creasing or decreasing the amount of sulfuric acid causes a lower yield. Absolute alcohol does not have any advantage over 95% alcohol nor does fuming sulfuric acid have any advantage over the ordinary concentrated acid.

The analysis of the crude diethyl sulfate was carried out as follows.

A 2 to 3 g. sample of diethyl sulfate, accurately weighed, is placed into a 250cc. Erlenmeyer flask, and 5 g. of barium hydroxide and 100 cc. of water are added. The mixture is heated just below the boiling point for three hours. It is allowed to cool and the excess of barium hydroxide removed by filtration. The filtrate is saturated with carbon dioxide, filtered and the residue thoroughly washed with distilled water. Sulfuric acid is then added to the filtrate until the barium is completely precipitated as barium sulfate. The mixture is then heated to boiling and filtered and the precipitate is washed, dried and weighed.

In two such analyses 51.03 and 51.27% of sulfur trioxide equivalent were found, as compared with the calculated value, 51.94.

Summary

A convenient process for the laboratory preparation of diethyl sulfate is given, together with a method for the analysis of this compound.

SEATTLE, WASHINGTON

[CONTRIBUTION FROM THE RESEARCH LABORATORY, EASTMAN KODAK COMPANY, No. 199]

A MODIFICATION OF THE SANDMEYER SYNTHESIS OF NITRILES

BY H. T. CLARKE AND R. R. READ

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The convenient method devised by Sandmeyer[1] for the replacement of aromatic amino groups by the nitrile radical involves the formation of a solution of potassium cuprocyanide by the addition of cupric sulfate to potassium cyanide, and the addition of an acid solution of a diazonium salt to the resulting mixture. During the reduction of the cupric salt to the cuprous condition cyanogen is liberated, while hydrogen cyanide is evolved on adding the acid solution to the cuprocyanide mixture. Modifications of the original process have been suggested[2] but apparently no attempt has ever been made to avoid the evolution of poisonous gases.

We have found that a solution of sodium cuprocyanide can be very satisfactorily prepared by dissolving cuprous chloride in sodium cyanide solution; when the diazonium solution is neutralized under suitable conditions, its reactivity is, in all cases which we have examined, unimpaired. When a solution of benzenediazonium chloride, which has previously been neutralized at 0–4°, is poured into a cold solution of sodium cupro-

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[1] Sandmeyer, *Ber.*, **17**, 2653 (1884); **18**, 1492, 1496 (1885).

[2] *Ber.*, **19**, 756 (1886); **23**, 1026 (1890).

cyanide, a light yellow precipitate of apparently oily nature at once separates; this appears to be extremely unstable even at 0° and soon collects on the surface of the watery liquid as a dark brown oil. When, now, the mixture is allowed to stand undisturbed, before many minutes an extremely vigorous reaction takes place in this surface layer and gas is violently disengaged with evolution of heat and the production of large volumes of a yellow fog smelling strongly of phenyl isocyanide. This decomposition cannot be prevented by holding the aqueous layer at a low temperature; the upper part of the vessel becomes warm even when ice is present in the lower part. We have, however, found it possible to control the decomposition of the addition product by vigorous stirring combined with the addition of an inert solvent, such as benzene, which not only acts as a diluent but facilitates the distribution of oily materials through the cold, aqueous liquid. In this way the spontaneous decomposition which takes place in the cold is prevented from raising the temperature to the point at which it may become violent. Under these conditions the product is free from isocyanide.

The yields obtained by this method are fully equal to those obtainable by the original Sandmeyer process or any of its suggested modifications in all the cases which we have tried. It is interesting to note that in one instance examined previously by one of the authors with W. R. Kirner[3] a smooth reaction (73% yield) was obtained with diazotized *p*-aminobenzoic acid without the addition of benzene and without mechanical stirring; in this case no separation of intermediate product took place, owing to the presence of the acid group.

Experimental Part

The cuprous chloride prepared from 1250 g. of crystallized cupric sulfate by the method recommended by Marvel and McElvain[4] is suspended in 2 liters of cold water in a 15-liter stone crock provided with a mechanical stirrer, and a solution of 650 g. of commercial (96–98%) sodium cyanide in 1 liter of water is added with stirring.[5] The cuprous chloride dissolves with evolution of heat. The resulting solution is then cooled by surrounding the crock with ice water and is finally chilled to 0–5° by the addition of ice. One liter of benzene is then poured onto the surface, and a cold solution of the diazotized amine (4 g.-mols.) which has previously been neutralized at 0–5° by means of sodium carbonate[6] is slowly added, such vigorous stirring being maintained that the benzene is continually drawn under the surface. During the addition, which occupies about 30 minutes, the temperature is held at 0–5° by the occasional addition of ice. As soon as the diazonium solution comes into contact with the cuprous cyanide, a

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[3] Unpublished observation.

[4] "Organic Syntheses," John Wiley and Sons, **1923**, vol. 3, p. 33.

[5] For the preparation of large quantities at a time it has been found advantageous to suspend the cuprous chloride in water, add the sodium cyanide in solid form, and stir until solution is complete.

[6] The use of sodium hydroxide avoids the evolution of gas but is not recommended on account of the difficulty in maintaining a low temperature.

dark yellow oily precipitate is formed which at once begins to give off nitrogen; the resulting nitrile is taken up by the benzene as soon as it forms. When all has been added the temperature is held at 0–5° for 30 minutes longer and is then allowed to rise to that of the room (20–25°), which usually requires about three hours. After the mixture has been stirred for two hours longer the crock is surrounded by hot water or steam and warmed to 50° without the stirring. The mixture is then allowed to stand until cool, when the aqueous layer is drawn off and the upper, oily layer distilled, first in a current of steam and finally under atmospheric or reduced pressure.

In this manner yields of nitriles amounting to 60–70% of the calculated quantity have been obtained from aniline, *o*-toluidine, *p*-toluidine and *p*-bromo-aniline, while a 55% yield of α-naphthonitrile[7] was obtained from α-naphthylamine. The reaction can be carried out on a considerably larger scale (over 50 g.-mols.) with no diminution of yield.

Summary

The conversion of primary aromatic amines into the corresponding nitriles by diazotization and treatment with cuprocyanide solutions can be carried out in neutral or weakly alkaline solution, so that the liberation of hydrogen cyanide is avoided. The yields fully equal those obtainable by the older method.

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[Contribution from the Chemical Laboratory of Harvard University]

THE MECHANISM OF THE DECOMPOSITION OF BETA-BROMOPHOSPHONIC ACIDS IN ALKALINE SOLUTION

By James B. Conant and Ernest L. Jackson

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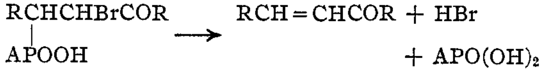
Certain β-bromophosphonic acids are rapidly and quantitatively decomposed by dissolving in aqueous alkaline solutions[1] according to the following equation.



$$\mathrm{R\underset{\displaystyle APOOH}{\underset{|}{C}}HCHBrCOR} \longrightarrow \mathrm{RCH{=}CHCOR + HBr + APO(OH)_2}$$

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$(\mathrm{R} = \text{aryl};\ \mathrm{A} = \mathrm{OH},\ \mathrm{C_6H_5}\ \text{or}\ \mathrm{C_6H_5O})$

In an earlier paper[2] it was suggested that the mechanism of this reaction might be similar to that proposed by Erlenmeyer[3] for the decomposition of β-halogen acids, and might involve the formation of an inner ester

[7] For the isolation of the nitrile, steam distillation under reduced pressure has been found most satisfactory.

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[1] (a) This Journal, **42,** 830 (1920); (b) *ibid.*, **43,** 1665 (1921); (c) *ibid.*, **44,** 2530 (1922); see also (d) *ibid.*, **43,** 1677 (1921).

[2] *Ibid.*, **43,** 1665 (1921).

[3] Erlenmeyer, *Ber.*, **13,** 305 (1880).