# Catalytic Addition of Hydrogen Cyanide to Non-activated Olefins

By E. S. BROWN* and E. A. RICK

(*Research and Development Department, Union Carbide Corporation, Chemicals and Plastics, South Charleston, West Virginia 25303*)

ALTHOUGH soluble transition-metal complexes are used as catalysts for the synthesis of nitriles from non-activated olefins and hydrogen cyanide, their use is limited by the large amount of catalyst required.[1-3] We report the first useful homogeneous process for the addition of hydrogen cyanide to non-activated olefins.

Zerovalent palladium and nickel complexes act as efficient catalysts for the addition of hydrogen cyanide to olefins under certain conditions. Reaction of hydrogen cyanide with bicyclo[2,2,1]heptene in the presence of catalytic quantities of tetrakis(triphenylphosphite)palladium[0] gives only poor yields of 2-cyanobicyclo[2,2,1]-heptane. However, in the presence of triphenylphosphite (Table) the yield of product and, more importantly, the catalyst turnover is increased (see last example). With bicyclo[2,2,1]heptene, the product is almost exclusively the *exo*-isomer of 2-cyanobicyclo[2,2,1]heptane.

When the reactants are charged simultaneously, optimum results are obtained when the phosphite concentration approximates the hydrogen cyanide concentration. This large phosphite requirement, however, can be greatly reduced if hydrogen cyanide is added continuously to the reaction mixture at such a rate that the concentration of hydrogen cyanide remains close to that of the phosphite.

We suggest that the initial reaction is formation of the hydride (II) by oxidative addition of hydrogen cyanide. This is reasonable since Pd$^0$ complexes add oxidatively to a variety of molecules.[4] Co-ordinated olefin may then "insert" into the H–Pd bond of (II) to form (III). Formation of product may occur either by a collapse of (III) or

| Catalyst, (M) | Bicyclo[2,2,1]heptene, (M) | HCN, (M) | $P(OPh)_3$, (M) | 2-Cyanobicyclo[2,2,1]heptane yield % (on HCN) | Catalyst turnover |
|---|---|---|---|---|---|
| $Pd[P(OPh)_3]_4$ 0·01 | 1·24 | 0·66 | 0·0 | 5·9 | 4 |
| 0·01 | 1·24 | 0·66 | 0·32 | 70·0 | 47 |
| 0·01 | 1·24 | 0·66 | 1·1 | 83·0 | 55 |
| 0·01 | 1·24 | 0·66 | 1·9 | 68·6 | 45 |
| 0·0005* | 3·0 | 1·05 | 1·0 | 59 | 1260 |

* 190°, 6 hr., in benzene. All other reactions shown, 120°, 8 hr., in benzene.

by reaction of (III) with hydrogen cyanide or phosphite with concomitant regeneration of (I) or (II).

$$\underset{\text{(I)}}{PdL_4} + HCN \rightarrow \underset{\text{(II)}}{H\text{–}PdL_2(CN)} + 2L$$

$$H\text{–}PdL_2(CN) + \text{olefin} \rightarrow \underset{\text{(III)}}{\text{alkyl–}PdL_2(CN)}$$

$$\text{alkyl–}PdL_2(CN) \rightarrow \text{alkyl–CN}$$

The role of the added phosphite in this sequence is unclear. Its presence may be required to retard conversion of the hydride (II) to $PdL_2(CN)_2$. Since this complex has been observed as a by-product of the reaction, and has been shown to be catalytically inactive under the reaction conditions.

The catalytic addition of hydrogen cyanide to ethylene is equally easy.

Zerovalent nickel complexes, *e.g.* $Ni[P(OPh)_3]_4$, catalyze the addition of hydrogen cyanide to bicyclo[2,2,1]heptene with similar efficiency. Several patents disclose the use of zerovalent nickel complexes promoted with borohydrides or zinc or cadmium salts and excess phosphorous ligand for addition of hydrogen cyanide to nonconjugated pentene nitriles to form adiponitrile.[2,5]

(*Received, November 25th,* 1968; *Com.* 1601.)

---

[1] P. Arthur, jun., D. C. England, B. C. Pratt, and G. M. Whitman, *J. Amer. Chem. Soc.*, 1954, **76**, 5364.

[2] W. C. Drinkard, jun., Belg. P. 698,332/1967.

[3] W. C. Drinkard, jun., and R. V. Lindsay, Belg. P. 698,333/1967.

[4] P. Fitton and J. E. McKeon, *Chem. Comm.*, 1968, 4; P. Fitton, M. P. Johnson, and J. E. McKeon, *ibid.*, p. 6; R. Ugo, *Co-ordination Chem. Rev.*, 1968, **3**, 319.

[5] W. C. Drinkard, jun., and R. J. Kassal, Belg. P. 700,420/1967.