



Fig. 1.

It will be necessary to adduce further proof, especially in the way of reactions of this new compound, before giving it a name or attempting to decide with certainty just what structure is actually present. This work is being extended to other nitrosochlorides.

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CONTRIBUTIONS TO THE KNOWLEDGE OF FOREST PRODUCTS.

III. IDENTIFICATION OF PHENOLS AS 3,5-DINITROBENZOIC-ACID ESTERS.¹

BY R. C. BROWN AND ROLAND E. KREMERS.

Introduction.—In the course of an investigation of some cohobated aqueous distillates, one of us became interested in the use of 3,5-dinitrobenzoic acid as a reagent for identifying the lower saturated alcohols.² By means of it a solid characteristic derivative of methyl alcohol was readily obtained.³ Encouraged by this fact, the same reagent was used in the course of some as yet unpublished work on guaiacol. From this it was but a step to the thought of applying this acid as a reagent in the identification of phenols as a group.

Theoretical Considerations.—The phenols, like the alcohols, are hydroxy substitution products of hydrocarbons. The chief difference is that the rest of the molecule has an "acidifying" effect on the fundamental properties of the —OH group. Hence it is that the reactions involving the —OH group of phenols differ in degree rather than in kind from the reactions of the alcohols. For the same reason, practically all general methods of identifying alcohols have been tried with phenols with suitable modifications.

Of these the most important is perhaps the formation of phenylurethanes from phenylisocyanate. The method itself is excellent and the resulting products apparently are uniformly crystalline. However, it is not in general use, probably due to the cost of the reagent and its instability. The benzoic acid esters, prepared by the Schotten-Baumann reaction, are most generally used, but have a

¹ Based on part of a thesis submitted by R. C. B. to the Graduate Faculty of Vanderbilt University in partial fulfillment of the requirements for the degree of M.S., June 1922.

² Univ. of Wis. Pharm. Expt. Sta., Circular 11, Oct. 1920.

³ See Mulliken, "Identification of Pure Organic Compounds," Vol. I, p. 68.

serious drawback in that some are liquids. Hence it becomes impossible to distinguish at times between the presence of a truly liquid ester, or a mixture rendered liquid by impurity. The fact that the nitro group raises the melting point suggested that this difficulty might be obviated in that all 3,5-dinitrobenzoic acid esters might be crystalline. Hence a liquid or resinous product would point clearly to contamination.

Another method that has been used somewhat is the conversion of the phenol into the carbonate by means of phosgene. The objection to this lies in the toxicity of the reagent and in the difficulty of procuring it. Of other methods which do not involve esterification, the formation of nitro- and brom-substitution products may be mentioned. The resultant compounds appear to be characteristic only in certain instances, and the reactions involved are not among those best suited for identification. A recent method suggested by Reid depends upon ether formation.¹

Preparation of Esters.—The first step in the preparation of the esters was the conversion of 3,5-dinitrobenzoic acid² into the acid-chloride.³ This was accomplished by warming together in a small distilling flask 10 Gm. of acid and 10 Gm. of phosphorus pentachloride. When the reaction was complete the phosphorus oxychloride was distilled off under diminished pressure from a water-bath. The acid chloride was then poured out while still liquid, allowed to crystallize, and kept on a porous tile in a desiccator.

The next step was the formation of the sodium or potassium phenolate by allowing a slight excess of phenol to act on the metal suspended in dry xylene. Heat was used to facilitate reaction. After the complete disappearance of the metal, the acid chloride was added. The slightly exothermic reaction was completed by heating. The sodium or potassium chloride precipitated and the ester went into solution. Accordingly the xylene solution, after cooling, was transferred to a separatory funnel, washed with water to remove salts, with 5 percent NaOH to remove unchanged acid, acid-chloride, and phenol, and again with water until neutral. The ester was then recovered by the spontaneous evaporation of the solvent and recrystallized from alcohol.

The following compounds were prepared and analyzed:

Ester of.	Melting point.	Esterification.	N ₂ calculated.	N ₂ found.
Phenol	145-46° C.	Fairly rapid	9.72	9.73
<i>o</i> -Cresol	133-34° C.	Slow	9.27	9.34
<i>m</i> -Cresol	160-62° C.	Slow	9.27	9.30
<i>p</i> -Cresol	180-82° C.	Fairly rapid	9.27	9.34
Guaiacol	138-39° C.	Fairly rapid	8.81	8.75
Carvacrol	76-77° C.	Fairly rapid	8.14	8.33
Thymol	102-03° C.	Fairly rapid	8.14	8.32

The esters so far prepared have all been crystalline and are characterized by definite, rather widely separated melting points. Whereas the benzoic acid esters of *o*-cresol and carvacrol are liquids, the 3,5-dinitrobenzoic acid esters are solids.

¹ E. E. Reid, "Identification of Phenols," *J. Am. Chem. Soc.*, 39, 1917, 304.

² This acid can now be procured from the Eastman Kodak Co., presumably also from Kahlbaum. For preparation in smaller quantities see *Ber.*, 28, 1800, 1895.

³ *J. prakt. Chem.*, [2] 69, 455, 1904.