September, 1983] © *1983 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, ***56***, *2863—2864 (1983)* 2863

Hydrocyanation of α,ω-Diynes Catalyzed by Tetracyanonickelate. Regiospecific Synthesis of a New Series of Acyclic Dinitriles

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(Received February 17, 1983)

Synopsis. Hydrocyanation of α,ω-diynes without the use of HCN has been described. Cyanonickelate, prepared by reducing $[Ni(CN)_4]^{2-}$ with $NaBH_4$ or Zn in the presence of excess KCN in water or ethylene glycol, catalyzes hydrocyanation of α,ω-diynes, $HC{\equiv}C(CH_2)_nC{\equiv}CH$ to give quantitatively $CH_3CH(CN)(CH_2)_nCH(CN)CH_3$, a new series of acyclic dinitriles. Importance of the preliminary formation of a (π-acetylene)nickel(0) complex for the hydrocyanation has been suggested.

Previously we have reported the hydrocyanation of acetylenes, without the use of hydrogen cyanide, catalyzed by cyanocobaltate[1] and cyanonickelate.[2] The reaction is useful not only for synthesis of secondary saturated nitriles from acetylenes, but also for elucidation of mechanisms of hydrocyanation with the use of hydrogen cyanide, which have been little clarified. To extend the utility of this new method of synthesis of nitriles, we have studied the reaction of α,ω-diynes, $HC{\equiv}C(CH_2)_nC{\equiv}CH$ ($n=3$—6). The diynes were hardly hydrocyanated by cyanocobaltate. However, they were readily hydrocyanated by cyanonickelate to form $CH_3CH(CN)(CH_2)_nCH(CN)CH_3$ selectively. The nitriles synthesized here are new compounds except for the case $n=3$, in which the nitrile has been obtained by a complicated procedure, *i.e.*, by hydrogenation of $CH_3CH(CN)(CH_2)_2CH{=}C(CN)CH_3$ derived from 3,7-dicyano-3,7-dimethylperhydro-1,2-diazepine.[3] The chemistry of these dinitriles has not been studied, but it is well expected that the present method is applicable to the diynes irrespective to its chain length and that they are useful as starting materials for organic and polymer synthesis.

Results and Discussion

Hydrocyanation was performed under three different conditions, *i.e.*, $[Ni(CN)_4]^{2-}$ was reduced 1) by $NaBH_4$ in water, 2)by $NaBH_4$ in ethylene glycol (EG), or 3)by Zn in water, in the presence of excess cyanide ion. The results of hydrocyanation and the data for identification of products are shown in Tables 1 and 2, respectively. The reactivity of the diynes under the condition (1) ($NaBH_4$–H_2O) was low in contrast to the high reactivity of terminal monoacetylenes under the same condition.[2] The reactivity and selectivity for formation of dinitriles decreased with increasing chain length of the diyne. The reaction under the condition (2) ($NaBH_4$–EG) gave good yields of dinitriles regardless of the chain length, but the selectivity for the dinitrile synthesis decreased slightly with increasing chain length. The reactivity under the condition (3) (Zn–H_2O) was as high as that under the condition (2), but 1,6-heptadiyne formed mainly unsaturated mononitrile, $CH_2{=}C(CN)(CH_2)_4CH_3$. The reason for this peculiar reactivity is not clear at present.

Recently,[4] hydrocyanation of monoacetylenes has been performed by $Ni[P(OPh)_3]_4$ in the presence of hydrogen cyanide, but the hydrocyanation of terminal acetylenes forms not only the internal but also terminal nitriles, indicating that the regioselectivity is not so high as that in the present case. In addition, our procedure does not require the use of HCN. The yields of dinitriles in Table 1 indicate that the hydrocyanation proceeds catalytically. Because of good yields, very high regioselectivity, and experimental simplicity, the present hydrocyanation procedure is more useful for synthesis of internal dinitriles from α,ω-diynes than the conventional method.[4]

Table 1. Hydrocyanation of $HC{\equiv}C(CH_2)_nC{\equiv}CH$ by cyanonickelate[a)]

α,ω-Diyne n	Conditions[b)]	Conv.[c)] %	Yield[d)] %	Composition of products (mol%) $CH_3CH(CN)(CH_2)_n$-$CH(CN)CH_3$	$CH_2{=}C(CN)$-$(CH_2)_{n+1}CH_3$	$CH_3CH(CN)$-$(CH_2)_{n+1}CH_3$
3	$NaBH_4$-H_2O	46	28	86	0	16
4		46	28	50	0	50
5		21	8	13	0	83
6		11	2	0	0	100
3	$NaBH_4$-EG	100	96(81)	94	0	6
4		100	86(80)	93	0	7
5		97	76(75)	88	0	12
6		89	78(76)	77	0	23
3	Zn-H_2O	100	85(81)	35	52	13
4		100	98(92)	92	0	8
5		100	90(89)	96	0	4
6		100	99(91)	95	0	5

a) $K_2[Ni(CN)_4]$ (0.8 mmol), KCN (1.6 mmol), diyne (0.8 mmol), at 45 °C, reaction time 6 h. b) $NaBH_4$ (4 mmol) or Zn (4 mmol) in 4 cm³ H_2O or ethylene glycol (EG). c) Determined by GLC analysis, based on added acetylenes. d) GLC and isolated (in parentheses, the reactions were performed in 20 cm³ of solvents) yields, based on added acetylenes.

It is known that in the presence of hydrogen cyanide $K_4[Ni(CN)_4]$ catalyzes hydrocyanation of activated olefins, and nonactivated olefins are hydrocyanated by other zero-valent nickel complexes such as $Ni[P(OR)_3]_4$.[5] In the absence of hydrogen cyanide, cyanonickelate catalyzes hydrogenation of olefins,[6] but not hydrocyanation. It has been proposed that in the hydrocyanation of olefins catalyzed by low-valent transition metal complexes (M) in the presence of HCN, H–M–CN is formed as an active species and olefins react with H–M–CN to form a σ-alkyl–M–CN complex (Eqs. 1 and 2).[5] Previously,[2] we have proposed a mechanism for hydrocyanation of acetylene, in which acetylene reacts directly with $[Ni(CN)_3H]^{2-}$ to form $[Ni(CN)_3(\sigma\text{-vinyl})]^{2-}$ in a similar way as shown in reactions (1) and (2). However, the mechanism cannot explain why olefins are not hydrocyanated in the absence of HCN. The peculiar reactivity of the complex with acetylene seems to be explained by assuming that the hydrocyanation proceeds *via* a (π-acetylene)nickel(0) complex. It is known that low-valent transition metal complexes form fairly stable

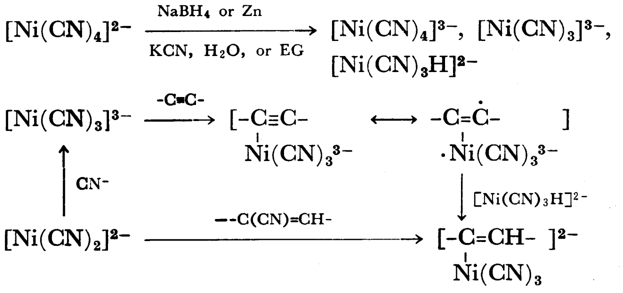
$$M + HCN \rightleftarrows H\text{-}M\text{-}CN \qquad (1)$$

$$H\text{-}M\text{-}CN + {>}C{=}C{<} \longrightarrow {>}CH\text{-}\overset{|}{\underset{|}{C}}\text{-}M\text{-}CN \qquad (2)$$

Table 2. Characterization of dinitriles

Dinitriles[a)] *n*	Bp θ_b/°C[b)]	Ret. time[c)]/min	IR[d)] $\tilde{\nu}$/cm^{-1}	^{1}H NMR[e)] δ	^{13}C NMR[e)] δ	Analysis Found (%) C	H	N	Calcd (%) C	H	N
3	110/0.3	4.88	2230	1.34 (d, J=7.08 Hz) 1.67 (m) 2.65 (m)	17.9 (q)[f)] 24.5 (t) 24.7 (t) 25.3 (d) 25.4 (d) 33.3 (t) 33.5 (t) 122.6 (s, CN)	71.84	9.67	18.36	71.96	9.39	18.65
4	115/0.3	7.33	2230	1.33 (d, J=7.08 Hz) 1.56 (m) 2.64 (m)	18.0 (q) 25.4 (d) 26.5 (t) 33.7 (t) 122.8 (s, CN)	73.38	9.99	16.80	73.26	9.81	17.06
5	140/0.3	11.02	2232	1.32 (d, J=7.08 Hz) 1.54 (m) 2.62 (m)	18.0 (q) 25.4 (d) 26.7 (t) 28.5 (t) 33.8 (t) 122.7 (s, CN)	73.87	10.45	15.95	74.11	10.18	15.71
6	155/0.3	14.97	2230	1.32 (d, J=7.08 Hz) 1.51 (m) 2.62 (m)	18.0 (q) 25.5 (d) 26.9 (t) 28.8 (t) 34.0 (t) 123.0 (s, CN)	74.82	10.64	14.53	74.95	10.48	14.57

a) $CH_3CH(CN)CH_2)_nCH(CN)CH_3$. b) Oven temperature of Kugelrohr apparatus in the vaccum distillation (1 mmHg=133.322 Pa). c) A 3 m column of Silicone SE-30 (10% on Uniport B (60-80 mesh)), carrier gas flow 40 cm^3 min^{-1}, column temp 180 °C. A Shimadzu GC-4CM gas chromatograph was used, and data were analyzed by a Shimadzu Chromatopac E1A. d) ν_{CN}, observed with the neat film. e) Observed in $CDCl_3$, using TMS as an internal reference. JEOL FX-100 NMR spectroscopy was used. f) A mixture of two stereoisomers (the ratio is 2:3).



Scheme 1.

π-acetylene complexes.[7)] The reaction solution may involve both zero- and univalent cyanonickelate,[6)] but formation of the π-acetylene complex with Ni(0) seems more probable than with Ni(I). The coordinated acetylene may have some radical character,[7)] and react with $[Ni(CN)_3H]^{2-}$ to form a (σ-vinyl)nickel(II) complex as shown in Scheme 1.

Experimental

The reaction was performed in a three-necked flask equipped with a cold finger at 45 °C under an atmosphere of nitrogen. $K_2[Ni(CN)_4]$ (0.8 mmol, 0.193 g), KCN (1.6 mmol, 0.101 g), $NaBH_4$ (4 mmol, 0.151 g), or Zn (4 mmol, 0.262 g) were placed in the flask. After purging the reaction vessel thoroughly with nitrogen, diyne, $HC{\equiv}C(CH_2)_nC{\equiv}CH$, (0.8 mmol, 0.09 cm^3 ($n$=3), 0.10 cm^3 ($n$=4), 0.12 cm^3 ($n$=5), 0.13 cm^3 ($n$=6), purchased from Tokyo Kasei Co. LTD) and 4 cm^3 of solvent (water or ethylene glycol) were added with syringes through a rubber serum cap, and the solution was stirred magnetically. The yellow reaction solution became dark red when the reaction was complete. The products were extracted with dichloromethane and analyzed by GLC, using a 3 m column of Silicone SE-30, with carrier gas flow of 40 cm^3 min^{-1}, at 180 °C. A larger scale reaction was also performed in a 20 cm^3 solvent, and the products were distilled by using Kugelrohr apparatus (Büchi's Glass Tube Oven KGR-50). Pure products were obtained by a preparative GLC. They gave satisfactory elemental analyses. Their structures were characterized by IR, ^{1}H, and ^{13}C NMR spectroscopy.

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