similar to that used for paraffin hydrocarbons and the calculated products are in good agreement with the experimental data available.

Summary

The decomposition products of all paraffin hydrocarbons can be calculated quantitatively by assuming, first, that they decompose according to a chain mechanism; second, that methyl and ethyl groups are the only stable radicals; a larger radical apparently decomposes to yield one or more molecules of an olefin, and either a methyl group, an ethyl group or atomic hydrogen; and third, that the relative chances of reactions of primary, secondary and tertiary hydrogen atoms are 1:2:10, respectively.

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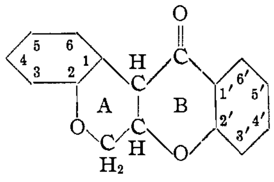
[Contribution from the Insecticide Division, Bureau of Chemistry and Soils]

Rotenone. XXVI. Synthesis of the Parent Substances of Some Characteristic Rotenone Derivatives

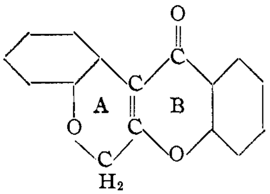
By F. B. LaForge

The investigation presented in this article deals with the synthesis of the parent substances of some of the characteristic rotenone derivatives, derritol, anhydroderritol, derrisic acid, dehydrorotenone and rotenonone.

Rotenone has been shown to be derived from the nucleus I,[1] with substituting groups occupying the positions 4 and 5 and 3′ and 4′

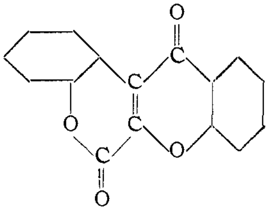


I

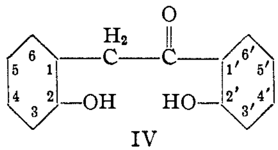


II

Dehydrorotenone has the same substituting groups as rotenone but contains two hydrogen atoms less in the dihydro-γ-pyrone system B and is derived from the nucleus II.



III



IV

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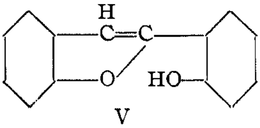
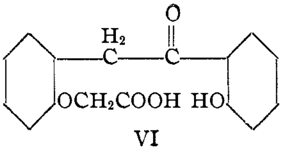
[1] LaForge and Haller, This Journal, **54**, 810 (1932); Butenandt, *Ann.*, **495**, 17 (1932); Takei, Miyajima and Ono, *Ber.*, **65**, 1041 (1932).

Rotenonone is derived from the nucleus III and differs from dehydrorotenone in having the two hydrogen atoms of the α-benzopyran A replaced by oxygen, the α-benzopyran becoming an α-benzopyrone system.

Derritol is derived from 2,2′-dihydroxydesoxybenzoin (IV), anhydroderritol from anhydro 2,2′-dihydroxydesoxybenzoin (V), and derrisic acid from 2-carbomethoxy-2′-hydroxydesoxybenzoin (VI).



V



VI

Derritol, anhydroderritol and derrisic acid have the same substituting groups occupying the same positions on the aromatic rings as rotenone.

Although none of the attempts to prepare the nucleus of rotenone I have been successful, it seemed advisable to record the results obtained, especially since a number of new and interesting compounds have been prepared as intermediates for the various synthetic plans.

Synthesis of the Parent Substances of Derritol and Anhydroderritol.—2,2′-Dihydroxydesoxybenzoin (IV), the parent substance of derritol, has not been described in the literature. It is of special importance because it also formed the starting material for the synthesis of the analogs of the rotenone derivatives described below. It differs from derritol in one important respect. Whereas both of the phenolic hydroxyls in 2,2′-dihydroxydesoxybenzoin are of approximately equal reactivity, the hydroxyl group of derritol in 2′ is diortho-substituted and hence is relatively unreactive.

The first attempt to prepare 2,2′-dihydroxydesoxybenzoin by demethylation of 2,2′-dimethoxydesoxybenzoin with hydriodic acid resulted in a small yield of the corresponding anhydride of formula V.

The 2,2′-dimethoxydesoxybenzoin used for this reaction was prepared from 2,2′-dimethoxydesyl chloride by reduction with zinc dust in aqueous alcoholic alkaline solution. The observation was subsequently made that 2,2′-dimethoxybenzoin[2] is itself reduced to the desoxy compound in good yield by zinc in alkaline solution. This method seems to be generally applicable to 2,2′-disubstituted benzoins although it has failed to give satisfactory results with other benzoins.[3]

Based on this observation, 2,2′-dihydroxydesoxybenzoin was prepared in considerable quantities by zinc–alkali reduction of the corresponding 2,2′-dihydroxybenzoin. This last-mentioned compound was prepared by applying the usual benzoin condensation to methoxymethylsalicylaldehyde, followed by elimination of the methoxymethyl groups.

(2) Rotenolone, which is a 2,2′-disubstituted benzoin derivative, is partly converted into derritol, a desoxybenzoin derivative, by zinc alkali reduction [LaForge and Smith, THIS JOURNAL, **52**, 1095 (1930)].

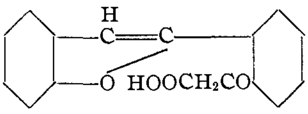
(3) Ballard and Dehn, *ibid.*, **54**, 3169 (1932).

Like derritol, 2,2′-dihydroxydesoxybenzoin is easily converted by dehydrating agents into its anhydride (V).

Synthesis of the Parent Substances of Derrisic Acid and Dehydrorotenone.—Derritol reacts with bromoacetic ester and sodium ethylate with the formation of derrisic acid. The reaction is accompanied by dehydration of part of the derrisic acid formed to dehydrorotenone and both compounds are products of the reaction.[4] Derrisic acid also results from alkaline hydrolysis of dehydrorotenone with addition of two moles of water.[5]

As applied to 2,2′-dihydroxydesoxybenzoin the first-mentioned reaction is more complicated than in the case of derritol because both phenolic groups of 2,2′-dihydroxydesoxybenzoin are equally reactive whereas in derritol the one in 2′, being diortho-substituted, is comparatively inert. Consequently, when 2,2′-dihydroxydesoxybenzoin reacts with one mole of sodium ethylate and one of bromoacetic ester, the 2- or the 2′-monosubstituted dihydroxydesoxybenzoin, a dibasic acid or a mixture of any of these might be expected.

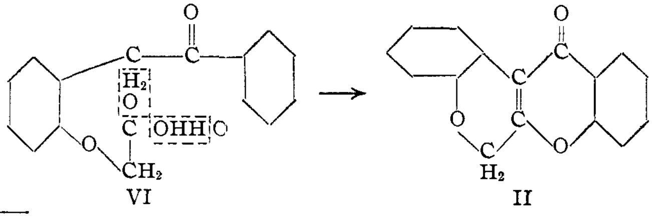
However, with the conditions described above, only one acid was isolated after saponification of the ester primarily formed. This acid, of formula $C_{16}H_{12}O_4$, was identical with the one obtained in good yield when anhydro-2,2′-dihydroxydesoxybenzoin (V) was allowed to react with one equivalent of sodium ethylate and one of bromoacetic ester. This acid can be expressed only by formula VII. It is apparent that substitution has occurred at 2′ and that dehydration has taken place during the reaction as indicated.



VII

When 2,2′-dihydroxydesoxybenzoin and two equivalents of sodium ethylate and one of bromoacetic ester are employed, in addition to the acid of formula VII, a considerable quantity of a compound of formula $C_{16}H_{10}O_3$ is obtained. This compound results from the dehydration of the acid of formula VI, formed by substitution of the CH_2COOH group at the 2 phenolic hydroxyl group.

Dehydration of the acid VI with loss of 2 moles of water has resulted in the formation of α-benzopyrano-γ-benzopyrone (II), the analog of dehydrorotenone.



VI II

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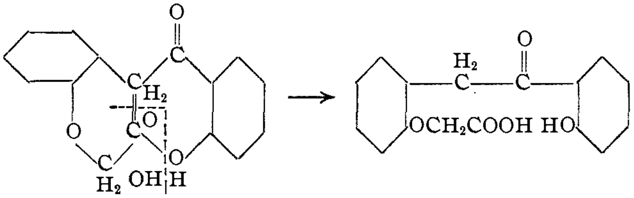
(4) LaForge, Haller and Smith, THIS JOURNAL, **53**, 4405 (1931).

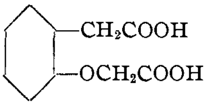
(5) Butenandt, *Ann.*, **464**, 253 (1928).

Analogous to the behavior of dehydrorotenone, α-benzopyrano-γ-benzopyrone (II) is hydrolyzed by alkali with addition of two moles of water to 2-carbomethoxy-2′-hydroxydesoxybenzoin (VI), the analog of derrisic acid, which can be obtained only in this indirect manner.



II VI

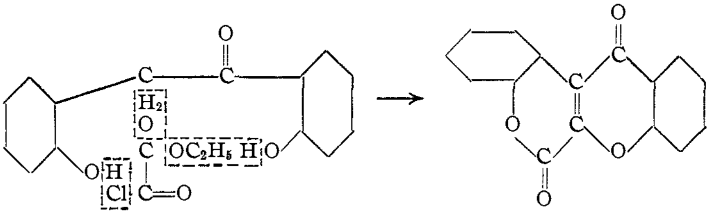
Like dehydrorotenone, α-benzopyrano-γ-benzopyrone (II) is not reduced by catalytic hydrogenation.



VIII

Hydrogen peroxide, in alkaline solution, oxidizes 2-carbomethoxy-2′-hydroxydesoxybenzoin to the known 2-carbomethoxyphenylacetic acid (VIII).[6] The oxidation takes the same course as in the case of derrisic acid,[7] and the oxidation product (VIII) is the analog of derric acid.

Synthesis of the Parent Substance of Rotenonone.—Rotenonone, an oxidation product of dehydrorotenone, has been synthesized by the action of chloro-oxalyl ethyl ester on derritol in pyridine solution.[8] The reaction between 2,2′-dihydroxydesoxybenzoin and chloro-oxalyl ethyl ester is analogous and results in the formation of α-benzopyrono-γ-benzopyrone of formula III.



III

Rotenonone is a yellow compound, but contrary to expectation α-benzopyrono-γ-benzopyrone is colorless.

Experimental Part

2,2′-Dimethoxydesyl Chloride.—Two and seven-tenths grams of 2,2′-dimethoxybenzoin[9] was cooled in an ice-bath and 1.4 g. of cold thionyl chloride was added. The material went into solution with gas evolution, and after a few minutes at room temperature the reaction product crystallized to a solid mass. Two or three cc. of methyl

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(6) Czaplicki, Kostanecki and Lampe, *Ber.*, **42**, 829 (1909).

(7) LaForge and Smith, THIS JOURNAL, **52**, 2878 (1930); LaForge, *ibid.*, **53**, 3898 (1931).

(8) LaForge, *ibid.*, **54**, 3377 (1932).

(9) Irvine, *J. Chem. Soc.*, **79**, 670 (1901).

alcohol was added, and the crystalline mass broken up, filtered and washed with a little more of the solvent. It was recrystallized from methyl alcohol and melted at 87°.

Anal. Calcd. for $C_{14}H_9OCl(OCH_3)_2$: OCH_3 (2), 21.34. Found: 21.32.

Reduction of 2,2′-Dimethoxydesyl Chloride to 2,2′-Dimethoxydesoxybenzoin.—Three and seven-tenths grams of 2,2′-dimethoxydesyl chloride was dissolved in 75 cc. of 95% alcohol, 25 cc. of 15% aqueous potassium hydroxide added and the solution boiled with 6 g. of zinc dust on reflux for three hours. Part of the alcohol was distilled off, and the solution was filtered from zinc, cooled, acidified with hydrochloric acid and after addition of water extracted with ether. The ether solution was washed several times with water, dried and the solvent removed. Nearly all the colorless oil distilled at about 170° in a vacuum of 1 mm. The distillate crystallized on cooling and after recrystallization from petroleum ether melted at 57°. The yield was 2.5 g.

Anal. Calcd. for $C_{14}H_{10}O(OCH_3)_2$: OCH_3 (2), 24.21. Found: 23.87, 24.56.

2,2′-Dimethoxydesoxybenzoin can be prepared under these same conditions in the same yield by employing 2,2′-dimethoxybenzoin instead of the corresponding desyl chloride.

Anhydro-2,2′-dihydroxydesoxybenzoin from 2,2′-Dimethoxydesoxybenzoin.—Instead of the expected 2,2′-dihydroxydesoxybenzoin, the corresponding anhydro derivative was obtained by demethylation of 2,2′-dimethoxydesoxybenzoin with hydriodic acid.

One and five-tenths grams of 2,2′-dimethoxydesoxybenzoin was boiled for one hour with 15 cc. of 50% hydriodic acid and 1 g. of phenol. After removal of the phenol by steam distillation, the solution was extracted with ether. About 1 g. of oil was obtained, which, however, still contained methoxyl. The material was again boiled with hydriodic acid as before and the solution distilled with steam. After about an hour crystals collected in the condenser and receiver, which were filtered off and washed with water. The material melted at 95–98°, and the analysis indicated that it was the anhydride of 2,2′-dihydroxydesoxybenzoin.

Anal. Calcd. for $C_{14}H_{10}O_2$: C, 80.00; H, 4.76. Found: C, 79.68, 79.04; H, 4.93, 4.72.

The same compound was later prepared in a different manner.

Salicylaldehyde Methoxymethyl Ether.—This compound has been described by Hoering and Baum,[10] who reported a 33% yield. By a slight variation of the method, a yield of more than 90% was obtained.

Twenty-four grams of sodium salicylaldehyde[11] was suspended in about 150 cc. of dry toluene, 14 g. of chloromethyl ether added and the suspension was shaken from time to time at room temperature. After about six hours the yellow sodium compound had disappeared, leaving a white colloidal suspension of sodium chloride. Dilute sodium hydroxide solution was added and the reaction mixture extracted with ether. The ether–toluene solution was extracted with dilute alkali and finally with water, and dried, and the solvents were distilled off, leaving a colorless oil, practically all of which distilled at about 128–130° at 11 mm. The yield was equal to the quantity of salicylaldehyde sodium employed.

2,2′-Dimethoxymethyl Ether Benzoin.—Twenty-five grams of salicylaldehyde methoxymethyl ether was dissolved in about 30 cc. of hot 50% alcohol, and 4 g. of potassium cyanide added, and the solution was boiled for two hours on reflux. The reaction product was extracted with ether, washed with water, dried with anhydrous sodium sulfate, and the solvent was then removed. The light brown oily ether residue

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(10) Hoering and Baum, German Patent 209,608 (1909).

(11) Helbig, *J. prakt. Chem.*, **77**, 365 (1908).

was distilled in a vacuum of about 11 mm. until the thermometer registered 135°. This fraction consists largely of unchanged salicylaldehyde methoxymethyl ether which can be redistilled and used for a subsequent operation.

The residue was further distilled at about 1 mm. and the fraction boiling between 200 and 220° collected. This material, which consists very largely of 2,2′-dimethoxymethyl ether benzoin, was used for the preparation of 2,2′-dihydroxybenzoin; yield, 50–60%.

A part was redistilled at 1 mm. and the fraction boiling at 200–210° used for analysis.

Anal. Calcd. for $C_{18}H_{20}O_6$: C, 65.09; H, 6.02. Found: C, 64.69; H, 5.97.

2,2′-Dihydroxybenzoin.—Fifteen grams of 2,2′-dimethoxymethyl ether benzoin was boiled with 100 cc. of 50% acetic acid containing 0.4 g. of sulfuric acid for twelve to fifteen minutes. Longer boiling decreases the yield.

The solution was cooled and poured into a solution of 50 g. of sodium carbonate containing cracked ice. The product which separated was gummy at first, but crystallized in a short time, especially on seeding. The mass was ground in a mortar with benzene and filtered from the solvent. In this manner the occluded water was largely removed. The product was recrystallized by dissolving in hot benzene, in which it is difficultly soluble, filtering and concentrating the solution.

The yield of pure substance was about 9 g., or 80%. The melting point was not sharp, 142–149°, and was not changed by further recrystallization. It gave a strong purple color with ferric chloride.

Anal. Calcd. for $C_{14}H_{12}O_4$: C, 68.85; H, 4.91. Found: C, 68.85, 69.09; H, 4.99, 5.14.

2,2′-Dihydroxydesoxybenzoin.—Three-gram portions of 2,2′-dihydroxybenzoin were boiled for eight hours with 90 cc. of alcohol, 30 cc. of 15% aqueous potassium hydroxide and 8 g. of zinc dust. The hot solution was filtered into dilute hydrochloric acid, the alcohol was distilled off in vacuum, and the residue extracted with ether. The ether solution was dried and evaporated, leaving a colorless oil which soon crystallized. The crude product was washed with a little cold benzene and recrystallized from 2 to 3 parts of the same solvent. The compound melted at 104°. The benzene mother liquor contained some other very soluble products which were not examined. The yield was 70–75%. The compound gave a dark purple color with ferric chloride.

Anal. Calcd. for $C_{14}H_{12}O_3$: C, 73.68; H, 5.26. Found: C, 73.45, 73.63; H, 5.28, 5.37.

Anhydride from 2,2′-Dihydroxydesoxybenzoin.—One gram of 2,2′-dihydroxydesoxybenzoin was boiled for five to ten minutes in 15 cc. of toluene with about 1 g. of phosphorus pentoxide. The solution was decanted, filtered and the solvent removed. The residue, which crystallized at once, was recrystallized from dilute alcohol. It melted at 95–98°. The yield was quantitative. It gave no color with ferric chloride.

Anal. Calcd. for $C_{14}H_{10}O_2$: C, 80.00; H, 4.76. Found: C, 78.86; H, 4.70.

Anhydro-2-hydroxy-2′-carbomethoxydesoxybenzoin.—Three-fourths of a gram of 2,2′-anhydrodihydroxydesoxybenzoin was dissolved in 15 cc. of sodium ethylate solution containing 0.082 g. of sodium (1 mol). Seven-tenths of a gram of ethyl bromoacetate was added and the solution boiled for one hour on reflux. Two-tenths of a gram of sodium in 8 cc. of alcohol was then added and the solution boiled for fifteen minutes. Water was added and the solution extracted with ether. The ether solution was extracted with sodium bicarbonate solution; the aqueous solution was acidified and extracted with ether. The ether residue crystallized promptly and was recrystallized from benzene. The yield of pure product was 0.7 g. It melted at 170°.

Anal. Calcd. for $C_{16}H_{12}O_4$: C, 71.64; H, 4.47. Found: C, 71.86, 72.03; H, 4.62, 4.68.

The same acid is also obtained from 2,2′-dihydroxydesoxybenzoin under the same conditions.

One and fourteen-hundredths grams of 2,2′-dihydroxydesoxybenzoin was dissolved in 15 cc. of absolute alcohol containing 0.12 g. of sodium (1 mol) and 0.84 g. of ethyl bromoacetate was added. The solution was boiled for ten minutes on reflux, after which a solution of 0.12 g. of sodium in 5 cc. of alcohol was added and the boiling continued for a few minutes. The solution, which turned dark on the second addition of sodium ethylate, was cooled, diluted with water, filtered, acidified and extracted with ether. The ether solution was extracted with sodium bicarbonate and the alkaline solution treated as above. The ether residue crystallized readily, and the product, after recrystallization from benzene, melted at 170° and was shown by the mixed melting point and examination of the crystals to be identical with the acid obtained from the anhydride. The yield was small.

Anal. Calcd. for $C_{16}H_{12}O_4$: C, 71.64; H, 4.47. Found: C, 72.13, 71.59; H, 4.42, 4.33. *Titration.* Subs. 0.0313, 0.0319: *N*/20 KOH, 2.48, 2.42 cc. Mol. wt. calcd. 268. Found: 262 and 264.

α-Benzopyrano-γ-benzopyrone.—One and fourteen-hundredths grams of 2,2′-dihydroxydesoxybenzoin was dissolved in 15 cc. of absolute alcohol containing 0.23 g. of sodium (2 mols) and 0.84 g. of ethyl bromoacetate was added. The solution was boiled for three hours on reflux, after which an equal volume of hot water was added. On cooling, long rods separated which were filtered off and recrystallized from 90% alcohol. The crude product is colored orange-yellow, but the pure compound is only slightly yellow and melts at 135°. The yield was about 0.15 g.

Anal. Calcd. for $C_{16}H_{10}O_3$: C, 76.80; H, 4.00. Found: C, 76.64, 76.91; H, 4.14, 4.11.

From the mother liquors more or less of the anhydro-2-hydroxy-2′-carbomethoxydesoxybenzoin of melting point 170° may be isolated by the method described above.

2-Carbomethoxy-2′-hydroxydesoxybenzoin.—Sixty-six hundredths gram of α-benzopyrano-γ-benzopyrone was boiled for three hours in 20 cc. of alcohol, and 6.6 cc. of 15% aqueous potassium hydroxide with 1.5 g. of zinc dust. The dark red solution rapidly became colorless. It was filtered into dilute hydrochloric acid, extracted with ether, and the ether solution was extracted several times with sodium bicarbonate solution. The alkaline solution was acidified and extracted with ether. The ether residue soon crystallized, and the product was recrystallized from benzene. It melted at 129°. The yield was 0.6 g. of pure material. The compound gives a purple color with ferric chloride.

Anal. Calcd. for $C_{16}H_{14}O_5$: C, 67.13; H, 4.89. Found: C, 67.58; H, 5.09. *Titration.* Subs. 0.0283 g.: *N*/20 KOH, 2.00 cc. Mol. wt. calcd. 286; found, 283.

2-Carbomethoxyphenylacetic Acid.—Five-tenths gram of 2-carbomethoxy-2′-hydroxydesoxybenzoin was dissolved in 12 cc. of 5% potassium hydroxide, the solution heated to boiling and 3 cc. of 30% hydrogen peroxide was added in three portions. The solution heated spontaneously and was finally boiled for a few minutes to remove the excess of peroxide. The solution was cooled, acidified and extracted with ether. The acid was extracted from the ether with sodium bicarbonate solution, freed with hydrochloric acid and taken up in ether. The ether residue crystallized at once and was recrystallized from butyl ether, from which it separated in spherical aggregates. It melted at about 154° after it had softened at a few degrees lower. The melting point recorded in the literature is 158°.[6]

Anal. Calcd. for $C_{10}H_{10}O_5$: C, 57.14; H, 4.71. Found: C, 57.32, 57.32; H, 4.91, 4.94. *Titration.* Subs., 0.0203 g.: *N*/20 KOH, 3.82 cc. Mol. wt. calcd. for dibasic acid, 210; found, 211.

α-Benzopyrono-γ-benzopyrone.—Five-tenths gram of 2,2′-dihydroxydesoxybenzoin was dissolved in 5 cc. of pyridine and 0.3 g. of chlorooxalyl ethyl ester added. After about an hour the reaction product began to separate in needles. After it had stood for several hours alcohol was added and the compound filtered, washed and recrystallized from alcohol, in which it is difficultly soluble. It melts with decomposition at about 240°.

Anal. Calcd. for $C_{16}H_8O_4$: C, 72.72; H, 3.03. Found: C, 72.09; H, 3.03.

COMPOUNDS PREPARED DURING UNSUCCESSFUL ATTEMPTS TO SYNTHESIZE THE NUCLEUS OF ROTENONE (I)

	Compound	Reactants G.	Cpd.	G.	Cpd.
1	Disalicylaldehyde ethylene ether (A)	4.5	$C_2H_2Br_2$	6	Na salicylaldehyde
2	Oxime of (A)	0.7 Few drops	A HAc	0.7 0.8	$NH_2OH\cdot HCl$ NaAc anhyd.
3	2,2′-Dihydroxybenzoin et. ether (B)	2	A	1	KCN, 50 cc. 50% EtOH
4	2,2′-Dihydroxybenzil et. ether	0.2	B		*d*
5	Acetyl-2,2′-dihydrox. benzoin et. ether	0.55	B	0.2	NaAc anhyd., HAc few drops, 5 cc. $(AC)_2O$
6	2,2′-Dihydroxydesyl chloride et. ether	2.7	B	2	Thionyl chloride

	Solvent and cc.		Heated for	Treatment	Recryst. from	Yield, g.	M. p., °C.
1	Abs. EtOH	20	7 hrs. in sealed tube	[a]	Benzene	1.5	130
2			5 hrs. on reflux	[b]	50% EtOH	...	170
3	50% EtOH	50	2 hrs. on reflux	[c]	95% EtOH	1	165
4	EtOH	5	10 min.		(Colorless rods)		200
5	$(Ac)_2O$	5	3 hrs.	[e]	95% EtOH		165
6			15 min.	[f]	MeOH		105

	Formula	Analyses, % Carbon Calcd.	Found		Hydrogen Calcd.	Found	
1	$C_{16}H_{14}O_4$	71.11	70.94	70.84	5.18	5.60	5.48
2	$C_{16}H_{16}N_2O_4$	N, calcd. 9.33; found, 9.17					
3	$C_{16}H_{14}O_4$	71.11	71.44		5.18	5.35	
4	$C_{16}H_{12}O_4$	71.71	71.55		4.48	4.78	
5	$C_{18}H_{16}O_5$	69.23	69.25	69.29	5.13	5.31	5.22
6	$C_{16}H_{13}O_3Cl$	66.55	66.59		4.50	4.61	

[a] Cooled, cryst. matter washed with EtOH and water to sep. NaBr, and dried. [b] Separated crystalline on addn. of water. [c] Cooled in ice and salt to cause crystals to separate. [d] Soln. boiled and Fehling's soln. added in small amounts to permanent blue color. Soln. cooled, sep. cryst. matter and Cu_2O filtered off and extracted by boiling with 20 cc. of EtOH. Cu_2O then filtered off and soln. concd. to 10 cc. The compound belongs to the class of pseudo benzils and does not react with ketone reagents.[12] [e] Equal vol. of MeOH added and solvent nearly boiled off. The acetyl deriv. came out on cooling. [f] MeOH caused compound to cryst. out.

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(12) Schoenberg, *Ber.*, **55**, 3746 (1922).

Summary

The parent substance of derritol, 2,2′-dihydroxydesoxybenzoin, was synthesized through the following steps: salicylaldehyde methoxymethyl ether ⟶ 2,2′-dimethoxymethyl ether benzoin ⟶ 2,2′-dihydroxybenzoin ⟶ 2,2′-dihydroxydesoxybenzoin.

Anhydrodihydroxydesoxybenzoin was prepared from this 2,2′-dihydroxydesoxy compound.

The analog of dehydrorotenone, α-benzopyrano-γ-benzopyrone, was obtained by the action of ethyl bromoacetate on the disodium compound of 2,2′-dihydroxydesoxybenzoin.

Hydrolysis of the α-benzopyrano-γ-benzopyrone with alkali gave 2-carbomethoxy-2′-hydroxydesoxybenzoin, the analog of derrisic acid.

The analog of rotenonone, α-benzopyrono-γ-benzopyrone, was obtained by the action of chlorooxalyl ethyl ester on 2,2′-dihydroxydesoxybenzoin.

WASHINGTON, D. C.

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Notes

The Synthesis of Isomeric Unsymmetrical Benzoins

BY SANFORD S. JENKINS

A convenient method, where applicable, for the synthesis of the isomeric unsymmetrical benzoins is to start from the corresponding desoxybenzoins. The method is well illustrated in the preparation of *p*-methoxy-α-hydroxybenzyl phenyl ketone (anisbenzoin). To a solution of *p*-methoxybenzyl phenyl ketone in carbon tetrachloride is added a molar equivalent of bromine dissolved in the same solvent. The mixture is exposed to the rays of a 500-watt tungsten lamp for about five minutes. The solvent is evaporated under reduced pressure, the remaining desyl bromide is dissolved in a small amount of absolute alcohol and two or three equivalents of sodium ethylate are then added. The mixture is shaken until no more sodium bromide is precipitated and then poured into an excess of dilute hydrochloric acid. The benzoin is separated and recrystallized from dilute alcohol; yield 65%, m. p. 89°. When mixed with benzanisoin the melting point was lowered 7–10°.

Anisbenzoin readily rearranges in the presence of alcoholic potassium cyanide to benzanisoin; yields of 60 to 70% were obtained [Jenkins, THIS JOURNAL, **53**, 3117 (1931). The study of their rearrangement is being continued].

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