Activation of Co-ordinated Nitriles - Reduction and Carbanion Addition

By INGE I. CREASER and ALAN M. SARGESON*
(*Research School of Chemistry, Australian National University, Canberra, A.C.T.* 2600)

Summary Reduction of co-ordinated nitriles with BH_4^-, and Michael addition of a carbanion to co-ordinated acrylonitrile both occur more than 10^4 fold faster than the same reactions for the unco-ordinated nitriles.

Two activating effects have been demonstrated previously for co-ordinated nitriles; attack of OH^- at the nitrile C atom was enhanced about 10^6 fold when the nitrile was attached to the $(NH_3)_5M^{3+}$ grouping (M = Co, Ru, Rh)[1-3] and a similar enhancement in acidity was noted for a $CH_2<$ group adjacent to a co-ordinated nitrile group.[2,4] These effects prompted us to examine the scope and origin of the activation in terms of reaction type and the distance over which it might extend.

The reduction of nitriles by BH_4^- ion does not normally occur; usually a more potent reductant, such as $LiAlH_4$ is required in a non-aqueous medium. If a substantial electron-withdrawing group such as a metal ion is applied to the nitrile, the carbon centre should become more susceptible to attack by H^- or BH_4^- and thus reduction should be easier. The acetonitrile complex $[(NH_3)_5Co–N{\equiv}C–Me](ClO_4)_3$ was treated with aqueous $NaBH_4$ (*ca.* 0·2 M) in a pH 9 buffer for 6 min at 25 °C. The product $[(NH_3)_5CoNH_2CH_2Me](ClO_4)_3$ (*ca.* 50%) was obtained along with some Co^{II} salts and $[(NH_3)_5CoNHC(=O)Me]^{2+}$. Attempts to follow the rate of reduction by ^1H n.m.r. were negated by the production of some Co^{II} species but an estimated half-life of *ca.* 1 min, under these conditions, was obtained by sampling the reaction mixture and separating the complexes by ion-exchange chromatography. The rate of reaction showed a dependence on the BH_4^- ion concentration but it was difficult to assess quantitatively. Unco-ordinated acetonitrile treated under identical conditions showed no signs of reduction in 10 days. By this time a substantial amount of the BH_4^- ion had decomposed but the ^1H n.m.r. spectra still indicated the presence of H–B signals and thus reducing capacity. The reaction is accelerated at least 10^4 times compared with the unco-ordinated nitrile and the general applicability of the method has been established using $NCCH_2CO_2Et$, $NCCH_2CH_2CH(COMe)_2$, $NC(CH_2)_4CN$, and $NCCH_2CH_2CH_2NO_2$ as well as acetonitrile. These results imply that reduction of a nitrile group which is predominantly σ-bound to a metal ion should be accelerated regardless of whether the nitrile complexes are kinetically inert or labile provided they are stable around pH 9—10. The process could also be used to insert ^2H or ^3H at the α-carbon atom of an amine.

For the adipic nitrile, the cyanoacetic ethylester and the nitrobutyronitrile complexes, only the nitrile groups attached to Co^{III} were reduced while the other functional groups were untouched, so some specificity was built into the system. The corresponding *N*-bound amide complexes were not reduced by this method. We also note that metal oxidation states such as Co^{II}, Cu^{II}, Ni^{II}, Pt^{II}, and Os^{II} have been used[5] to accelerate reduction of nitriles by BH_4^-. However, these reagents are also capable of reducing amides and nitro compounds to primary amines and it may be significant that the effective metals are those which readily form metal hydrides. The reduction could then arise from a co-ordinated nitrile and metal hydride complex rather than directly from the BH_4^- reagent. In the present examples, the Co^{III}–nitrile entity remains intact during the reduction and as the resulting Co^{III}–amine is isolated the implication is that reduction is accomplished by BH_4^-. In more acidic solutions (pH <4) B_2H_6, which is generated rapidly, reduces Co^{III} to Co^{II} before reduction of the nitrile.

Another reaction of possible synthetic interest to organic chemists is the Michael addition exemplified by the reaction of acrylonitrile and acetylacetone (equation 1).

$$CH_2{=}CH{-}C{\equiv}N + \bar{C}H(COMe)_2 \xrightarrow{H^+} (MeCO)_2CHCH_2{-}CH_2{-}C{\equiv}N \quad (1)$$

In aqueous solutions, these reactions are slow and frequently occur with multiple additions which are difficult to control. It is interesting to know whether the activating influence of the metal ion extends to the distant carbon atom for these carbanion addition reactions, and whether there is any selectivity in the addition. The complex $[(NH_3)_5CoNC{-}CH{=}CH_2](ClO_4)_3$ was treated with acetylacetone (0·2 M) at pH 9 and 25 °C. The acetylacetone carbanion adds to the olefin bond in <5 s (equation 2).

$$[(NH_3)_5CoNC{-}CH{=}CH_2]^{3+} + \bar{C}H(COMe)_2 \xrightarrow{H^+} [(NH_3)_5Co{-}N{\equiv}C{-}CH_2{-}CH_2{-}CH(COMe)_2]^{3+} \quad (2)$$

The initial product is the cyanoethylated acetylacetone complex, (isolated as the perchlorate, *ca.* 50%) which converts to the amide over 15 min unless the reaction mixture is acidified. The reaction apparently ceases with the addition of the first carbanion. An equally fast reaction occurred between the acrylonitrile complex and nitromethane (*ca.* 1M) at pH 9 producing $[(NH_3)_5Co{-}N{\equiv}C{-}CH_2{-}CH_2{-}CH_2NO_2](ClO_4)_3$ (*ca.* 15 s, *ca.* 55%). Both reactions constitute examples of fast cyanoethylations. For the unco-ordinated acrylonitrile under the same conditions, the condensation is very slow ($t_{\frac{1}{2}} > 7$ h) which indicates an acceleration factor $>10^4$ by co-ordinating the nitrile activating group. The ligands can be readily removed from the Co^{III} complexes by reduction with acidic BH_4^-, V^{2+}, Cr^{2+}, or by treatment with CN^- or S^{2-}.

(*Received*, 19*th August* 1975; *Com.* 958.)

---

[1] D. Pinnel, G. B. Wright, and R. B. Jordan, *J. Amer. Chem. Soc.*, 1972, **94**, 6104.

[2] D. A. Buckingham, F. R. Keene, and A. M. Sargeson, *J. Amer. Chem. Soc.*, 1973, **95**, 5649.

[3] R. J. Balahura, P. Cock, and W. L. Purcell, *J. Amer. Chem. Soc.*, 1974, **96**, 2739; A. W. Zanella, and P. C. Ford, *Inorg. Chem.*, 1975, **14**, 42.

[4] I. I. Creaser and A. M. Sargeson, *J.C.S. Chem. Comm.*, 1975, 324.

[5] T. Satoh, S. Suzuki, Y. Suzuki, Y. Miyaji, and Z. Imai, *Tetrahedron Letters*, 1969, **52**, 4555.