Stereochemistry of the Nickel-catalysed Hydrocyanation of Olefins

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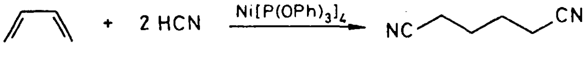
Summary Nickel-catalysed addition of deuterium cyanide to (*E*)-1-deuterio-3,3-dimethylbut-1-ene (**1**) and subsequent analysis of the dideuteriated nitrile (**2**) by ^{1}H n.m.r. spectroscopy shows that the addition of deuterium and cyanide occurs in a *cis*-fashion.

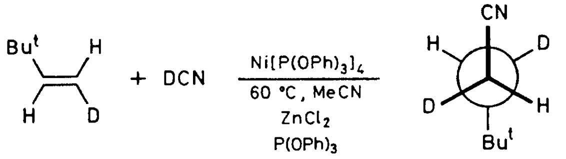
THE nickel(0)-catalysed addition of two molecules of hydrogen cyanide to butadiene is the basis for an industrial process for the manufacture of adiponitrile (equation 1).[1,2]



(1)

The reaction may be depicted as involving three steps: (i) 1,4-hydrocyanation of butadiene, (ii) double bond isomerization, and (iii) 1,2-hydrocyanation of pentene-4-nitrile.[1] Complexes of both nickel(0) and palladium(0) are known to catalyse the hydrocyanation of mono-olefins.[3–5] In spite of its importance, little is known about the mechanism of the hydrocyanation reaction. It has been suggested[5,6] that the initial step involves an oxidative addition of hydrogen cyanide to nickel(0) to give a hydridocyanide complex. In fact, such complexes have been isolated from the reaction of hydrogen cyanide with nickel(0) complexes.[6] We have now studied the stereochemistry of the nickel(0)-catalysed hydrocyanation and found that hydrogen and cyanide add *cis* across the double bond.

The nickel(0)-catalysed reaction of (**1**)[7] with deuterium cyanide[8] was performed in acetonitrile at 60 °C using tetrakis(triphenyl phosphite)nickel[9] as catalyst, using a procedure similar to that described by Taylor and Swift.[5] We found that a more convenient laboratory procedure was to add an acetonitrile solution of deuterium cyanide (*ca.* 4 M) to a mixture of the olefin (**1**) and the catalyst in acetonitrile. The deuteriated cyanide (**2**) formed in this way (equation 2)



(2)

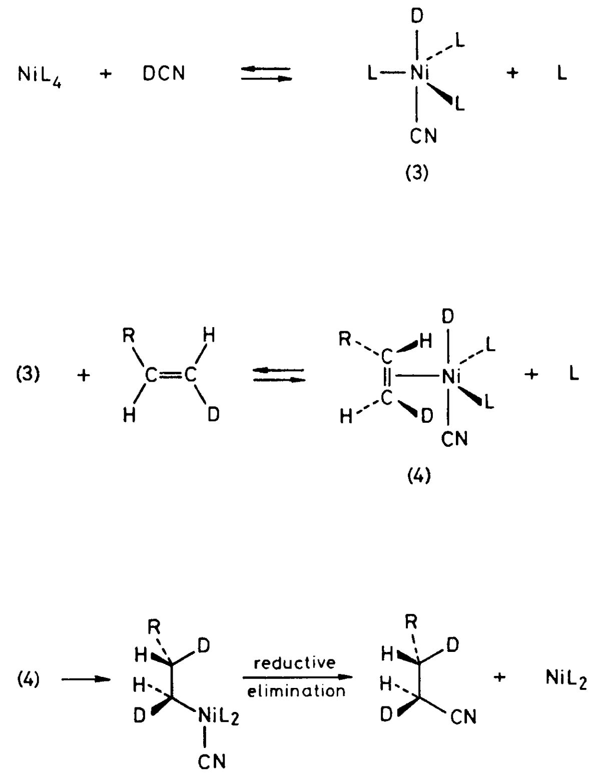
(1) (2)

J_{HH} 10·2 Hz[10]

was isolated and analysed by ^{1}H n.m.r. spectroscopy.[10] The vicinal coupling constant of the major compound in (**2**) was found to be 10·2 Hz, showing that (**2**) has the *erythro*-configuration. Thus, formation of *erythro*-(**2**) proves that the addition of DCN has occurred *cis*. A small amount of the *threo*-compound (J_{HH} 5·8 Hz[10]) was also observed. Estimation of the ratio of *erythro*-(**2**) to *threo*-(**2**) by ^{1}H n.m.r. spectroscopy indicated that the addition had occurred >90% *cis*.

In order to find the source of the small fraction of *threo*-(**2**) formed in the addition of DCN to (**1**), we isolated the remaining traces of unchanged olefin. N.m.r. analysis of the recovered olefin showed that no *E–Z*-isomerization had occurred (> 98% *E*), and hence olefin isomerization cannot account for the slight loss of stereoselectivity.

A likely mechanism for the reaction is depicted in the Scheme.† Oxidative addition of hydrogen cyanide to the nickel(0) catalyst would give a hydrido-nickel cyanide complex (**3**). Such complexes have previously been isolated and characterized.[6] Co-ordination of the olefin to the metal followed by hydride addition would give a σ-nickel complex, which on reductive elimination would yield the organic nitrile. Since transition-metal hydride additions to olefins are known[11] to proceed *cis*, the observed stereochemistry requires the reductive elimination to occur with retention of configuration at carbon.



SCHEME. R = Bu^t; L = P(OPh)$_3$.

During this study we observed that the addition of deuterium cyanide is very sensitive to trace amounts of H_2O. To ensure a high deuterium content in the organic nitrile it was necessary to use rigorously dried acetonitrile and to add 1% of D_2O to the solution. Moderately dried acetonitrile, without added D_2O, gave $(CH_3)_3C–CH_2–CHD–CN$ as the main product *via* a HCN addition.‡ Since the estimated concentration of H^+ is lower than the concentration of D^+ in the latter case, it appears that there is a considerable isotope effect in the reaction. We are presently investigating the isotope effect for the hydrocyanation reaction.

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† A similar mechanism has been proposed previously for both the nickel- and the palladium-catalysed reactions.[4b,5]

‡ A control experiment using CD_3CN gave the same result, indicating that the acetonitrile cannot be the source of protons.

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