Catalytic Hydrocyanation of Acetylenes by Tetracyanonickelate without the Use of Hydrogen Cyanide

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Summary Acetylenes are readily hydrocyanated to saturated secondary nitriles by tetracyanonickelate, $[Ni(CN)_4]^{2-}$, in ethylene glycol or water in the presence of excess of cyanide ion and $NaBH_4$ or Zn; in the two-step reactions (hydrocyanation and hydrogenation) hydridotricyanonickelate functions as an active species only in the former.

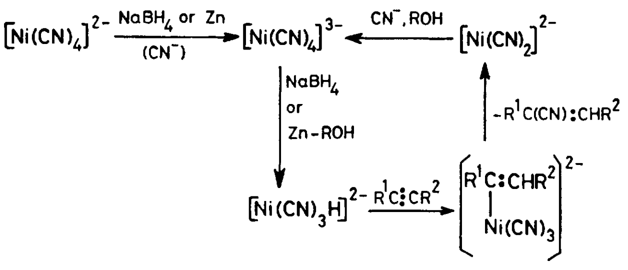
PREVIOUSLY,[1] we have described the hydrocyanation of acetylenes by $[Co(CN)_5]^{3-}$, in which HCN was not used and the hydrogen source was H_2, but the reaction proceeded only with CN:Co$<$5:1 and was stoicheiometric with respect to Co. We report here a catalytic process by tetracyanonickelate, in which the hydrogen source is not H_2 but $NaBH_4$ or solvent. Tetracyanonickelate, $[Ni(CN)_4]^{4-}$, has been used for the hydrocyanation of activated olefins under HCN,[2] but the present result is the first example of the hydrocyanation of acetylenes by $[Ni(CN)_4]^{2-}$ without using HCN under mild conditions.

Reactions were performed by the addition of solvent (ethylene glycol or water) to a mixture of $Na_2[Ni(CN)_4]$, KCN, $NaBH_4$ or Zn, and acetylenes at 45 °C under N_2. Results are shown in the Table. Similar results were obtained under H_2, which indicated that H_2 was not activated by the nickel complex. The reaction proceeded catalytically and was promoted by the presence of an excess of KCN. Terminal acetylenes RC⋮CH selectively produced RCH(CN)Me in good yields, and, interestingly, an internal acetylene PhC⋮CEt was also readily hydrocyanated to give equimolar amounts of two saturated nitriles. When $NaBH_4$ was used as a reductant, ethylene glycol was a better solvent than water, but in the case of Zn the reaction proceeded effectively only in water.

Table. Hydrocyanation of acetylenes by cyanonickelate in ethylene glycol[a]

$R^1C{:}CR^2$							Products (%)[c]						
R^1	R^2	KCN[b]	$NaBH_4$[b]	Zn[b]	$R^1C{:}CR^2$[b]	Time/h	A	B	C	D	E	F	G
Ph	H	2	5	0	2	4[d]	98	0	1	1	0	1	0
		2	5	0	2	2	83	0	7	1	6	2	1
		2	0	10	2	4[d]	86	1	0	0	10	2	1
		2	0	10	2	24	9	50	0	0	0	6	34
		2	5	0	4	4	87	0	4	2	2	2	3
		10	5	0	2	1	90	0	5	0	1	2	2
$PhCH_2CH_2$	H	2	5	0	2	3	92	0	0	0	1	1	6
c-C_6H_{10}(OH)	H	2	5	0	2	2	85	0	0	0	0	15	0
Ph	Et	10	10	0	2	2	47	0	45	0	7	0	0

[a] [Ni] = 0·2 mol dm^{-3} in 4 cm^3 solvent at 45 °C in N_2. [b] Relative to $Na_2[Ni(CN)_4]$. [c] Yield was almost quantitative. A: $R^1CH(CN)CH_2R^2$; B: $R^1C(CN){=}CHR^2$, C: $R^1CH_2CH(CN)R^2$, D: $R^1CH{=}C(CN)R^2$, E: $R^1CH_2CH_2R^2$, F: $R^1CH{=}CHR^2$, G: $R^1C{\equiv}CR^2$. [d] In water.



Scheme. ROH = H_2O or alcohol.

Saturated nitriles are obtained in two stages, hydrocyanation and hydrogenation. The former seems to be explained by the mechanism in the Scheme, in which the σ-vinyl–Ni complex is formed from nickel hydride and acetylene followed by insertion of the cyanide ligand into the σ-C–Ni bond.† It is known that $[Ni(CN)_4]^{2-}$–$NaBH_4$ in aqueous solvents is an effective catalyst for the hydrogenation of olefins.[3] The reaction has been explained in terms of reduction *via* an electron transfer mechanism involving Ni^I followed by protonation; nickel hydride is not an active species and water is the hydrogen source.[4] Hydrocyanation of PhC:CH in the $NaBH_4$–D_2O and $NaBD_4$–H_2O systems produced selectively $PhCD(CN)CH_2D$ and $PhCH(CN)CH_2D$, respectively. Since no exchange occurs between D_2O and $NaBH_4$,[5] this result clearly indicated that the nickel hydride is involved in the hydrocyanation and not in the hydrogenation of unsaturated nitriles. In the case of Zn–H_2O the hydrogen source is H_2O, and the hydrocyanation must proceed *via* the nickel hydride although the mechanism of its formation has not been clarified. Excess of cyanide ion is necessary for effective reduction of Ni^{II} to Ni^I and promotes the oxidation of Ni^0 with solvent to Ni^I.[5]

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† Insertion of the CN ligand into σ-vinyl–metal bond has been demonstrated with σ-styrylcyanocobaltates (T. Funabiki, S. Yoshida, and K. Tarama, *J.C.S. Chem. Comm.*, 1978, 1059).

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[4] W. H. Dennis, Jr., D. H. Rosenblatt, R. R. Richmond, G. A. Finseth, and G. T. Davis, *Tetrahedron Letters*, 1968, 1821.
[5] See B. R. James, 'Homogeneous Hydrogenation,' Wiley, New York, 1973, p. 314, and refs. therein.