	49.57	$C_{11}H_{14}O$	81.4	81.5, 81.5	8.71	8.81, 8.81
6-Methylchroman	111–112[b]	18	1.5392[b]	25	1.033[b]	44.22	44.87[b]	$C_{10}H_{12}O$	..	.....	...	....
7-Methylchroman	141–143	60	1.5380	26	1.028	44.22	45.03	$C_{10}H_{12}O$	81.0	80.8, 81.1	8.16	7.94, 8.09
7,8-Benzochroman	140–142	5	1.6315	22	1.123	54.95	58.43[c]	$C_{13}H_{12}O$	84.7	84.3, 84.9	6.57	6.67, 6.55
2-(γ-Hydroxypropyl)-4-methylphenol	153–154	3	1.5448	27	1.091	47.93	48.09	$C_{10}H_{14}O_2$	72.2	71.8, 71.9	8.50	8.70, 8.72
2-(γ-Hydroxypropyl)-5-methylphenol	156–157	4	M. p. 64.5–65° cor.					$C_{10}H_{14}O_2$	72.2	72.4, 72.2	8.50	8.69, 8.75
2-(γ-Hydroxy-*s*-butyl)-5-methylphenol	179–180	6	M. p. 73–74° cor.					$C_{11}H_{16}O_2$	73.3	73.2, 72.9	8.95	8.86, 8.86
2-(γ-Hydroxypropyl)-naphthol-1			M. p. 87–88° cor.					$C_{13}H_{14}O_2$	77.2	77.3, 77.4	6.99	7.24, 7.16

[a] The high value of the observed molecular refraction is in accord with the reported exaltation by the tetrahydronaphthalene nucleus.[14] The identity of this compound was confirmed by oxidation with potassium permanganate according to the usual procedure.[15] Phthalic acid was the only product isolated, m. p. 193–196° dec. This product was identified by sublimation to phthalic anhydride, m. p. 127–128°, mixed m. p. 128–129°. [b] $n^{14.5}_D$ 1.5428. Von Auwers reported[16] the following data on this compound: $n^{14.5}_D$ 1.5421, n^{20}_D 1.5395, d^{20}_4 1.032, M_D found 44.93. Von Braun, Grabowski and Kirschbaum reported[17] b. p. 107° (12 mm.). [c] Molecular exaltation would be expected in the presence of the naphthalene[14] and chroman[16] ring systems. The molecular exaltation approximates the sum of the values for naphthalene and chroman.

and 67.0 g. of malic acid, contained in a 500-ml. round-bottomed flask, was added slowly 150 g. of concentrated sulfuric acid. The mixture was heated in an oil-bath held at about 150° until the evolution of gas had ceased, and was then slowly poured onto about 500 g. of ice. The tarry precipitate was collected on a filter and dried. The dry tar was extracted with hot ligroin (b. p. 70–90°),

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(14) Gilman, "Organic Chemistry," Vol. II, John Wiley and Sons, Inc., 440 Fourth Avenue, New York, N. Y., 1938, p. 1742.

(15) Shriner and Fuson, "The Identification of Organic Compounds," John Wiley and Sons, Inc., 440 Fourth Avenue, New York, N. Y., 1935, p. 139.

(16) Von Auwers, *Ann.*, **415**, 153 (1918).

(17) Von Braun, Grabowski and Kirschbaum, *Ber.*, **46**, 1274 (1913).

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. 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

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

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

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW YORK UNIVERSITY]

Indano-indanes[1]

BY JOSEPH B. NIEDERL AND RICHARD H. NAGEL[2]

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-

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[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.