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.

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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].

CHEMICAL LABORATORY OF
THE JOHNS HOPKINS UNIVERSITY
BALTIMORE, MARYLAND

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A Method for the Identification of the Acyl Group in Certain Esters

BY C. F. KOELSCH AND DAVID TENENBAUM

The characterization of an ester is usually carried out by saponification followed by the preparation of a derivative from each of the resulting products. The alcohol is usually easily separated and converted into a solid derivative, but experience has shown that despite the variety of methods available,[1] the sodium salt, contaminated as it is with sodium hydroxide, is not so easily dealt with.

Esters may be ammonolyzed with aqueous ammonia, but the amides formed are usually too water soluble to be of value as derivatives. The reaction of aromatic amines with aliphatic esters takes place too slowly to be of use in this connection.

The present method, an adaptation of a reaction discovered by Bodroux,[2] leads to the direct formation of *p*-toluidides from esters.

$$2C_7H_7NHMgBr + RCOOR' \longrightarrow RC(NHC_7H_7)_2OMgBr + R'OMgBr$$
$$RC(NHC_7H_7)_2OMgBr + HCl \longrightarrow MgBrCl + C_7H_7NH_2HCl + RCONHC_7H_7$$

Procedure.—An ether solution of four equivalents of ethylmagnesium bromide is prepared, and to this is added slowly a dry ether solution of four equivalents of *p*-toluidine. An ether solution of 1 g. of the ester is then added with shaking. After the mixture has been refluxed for five

TABLE I

TOLUIDIDES FROM ESTERS

Ester used	Yield of toluidide G.	Yield of toluidide %	M. p. of toluidide, °C., uncorr. Obs.	M. p. of toluidide, °C., uncorr. Lit.
Benzyl formate[a]	..	..	52–53	53
Ethyl acetate	..	..	145–146	145.5
Cyclohexyl acetate[a]	..	..	145–146	145.5
Ethylene propionate	1.04	55.4	124	126
Isobutyl butyrate	..	..	70–71	73–74
Ethyl isovalerate	0.75	51.7	108–109	110
Methyl caproate	1.06	66.4	74.5–75	75
Phenyl benzoate	0.56	53.2	157–158	158
Ethyl β-chlorolactate	..	*ca.* 16	164–165	[b,c]
Ethyl salicylate	0.7	51	155–156	155–156

[a] The water insoluble alcohol may prevent the solidification of the toluidide. It can be removed by short steam distillation. [b] *Anal.* Calcd. for $C_{10}H_{12}O_2NCl$: C, 56.2; H, 5.6. Found: C, 56.2; H, 5.7. [c] In this reaction there is also formed a basic substance, precipitated from the hydrochloric acid extracts with sodium hydroxide and separated from the excess *p*-toluidine by crystallization from benzene and then from xylene. It melts at 168–169°, contains no halogen, and is shown by analysis to be the expected *p*-toluidide of N-*p*-tolyl-iso-serine.

Anal. Calcd. for $C_{17}H_{20}O_2N_2$: C, 71.8; H, 7.0. Found: C, 71.5; H, 7.0.

(1) Kamm, "Qualitative Organic Analysis," John Wiley and Sons, New York, 1932, 2d ed., pp 176–183.

(2) Bodroux, *Compt. rend.*, **138**, 1427 (1904).

minutes, it is cooled and hydrolyzed with dilute hydrochloric acid. The ether layer is washed again with dilute hydrochloric acid and evaporated. The crude toluidide is purified by crystallization from dilute alcohol.

Table I summarizes the results obtained in this laboratory. The method failed when applied to the following dibasic esters: benzyl succinate, ethyl malonate, methyl oxalate, and methyl phthalate.

SCHOOL OF CHEMISTRY
UNIVERSITY OF MINNESOTA
MINNEAPOLIS, MINNESOTA

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COMMUNICATIONS TO THE EDITOR

PLATINUM OXIDE AND CARBON MONOXIDE

Sir:

In a previous publication [THIS JOURNAL, **54,** 4498 (1932)] it was shown that the reduction of palladium oxide by carbon monoxide requires a higher temperature than is necessary for reduction by hydrogen. A cause was found in the exceptional adsorption of carbon monoxide and dioxide by the palladium oxide. Since Langmuir [*ibid.*, **40,** 1398 (1918)] and also Taylor and Burns [*ibid.*, **43,** 1282 (1921)] found a much stronger adsorption of carbon monoxide and oxygen on platinum than on palladium it was reasonable to suppose that platinum oxide might reduce in the usual manner.

We have prepared samples of platinum oxide using the procedure and apparatus previously described and have established that platinum oxide reduces with carbon monoxide at 0°. The reaction is autocatalytic in type, having an induction period, and is similar in all ways to the reduction of copper oxide described by Jones and Taylor [*J. Phys. Chem.*, **27,** 623 (1923)]. A powdery 2-g. sample at 0° in a tube of 1 cm. diameter at a flow rate of 20 cc. of carbon monoxide per minute had an induction period of twelve minutes followed by an extremely rapid reaction. A sample first washed free of air by nitrogen gave no reaction in one hour at 0°, nothing at 10° in thirty minutes, but at 25° reacted immediately. A layer of recently reduced platinum practically eliminated the induction period. Platinum oxide thus shows none of the exceptional behavior found in the case of palladium oxide.

RUTGERS UNIVERSITY
NEW BRUNSWICK, NEW JERSEY
PAUL V. MCKINNEY
EDWIN F. MORFIT

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