

# APPLICATION OF THE STEPHEN REDUCTION TO 4-CYANODIPHENYL\*

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The conversion of cyanides into aldehydes by the action of anhydrous stannous chloride in ethereal hydrogen chloride solution, followed by hydrolysis of the resulting aldimine stannichloride, has been applied to aliphatic,<sup>1</sup> aromatic,<sup>1</sup> and heterocyclic<sup>2</sup> cyanides. In the aromatic series, aldehydes are usually formed in excellent yield, except in the cases of *o*-tolualdehyde and  $\alpha$ -naphthaldehyde where the low yields have been attributed<sup>1</sup> to steric hindrance by *ortho* substituents. It was claimed<sup>3</sup> that the Stephen reduction failed when applied to 4-cyanodiphenyl, more than 90% of the cyanide being recovered unchanged. It seemed unlikely that the failure of 4-cyanodiphenyl to react could be due to steric effects so the reduction was repeated under modified conditions. In the original directions of Stephen,<sup>1</sup> hydrogen chloride is passed into anhydrous stannous chloride suspended in dry ether, until the stannous chloride dissolves and forms a viscous lower layer. Subsequently it has been reported<sup>4,5</sup> that reduction in homogeneous solution usually gives a better yield of aldehyde, and diethylene glycol diethyl ether<sup>4</sup> and ethyl formate or ethyl acetate<sup>5</sup> have been recommended as solvents for the reaction. During other work we found that passage of hydrogen chloride into dry ether-stannous chloride gives firstly a heavy viscous layer which, on passage of further quantities of hydrogen chloride, gradually increases in amount until the solution eventually becomes homogeneous. This solution gives efficient conversions of nitriles to aldehydes. When 4-cyanodiphenyl was added to such a homogeneous solution a solid soon separated and from this diphenyl-4-aldehyde was obtained in good yield.

## Experimental

Infrared spectra were determined on a Perkin-Elmer Infracord 137 for Nujol mulls. Analyses were performed by the Australian Microanalytical Service, Melbourne.

### 4-Cyanodiphenyl

This was prepared by the method of Friedman and Shechter<sup>6</sup> from 4-bromodiphenyl (B.D.H., 23.5 g) and cuprous cyanide (10.5 g) in refluxing dimethylformamide. The cyanide had m.p. 84–86° (lit.<sup>7</sup> 84–85°) and showed the characteristic CN infrared absorption band at 2230 cm<sup>-1</sup>.

\* Manuscript received April 9, 1965.

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<sup>3</sup> Shoppee, C. W., *J. Chem. Soc.*, 1933, **39**.

<sup>4</sup> Gardner, T. S., Smith, F. A., Wenis, E., and Lee, J., *J. Org. Chem.*, 1951, **16**, 1121.

<sup>5</sup> Stephen, T., and Stephen, H., *J. Chem. Soc.*, 1956, 4695.

<sup>6</sup> Friedman, L., and Shechter, H., *J. Org. Chem.*, 1961, **26**, 2522.

<sup>7</sup> Heilbron, Sir Ian, and Bunbury, H. M., "Dictionary of Organic Compounds." (Eyre & Spottiswoode: London 1953.)

*Anhydrous Stannous Chloride*

Analytical reagent stannous chloride dihydrate was dehydrated by the addition of acetic anhydride.<sup>8</sup> The solid was filtered off and washed well with anhydrous ether and stored in a vacuum desiccator.

*Diphenyl-4-aldehyde*

Anhydrous stannous chloride (10 g) and sodium-dried ether were placed in a flask protected from atmospheric moisture and cooled in ice while dry hydrogen chloride was passed in until a homogeneous solution was formed. 4-Cyanodiphenyl (5 g) dissolved in ether (35 ml) was then added with stirring and the mixture allowed to stand. The solid product was filtered off, washed with ether, and then dissolved in water. The solution was warmed on the water-bath, then cooled and extracted with ether, and the ether extract washed with water and dried over sodium sulphate. Evaporation of the ether yielded diphenyl-4-aldehyde, 3.9 g (77%), m.p. 58° (lit.<sup>7</sup> 60°) (infrared absorption bands at 1695  $\text{cm}^{-1}$  (strong) and 2720  $\text{cm}^{-1}$  and no CN peak near 2230  $\text{cm}^{-1}$ ). From the aldehyde there were formed, in the usual way, the semicarbazone, colourless platelets, m.p. 235° (capillary); 235° phase change, remelting 243–245° (Kofler block) (lit.<sup>7</sup> 243°) (Found: C, 70.8; H, 5.6; N, 17.8. Calc. for  $\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}$ : C, 70.3; H, 5.5; N, 17.6%) and the 2,4-dinitrophenylhydrazone (from nitromethane), red plates, m.p. 237° (lit.<sup>7</sup> 239°) (Found: C, 62.7; H, 4.2. Calc. for  $\text{C}_{18}\text{H}_{14}\text{N}_4\text{O}_4$ : C, 63.0; H, 3.9%).

<sup>8</sup> Stephen, H., *J. Chem. Soc.*, 1930, 2786.