Reaction with Potassium Permanganate.—To a solution of 2.1 g. of triphenylchloromethane in 30 cc. of alcohol-free acetone was added 0.8 g. of potassium permanganate, dissolved in the same solvent. The permanganate was reduced instantly and the chloride was converted quantitatively into the carbinol. Identical results were obtained with the fluoride.

It is our intention to study the lability of fluorine in tertiary aliphatic carbinol fluorides; these we hope to prepare by the action of acetyl fluoride on the carbinols.

Summary

Triphenylfluoromethane has been synthesized and described.

The ordinary method for the preparation of triphenylmethyl—action of silver, mercury or zinc on a solution of a triphenylhalomethane—fails in the case of the fluoride; no trace of fluorine is removed by these metals. In certain other reactions the fluoride behaves similarily to the chloride.

In general it may be stated that the fluorine in triphenylfluoromethane is much less labile than the chlorine in triphenylchloromethane.

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[Contribution from the Chemical Laboratory of the University of Illinois]

SIMPLIFICATION OF THE GATTERMANN SYNTHESIS OF AROMATIC ALDEHYDES. II

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In a recent communication from this Laboratory,[2] a convenient simplification of the Gattermann reaction for the synthesis of certain hydroxyaldehydes was described. Various phenols were treated in dry ether with zinc cyanide, and then dry hydrogen chloride was passed in. By this procedure, anhydrous hydrogen cyanide was formed in the reaction mixture and condensed with the hydrogen chloride and phenol to give a condensation product which was hydrolyzed to an hydroxyaldehyde. The zinc chloride which was produced at the same time acted as an effective condensing agent. Thus the most disagreeable feature of the Gattermann reaction, the handling of anhydrous hydrogen cyanide, was avoided. An easy method for the preparation of zinc cyanide was also described.

Gattermann[3] found that, in order to prepare aldehydes from certain phenols or phenol ethers, it was necessary to use anhydrous aluminum chloride as a condensing agent with the phenol or phenol ether, hydrogen cyanide and hydrogen chloride, zinc chloride being unsatisfactory. A study has been made of the synthesis of the aldehydes from various phen-

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[1] This communication is an abstract of a thesis submitted by Edna Montgomery in partial fulfilment of the requirements for the degree of Master of Science in Chemistry at the University of Illinois.

[2] Adams and Levine, This Journal, **45**, 2373 (1923).

[3] Gattermann, *Ann.*, **357**, 313 (1907).

ols and phenol ethers, using aluminum chloride, hydrogen chloride and zinc cyanide in place of hydrogen cyanide. The reactions run very smoothly, and the expected products were obtained thus making the synthesis of these aldehydes possible without the use of anhydrous hydrogen cyanide.

Phenols or phenol ethers and zinc cyanide were mixed with benzene as a diluent so that stirring could be accomplished more readily, and dry hydrogen chloride passed in to the saturation point. Anhydrous aluminum chloride was then added and hydrogen chloride again passed in. The imide hydrochlorides of the aldehydes separated. These were decomposed with hydrochloric acid and the aldehydes obtained by one or another of the usual procedures.

The zinc chloride which is formed in the reaction mixtures does not interfere in any way with the condensations. The only noticeable difference between this procedure and the one using anhydrous hydrogen cyanide is that the imide hydrochlorides almost always separate from the reaction mixtures as a sticky mass, probably a mixture or a compound with zinc chloride. In contrast to the imide hydrochlorides obtained from those phenols[2] which formed by condensation in dry ether with zinc cyanide and hydrogen chloride, these imide hydrochlorides were not so readily decomposed by water or very dilute hydrochloric acid, but required refluxing with 10–20% hydrochloric acid. They were then rapidly decomposed with the production of aldehydes in yields equal to those usually obtained, provided anhydrous hydrogen cyanide was used in place of zinc cyanide.

The method has been applied to the preparation of aldehydes from anisole, *p*-cresol methyl ether, resorcinol dimethyl ether, diphenyl ether, *β*-naphthol methyl ether, *o*-cresol and thymol with excellent results. These represent a sufficient number of condensations to warrant the conclusion that any aldehydes that can be synthesized by the older Gattermann procedure may be prepared equally well by this modification.

Experimental Part

Zinc Cyanide.—Zinc cyanide for this investigation was made according to the procedure described in the previous communication on the modification of the Gattermann reaction. It has been found that conversion of 200 g. of zinc chloride to zinc cyanide can easily be carried out in about 30 minutes. When the 96–98% potassium cyanide was used for the preparation, no magnesium chloride was necessary and the zinc cyanide was 95–98% pure.

Phenols and Phenol Ethers.—The phenols and phenol ethers were made by the usual procedures and boiled over a range of 2°.

General Method of Preparation of Various Phenols and Phenol Ethers.—A 600cc. wide-mouth bottle with a flat bottom was fitted with a stopper holding a mechanical stirrer with a mercury seal, an adapter holding a reflux water condenser, and an inlet tube, preferably with wide mouth to prevent any chance of clogging from the precipitate, extending nearly to the bottom of the flask or bottle. To the inlet tube was attached a dry hydrogen chloride generator. To the top of the condenser was connected a tube leading to a wash bottle containing sulfuric acid; from this a tube was led to a safety bottle and from the latter a tube to the surface of a sodium hydroxide solution.

In the bottle was placed about 30 g. of the phenol or phenol ether in approximately three times its volume of dry benzene. Sufficient powdered dry zinc cyanide was then added, equivalent to about two molecules for every molecule of phenol or phenol ether. The mixture was cooled, the mechanical stirrer was started and dry hydrogen chloride was passed in rapidly for half an hour to an hour. After this treatment, the mixture was kept cool, and then, without stopping the stirring, the condenser was removed and 1.5 molecular equivalents of powdered anhydrous aluminum chloride was slowly added at one time. Stirring was continued and hydrogen chloride again passed in very slowly while the mixture was heated at 40–45° for three to four hours.

The material was added to an excess of 10% hydrochloric acid, which generally caused a heavy precipitate of imide hydrochloride to separate. This mixture was refluxed for half an hour, thus causing a rapid decomposition with the formation generally of an oily product, the aldehyde. The aldehyde could then be extracted directly or filtered from this hydrogen chloride-benzene mixture or it could be steam-distilled and then extracted from the distillate and finally purified by distillation or crystallization.

The benzene was used so that mechanical stirring could be carried on more satisfactorily. Although Gattermann did not use this solvent in all cases, it is necessary to do so when zinc cyanide is employed.

An attempt was made merely to use powdered sodium or potassium cyanide in the above reaction in place of zinc cyanide. The results were entirely unsatisfactory, the yields of products being very low. An attempt was also made without success to replace the benzene by other solvents.

The same conditions as were found most suitable by Gattermann for the preparation of each of a large number of aldehydes can undoubtedly be used when zinc cyanide is employed in place of hydrogen cyanide. The only difference is the more vigorous hydrolysis of the imide hydrochlorides after they have formed and the necessity of always using a solvent in the initial condensation.

Anisole.—From 30 g. of anisole, 52 g. of zinc cyanide, 45 g. of aluminum chloride and 65 g. of benzene was obtained 35.5 g. (quantitative) of anisaldehyde boiling at 246–248°.

After decomposition with hydrochloric acid, the mixture was steam-distilled. The benzene was removed and the anisaldehyde, with traces of anisole, collected. This was separated and shaken with sodium bisulfite. The traces of anisole were thus removed, and the anisaldehyde was obtained by the action of alkali and then distilled.

p-Cresol Methyl Ether.—From 30 g. of p-cresol methyl ether, 52 g. of zinc cyanide, 45 g. of aluminum chloride and 75 g. of benzene, was obtained 29.5 g. (80% of the calculated amount) of aldehyde boiling at 250–252°.

It was obtained from the reaction mixture in exactly the same way as the anisaldehyde.

Resorcinol Dimethyl Ether.—From 25 g. of resorcinol dimethyl ether, 40 g. of zinc cyanide, 38 g. of aluminum chloride and 100 g. of benzene, was obtained 25 g. of aldehyde (an 80% yield).

The product was obtained as described under the two previous aldehydes but was purified by crystallization from ligroin, from which white needles were formed melting at 71°.

Diphenyl Ether.—From 30 g. of diphenyl ether, 52 g. of zinc cyanide, 45 g. of aluminum chloride, and 70 g. of benzene, was obtained 18 g. of aldehyde (a 50% yield); b. p., 188–190° (20 mm.).

The aldehyde was obtained as described above.

o-Cresol.—From 30 g. of o-cresol, 52 g. of zinc cyanide, 45 g. of aluminum chloride and 90 g. of benzene, was obtained 14.5 g. of aldehyde (a 38% yield).

Since the aldehyde could not be steam-distilled, the unchanged o-cresol and benzene were removed by steam distillation and the aldehyde salted out from the residual solution, then extracted with ether. It was readily purified by crystallization from hot water with boneblack. It yielded white crystals melting at 118°.

Thymol.—From 20 g. of thymol, 37 g. of zinc cyanide, 30 g. of aluminum chloride and 60 g. of benzene, was obtained 23.5 g. of aldehyde (a quantitative yield).

The aldehyde was isolated in exactly the same way as that from o-cresol and formed white needles melting at 133°.

β-Naphthol Methyl Ether.—From 30 g. of β-naphthol methyl ether, 52 g. of zinc cyanide, 45 g. of aluminum chloride and 150 g. of benzene, was obtained 36 g. of aldehyde (a quantitative yield).

The aldehyde was isolated as were those from thymol and o-cresol. It was purified by crystallization from ligroin, giving white needles; m. p., 83°.

Summary

The introduction of an aldehyde group into phenols and phenol ethers by the Gattermann method, using hydrogen cyanide, hydrogen chloride and aluminum chloride, may be carried out more conveniently and in equally good yields by the substitution of zinc cyanide for hydrogen cyanide.

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