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SYNTHESIS OF AROMATIC NITRILES BY THE METAL-CYANIDE EXCHANGE REACTION BETWEEN ARYL-LITHIUM COMPOUNDS AND PENTACHLOROBENZONITRILE

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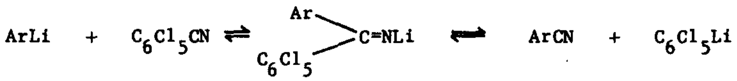
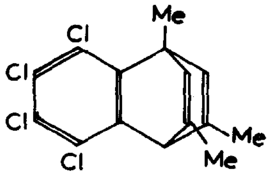
We have demonstrated[1] that the addition of pentachlorophenyl-lithium to aromatic nitriles[2] is reversible. We now report that if the adduct is approached from the other direction, i.e. by the reaction of an aryl-lithium compound with pentachlorobenzonitrile, pentachlorophenyl-lithium and the aromatic nitrile are formed:



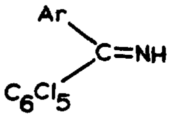
$$\mathrm{ArLi} + \mathrm{C_6Cl_5CN} \rightleftharpoons \begin{matrix}\mathrm{Ar}\\ \mathrm{C_6Cl_5}\end{matrix}\!\!>\mathrm{C{=}NLi} \rightleftharpoons \mathrm{ArCN} + \mathrm{C_6Cl_5Li}$$

The overall result is 'metal-cyanide exchange', formally analogous to metal - halogen exchange[3] (though quite different mechanistically).

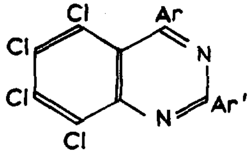
The equilibrium may be displaced in the forward direction if the reaction is conducted in a medium containing an aromatic hydrocarbon such as mesitylene, and the temperature is raised to the level at which pentachlorophenyl-lithium decomposes to tetrachlorobenzyne, which is trapped as the adduct (I)[1,4]. Using this procedure we have prepared benzonitrile (34%), p-tolunitrile (24%), p-bromobenzonitrile (25%), p-chlorobenzonitrile (30%), 4-cyanobiphenyl (35) and 1-naphthonitrile (45%) from the corresponding aryl-lithium compounds.



(I)



(II)

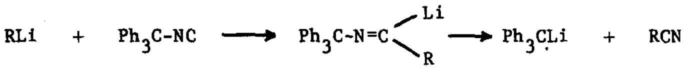


(III)

Ar′= Ar or C_6Cl_5

The reactions gave a number of by-products, including the imines (II) and the diarylquinazolines (III). The latter are formed by the addition of the N-lithio derivative of compound (II) to a nitrile (which may be the product nitrile or pentachlorobenzonitrile) followed by cyclisation[2]. The modest yields quoted above should be capable of improvement, at the expense of the by-products, and we are now undertaking a search for the optimum experimental conditions.

Walborsky *et al.*[5] have recently reported an 'isonitrile - metal exchange reaction' involving the addition of organolithium compounds to isonitriles such as triphenylmethylisonitrile, followed by elimination of triphenylmethyl-lithium:



$$RLi + Ph_3C\text{-}NC \longrightarrow Ph_3C\text{-}N{=}C\begin{smallmatrix}Li\\R\end{smallmatrix} \longrightarrow Ph_3CLi + RCN$$

For alkyl-lithium compounds, this reaction gave mixtures of the nitrile and the ketone formed by the reaction:

$$RLi + RCN \longrightarrow R_2C{=}NLi \xrightarrow{H_3O^+} R_2CO$$

With hindered alkyl-lithium compounds (e.g. t-butyl-lithium) the nitrile could be made the main product, but with phenyl-lithium only benzophenone was obtained. In contrast, although our reactions with aryl-lithium compounds gave the nitriles, the reaction of alkyl-lithium compounds with pentachlorobenzonitrile failed to yield identifiable products[6]. No ketones were obtained from any of our experiments. Our reaction and that of Walborsky are thus complementary, and together should furnish a general route for the conversion of organolithium compounds into nitriles or ketones.

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6. D. J. Berry, unpublished work.