Stoicheiometric Dimerisation of Acrylonitrile to Adiponitrile by a Cobalt Complex

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WE report a novel stoicheiometric procedure for dimerising acrylonitrile to adiponitrile,¹ based on the use of powdered manganese and cobalt chloride in dimethylformamide, according to the overall equation:

 $2 \text{ CH}_2 = \text{CHCN} + \text{Mn} + \text{CoCl}_2 + 2\text{H}_2\text{O} \rightarrow \\ \text{NC}[\text{CH}_2]_4\text{CN} + \text{MnCl}_2 + \text{Co(OH)}_2$

The process occurs in two stages: in the first, a dimethylformamide-solvated complex, derived from one atom of cobalt and two molecules of acrylonitrile, is formed at room temperature and atmospheric pressure; in the second stage the complex is decomposed by warming it with water in the presence of an organic base. Adiponitrile and cobalt hydrate are formed. Alternatively, the decomposition can be carried out by treating the complex with hydrogen sulphide at room temperature. Adiponitrile and cobalt sulphide are formed in this case. In a typical experiment an excess of powdered manganese (0.050 mole), cobalt chloride (0.030 mole), acrylonitrile (stabilised with hydroquinone) (0.060 mole), and dimethylformamide (50 ml.), are mixed and shaken for 20 hours at 20°. During this time the colour of the mixture changes from dark blue to green and finally to dark red. The unchanged manganese is filtered off and hydrogen sulphide is passed into the solution. Adiponitrile (0.029 mole) containing about 0.1% of 2-methyl-glutaronitrile are obtained by distillation. No hydrogenation of acrylonitrile occurs by this procedure. The yield, based on converted acrylonitrile, exceeds 95%.

The intermediate complex precipitates from the solution if other solvents in which it is insoluble are added. Attempts to separate it from dimethylformamide gave a completely insoluble form, probably polymeric.

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¹ For dimerisation of acrylonitrile on transition-metal complexes, see P. Chabardes, C. Gerard, and M. Thiers (Rhone Poulenc) F. P. 1,377,425/1964; J. D. McClure, R. Owyang, and L. H. Slaugh, *J. Organometallic Chem.*, 1968, 12, P8; A. Misano, Y. Uchida, M. Hidai, and H. Kanai, *Chem. Comm.*, 1967, 357.