Summary

The Clerget-invertase hydrolysis constant of sucrose was determined. The relation between sucrose concentration and this constant is expressed by the equation, constant = 131.17 + 0.073 c, where c is the number of g. of sucrose in 100 cc.

The value 0.521, which shows negligible variation over a considerable range of concentration, was found for the ratio of polarization of raffinose after invertase hydrolysis to the original polarization. The above values are applicable in enzymic analytical methods for the determination of sucrose and of sucrose and raffinose in mixture.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF SWARTHMORE COLLEGE]

ACTION OF ANHYDROUS ALUMINUM CHLORIDE ON CRESYL BENZOATES

BY EDWARD H. COX

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The action of anhydrous aluminum chloride on monohydric phenolic esters (the Fries reaction) as a method for preparing aromatic hydroxy ketones has been successfully applied.[1] Thus far, the method has been almost entirely limited to the action of aluminum chloride on the fatty acid esters of phenols. The yields of the resulting products, acyl phenols, have been variously reported as from poor to excellent. The present work deals with the action of aluminum chloride on the benzoic acid esters of the cresols as a method for preparing benzoyl cresols.

That this method possesses advantages over that of Friedel and Crafts for the preparation of benzoyl cresols there seems little doubt, from a review of the literature. The reaction of benzoyl chloride with phenols in the presence of anhydrous aluminum chloride often fails altogether or results in low yields of the benzoyl phenols,[1a,2] unless the hydroxyl group has been previously protected or the reaction carried out in nitrobenzene. On the other hand, benzoyl cresols are produced in excellent yields by the action of aluminum chloride directly on the cresyl benzoates.

The procedure for the conversion of each cresyl benzoate into its respective benzoyl cresol is described, but since they are all known and found in Beilstein,[3] only a tabular review of them is given. Although the structure of one of the benzoyl cresols has been assumed, their constitutional

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[1] (a) Fries and Finck, *Ber.*, **41,** 4276 (1908). (b) Fries and Pfaffendorf, *Ber.*, **43,** 214 (1910). (c) Auwers, *Ber.*, **47,** 3319 (1914); **49,** 813 (1916); (d) *Ann.*, **421,** 36 (1920); **447,** 162 (1926). (e) Fries and co-workers, *Ber.*, **54,** 717 (1921); **56,** 1304 (1923).

[2] Heller, *Ber.*, **46,** 1498 (1913).

[3] Beilstein, "Handbuch der organischen Chemie," Julius Springer, Berlin, **1925,** 4th ed., vol. 8.

formulas have not been determined. Since all are readily converted into substituted toluic acids of known constitution, by treatment with fused potassium hydroxide,[4] definite proof of their structure is now established. The substituted toluic acids are also shown in tabular review.[5]

Experimental Part

_p_-Benzoyl-_o_-cresol,[6] $C_6H_3(OH).(CH_3).(COC_6H_5)(1,2,4)$. **Action of Anhydrous Aluminum Chloride on _o_-Cresyl Benzoate.**—To 50 g. of the ester, stirred and heated to 130°, is added in small portions 40 g. of anhydrous aluminum chloride. After the addition the temperature is slowly increased to 160° for about three-quarters of an hour. The melt is decomposed in warm dilute hydrochloric acid, and the resulting residue is filtered, washed and dried. The residue is best purified by distillation (240–260°, at 12–15 mm.); yield, 45.5 g.

This ketone is readily converted into *o*-homo-*p*-hydroxybenzoic acid when fused at 350° with potassium hydroxide.

_o_- and _p_-Benzoyl-_m_-cresols,[2] $C_6H_3(OH).(CH_3).(COC_6H_5)$, (*a*) (1,3,4), (*b*) (1,3,6). **Action of Anhydrous Aluminum Chloride on _m_-Cresyl Benzoate.** (*a*).—This ketone (16 g.) is formed along with its isomer (*b*) (25 g.) when 50 g. of the ester is treated with 40 g. of aluminum chloride in carbon disulfide for three hours. The carbon disulfide is distilled off and the reaction mixture is heated and stirred for a short time at 90°. An oil results upon decomposing the melt and is distilled in a vacuum. The fraction distilling at 195–215°, at 14 mm., is a yellow oil and solidifies after long standing, while the portion distilling at 220–240°, at 13 mm., is colorless; total yield, 41 g. The second fraction is further purified by treating it with hot petroleum ether which removes the *ortho* isomer.

p-Benzoyl-*m*-cresol yields *m*-homo-*p*-hydroxybenzoic acid when treated with fused

TABLE I

MELTING POINTS, ANALYSES AND YIELDS OF THE BENZOYL CRESOLS

		Analyses[a]					
	M. p., °C.	Subs., g.	H_2O, g.	CO_2, g.	C, %	H, %	Yield, %
p-Benzoyl-*o*-cresol	173–174	0.2218	0.1103	0.6426	79.01	5.56	91
p-Benzoyl-*m*-cresol	129	.1353	.0690	.3934	79.29	5.71	32[b]
o-Benzoyl-*m*-cresol	63	.2531	.1323	.7332	79.01	5.85	50[b]
o-Benzoyl-*p*-cresol	87	.1989	.1049	.5769	79.10	5.88	94

[a] Calcd. for $C_{14}H_{12}O_2$: C, 79.21; H, 5.70.

[b] Combined yield, 82%.

TABLE II

MELTING POINTS AND ANALYSES OF THE HYDROXYTOLUIC ACIDS

		Analyses,[a]				
	M. p., °C.	Subs., g.	H_2O, g.	CO_2, g.	C, %	H, %
o-Homo-*p*-hydroxybenzoic acid	174–175	0.1900	0.0931	0.4395	63.08	5.48
m-Homo-*p*-hydroxybenzoic acid	176–178	.1796	.0875	.4163	63.22	5.45
m-Homosalicylic acid	177–178	.2101	.1034	.4873	63.25	5.49
p-Homosalicylic acid	149–150	.0883	.0440	.2047	63.22	5.57

[a] Calcd. for $C_8H_8O_3$: C, 63.13; H, 5.30.

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[4] Doebner, *Ber.*, **10**, 1971 (1877); *Ann.*, **210**, 253 (1881).

[5] Ref. 3, 3rd ed., **1920**, vol. 2, pp. 1544–1549.

[6] Ref. 2, p. 1502; Ref. 3, p. 178.

potassium hydroxide, while *o*-benzoyl-*m*-cresol gives a good yield of *m*-homosalicylic acid when treated in the same way.

When *m*-cresyl benzoate reacts with aluminum chloride without a solvent at about 130° it is converted practically quantitatively into the *o*-benzoyl-*m*-cresol. Apparently, high temperatures favor the formation of the *ortho* isomer.

o-Benzoyl-*p*-cresol, $C_6H_3.(OH).(CH_3).(COC_6H_5)(1,4,2)$. Action of Anhydrous Aluminum Chloride on *p*-Cresyl Benzoate.—This ketone is formed when 40 g. of the chloride is added in small portions to 50 g. of the ester which is stirred and heated to 140° for 15–20 minutes. The reaction is completed at 200°. The solid residue which results upon decomposing the melt is purified by repeatedly dissolving it in 20% sodium hydroxide solution and reprecipitating with hydrochloric acid. The dry residue weighs 47 g.

p-Homosalicylic acid is formed when *o*-benzoyl-*p*-cresol is fused with potassium hydroxide.[7]

Summary

Direct action of anhydrous aluminum chloride on the cresyl benzoates offers a good method for producing benzoyl cresols in excellent yields. The method possesses advantages over that of Friedel and Crafts.

The constitution of the benzoyl cresols has been proved by converting them into hydroxytoluic acids of known constitution by means of fused potassium hydroxide.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PRINCETON UNIVERSITY]

THE ELECTRIC MOMENTS OF SUBSTITUTED BENZENE MOLECULES AND THE STRUCTURE OF THE BENZENE RING

BY CHARLES P. SMYTH AND STANLEY O. MORGAN

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Information concerning molecular structure may often be obtained from a consideration of the distribution of the electric charges in a molecule as revealed by the dielectric behavior of the substance. If the center of gravity of the positive charges does not coincide with that of the negative, the molecule may be regarded as containing an electric doublet, that is, two charges of equal size but opposite sign, very close together, the imaginary line joining the two charges being termed the axis of the doublet and the magnitude of the doublet being measured by its electric moment, the product of one of the charges by the length of the axis. A method of calculating the electric moment of a molecule from its structure has been discussed in an earlier paper.[1] It may be convenient to resolve the system of positive and negative charges in a molecule into two or more doublets, the resultant of the moments of these doublets being the moment of the molecule as a whole.

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[7] Jacobsen, *Ber.*, **14**, 2352 (1881).

[1] Smyth, *Phil. Mag.*, **47**, 530 (1924).