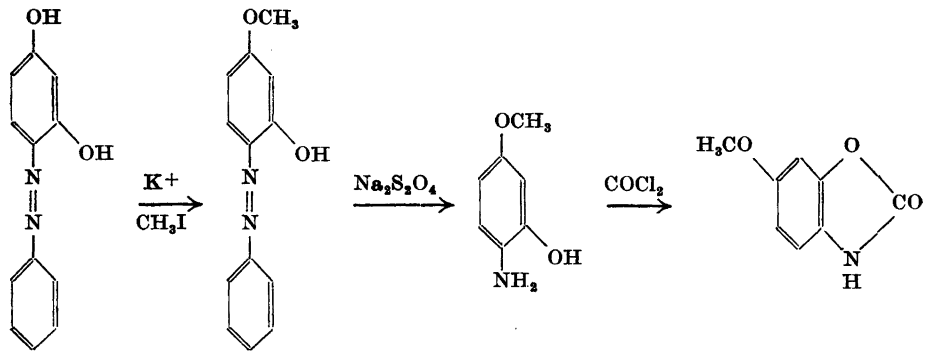

I II III IV

Pure *p*-benzene-azo-resorcine (I) was obtained by the method of Will and Pukall [2].

The methylation was done by the method of Bechold [3], with the following modifications: a) methyl iodide was used in the proportion 2 moles to 1 mole of the dry potassium salt of I; b) the reaction time was reduced from 6 h to 3 h (yield: 6 h, 1.5 %; 3 h, 14 % theor.).

2-Hydroxy-4-methoxy-aniline (III) is very easily oxidized wherefore the following stages were carried out in a carbon dioxide atmosphere: a) II was reduced in a boiling alcohol solution with a slight excess of a saturated solution of sodium hyposulphite in water [4], the mixture was neutralized with barium carbonate and evaporated almost to dryness (the aniline is removed with the vapour); b) III was extracted from the remaining mixture by peroxide-free ether and after evaporation of the ether it was mixed with glacial acetic acid, about ten times its weight, when the acetate of III precipitated. Phosgene was bubbled through the mixture [5] until the precipitate had dissolved.

After evaporation of the acetic acid *in vacuo*, dissolving the residue in hot water, treating with active carbon to decolourize the solution, and filtrating, IV crystallizes on cooling. Yield 15 % of the theoretical. Through recrystallization from alcohol colourless needles, m. p. 156°, were obtained.

The mixed melting point of this substance and the anti-fungal substance of wheat and maize plants showed no depression. Acetyl derivative m. p. 150° C (no depression).

UV spectra (in water): Synthetic product: Max. 229–230 mμ and 285–286 mμ; Min. 255 mμ; Log ε 286 mμ = 3.74.

Isolated anti-fungal substance: Max. 285–286 mμ; Min. 255 mμ.

Acknowledgement. We are indebted to Professor A. I. Virtanen for his great interest in this work and to the *Rockefeller Foundation* for a grant awarded to the Foundation for Chemical Research.

1. Virtanen, A. I., Hietala, P. K. and Wahlroos, Ö. *Suomen Kemistilehti* **B 29** (1956) 143.
2. Will, W. and Pukall, W. *Ber.* **20** (1887) 1119.
3. Bechold, J. *Ber.* **22** (1889) 2374.
4. Grandmougin, E. *Ber.* **39** (1906) 2494.
5. Zinner, H. and Herbig, H. *Ber.* **88** (1955) 1241.

Received September 18, 1956.

On the Preparation of Alkyl Cyanides

ÅRNE BRÄNDSTRÖM

Research Laboratory, Pharmacia Ltd., Uppsala, Sweden

In an interesting paper Lewis and Susi [1] report that the preparation of alkyl cyanides from the corresponding primary bromides gives very good yields when ethylene glycol is used as solvent.

Glycols seem to be excellent for this reaction, being good solvents of alkali cya-

nides and easily obtainable in a sufficiently anhydrous state to prevent hydrolysis of the alkyl cyanide under the condition of the reaction. The boiling-point of ethylene glycol is, however, somewhat too low to permit easy separation of the alkyl cyanide by means of distillation. In order to eliminate this disadvantage some polymers of ethylene glycol, such as diethylene glycol and polyethylene-glycol-300, have been tried. In these experiments it was surprisingly found that, although the yields were moderate and the reaction slow when bromides were employed, the yields were excellent and the reaction rapid and sometimes vigorous when the corresponding chlorides were used. The reason for this is probably that the reaction is heterogeneous, making solubility a very important factor.

The fact that excellent yields of alkyl cyanides can be obtained from the corresponding alkyl chloride is of great value, since alkyl chlorides are readily available by the chlorination of hydrocarbons and by other methods.

When an alkyl chloride is refluxed with sodium cyanide in polyethylene glycol the temperature in the reaction-flask is at first equal to the boiling-point of the chloride. Since the alkyl cyanide has a much higher boiling-point than the corresponding alkyl chloride, the reaction-temperature will rapidly rise as long as the alkyl cyanide is being formed from the alkyl chloride. This permits an exact determination of the end-point of the reaction as the point where the temperature in the flask no longer rises. The alkyl cyanide is then easily removed from the reaction-mixture by distillation. The crude product obtained in this way contains very little by-products, and is pure enough for most purposes.

If necessary it can easily be purified by means of distillation.

Experimental. In a 5-l round-bottomed flask fitted with an efficient stirrer, a reflux condenser, and a thermometer, were placed 1.5 l of polyethylene-glycol-300, 300 g of sodium cyanide, and 5 moles of the alkyl chloride. The flask was heated by means of an electric heating-mantle so arranged that it could easily be removed if the reaction showed any tendency to become violent. The flask was heated until the temperature was practically constant. The refluxing time varied from about 15 min for *n*-octyl chloride to about 4 h for *n*-butyl chloride. The nitrile was then removed by distillation under reduced pressure as long as any product came over. A temperature of 200° at a pressure of 10 mm was often required to ensure complete removal of the nitrile from the reaction-product. Practically no polyethylene glycol distilled under these conditions. The yield of the crude product varied between 90—95 %, and the yields of the redistilled alkyl cyanides were all in the region of 85—95 % when the chlorides from *n*-butyl to *n*-octyl were employed. When the reaction tended to become violent, which was the case when chlorides higher than *n*-hexyl were used, the reaction was easily controlled by stopping the stirrer and removing the heating-mantle.

1. Lewis, R. N. and Susi, P. V. *J. Am. Chem. Soc.* **74** (1952) 840.

Received September 24, 1956.