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## Preparation of Benzonitrile, Isotopically Labelled in the Cyanide Group

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As a pre-requisite for the study of infrared and microwave spectra of benzonitrile(I), species isotopically labelled in the cyanide group were prepared.

$C_6H_5{}^{13}CN$. 2.65 g (0.0134 mole) of commercial $BaCO_3$ (52 % enriched in $^{13}C$) was converted to carbon dioxide(II), which was distilled at −80°C for purification. Bromobenzene (2.62 g, 0.0167 mole) was converted to phenylmagnesium bromide and afterwards to benzoic acid (III) by addition of (II), roughly following Ref.[1] For the present purpose it was found useful to omit the prescribed extraction of (III) by ether. The yield of (III), contaminated by a small amount of inorganic substance, was 1.70 g. Refluxing for 3 h of (III) with 13 ml dry benzene and 2.3 ml $SOCl_2$ produced a quantity of benzoyl chloride (IV), mixed with traces of benzene and $SOCl_2$ after its distillation. (IV) was converted to benzamide (V), following the indications by Swan and Kelly [2], but using concentrated ammonium hydroxide in excess instead of $NH_4NO_3$ and base. Yield 1.02 g (0.0084 mole). The infrared absorption curve showed the substance to be pure. Following Ref.[1], (V) was converted to (I). The problem of removing the last traces of HCl in samples of the present magnitude was solved by pumping off the vapors in equilibrium with the liquid phase at room temperature six times with 2 h intervals after which the vapor pressure became normal. The infrared absorption curve of the undiluted sample showed that it consisted of the expected mixture of 52 % $C_6H_5{}^{13}CN$ and 48 % $C_6H_5CN$ as evidenced by the relative intensity of the bands at 2 180 $cm^{-1}$($C_6H_5{}^{13}CN$) and at 2 230 $cm^{-1}$($C_6H_5CN$). This disclosed that the weak line observed in non-enriched benzonitrile at 2 180 $cm^{-1}$ is due to the presence of 1 % $C_6H_5{}^{13}CN$. The yield of (I) obtained was 0.566 g (0.0055 mole) or 41 % with respect to the enriched $BaCO_3$ applied.

$C_6H_5C^{15}N$. Following Ref.[2], 720 mg (0.0090 mole) of commercial $NH_4NO_3$ (33 % enriched in $^{15}N$), dissolved in 30 ml of water, was treated with 1.35 g benzoyl chloride (0.0096 mole), dissolved in 70 ml chloroform, and 0.0190 mole of 1 N NaOH aq. for 1 h at room temperature under vigorous shaking. On evaporation of the chloroform layer and the small portions of chloroform used for extraction of the aqueous phase, a residue of 860 mg (0.0071 mole) enriched benzamide (VI) was obtained. The infrared spectrum showed (VI) to be pure. Hence, the suggested extraction by petrol ether is unnecessary, at least for the present purpose. (VI) was converted to $^{15}N$-enriched benzonitrile(VII) by the same procedure as above, the yield being 540 mg (0.0052 mole) or 58 % with respect to enriched $NH_4NO_3$. The infrared absorption curve of the undiluted sample showed it to consist of the expected mixture of 33 % $C_6H_5C^{15}N$ (absorbing at 2 200 $cm^{-1}$) and 67 % $C_6H_5CN$ (absorbing at 2 230 $cm^{-1}$). The spectral isotope effect of $^{15}N$ as compared to $^{13}C$ in benzonitrile is only 2/3. In natural abundance (1/3 %), $^{15}N$ in benzonitrile may still give rise to observable absorption at 2 200 $cm^{-1}$, if sufficient spectroscopic power of resolution is available.

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