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Catalytic Hydrocyanation of Dienes and Trienes

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The hydrocyanation of dienes and trienes using nickel-(0)-phosphite complexes as catalysts yielded various mono- and dinitriles, which can be important starting materials in organic syntheses. The reactivities of conjugated and isolated dienes were compared and the products formed could be explained by either an alkyl or an allyl mechanism. The hydrocyanation of conjugated dienes yielded mainly 1,4-adducts. The conversion of the diene decreased in the series butadiene > piperylene > isoprene indicative for the formation of η^3-allyl systems, which show different stability. The hydrocyanations of nonconjugated α-ω-diolefins, such as 1,4-pentadiene, 1,5-hexadiene, and 1,7-octadiene, yielded various nitriles depending on the number of methylene groups separating the two double bonds. Whereas 1,4-pentadiene and 1,5-hexadiene yielded mainly products originating from conjugated dienes formed by isomerization, 1,7-octadiene gave sebacic dinitrile in a yield of 22%. 1,3,7-Octatriene, which contains an isolated double bond and a conjugated diene system combined in one molecule, gave six nitriles in which the cyano groups are attached to carbon number 2 or 4 of the C_8 chain. The products can be explained by an allyl mechanism and concomitant isomerization.

INTRODUCTION

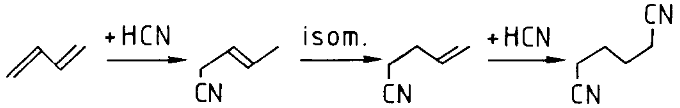
The catalytic hydrocyanation of olefins and diolefins is a new synthetic method to prepare alkyl nitriles and dinitriles, which can be important starting materials for amides, amines, and acids (*1*).

Taylor and Swift (*2*) report the hydrocyanation of 1-hexene by zerovalent nickel phosphite complexes promoted by Lewis acids such as $ZnCl_2$ yielding isomeric heptanenitriles. Using *n*-octenes as starting materials, we found that, irrespective of the position of the double bond, the anti-Markownikow-adduct perlargonic nitrile was formed with 80% selectivity, if $AlEtCl_2$ was used as co-catalyst (*3*). Also hydrocyanation of substituted olefins like pentenenitrile (*4–8*), styrene, acrylonitrile (*1*), vinylsilanes (*9*), and sulfolene (*10*) has been reported.

Mechanistically all these reactions can be explained by what we wish to call the "alkyl mechanism," which is illustrated in Fig. 1.

The oxidative addition of HCN to a NiL_4 complex yields the nickel-hydrido-cyano species **1**, which alone or activated by a Lewis acid coordinates an olefin followed by insertion yielding the nickel-alkyl species **2**. Elimination affords the nitrile and the coordinatively unsaturated complex NiL_3, which again can add a further ligand forming the initial complex NiL_4. Also direct addition of HCN on NiL_3 is possible giving the nickel-hydrido-cyano species **1** thus closing the catalytic cycle.

Of special industrial importance is the hydrocyanation of butadiene shown in Eq. (1).



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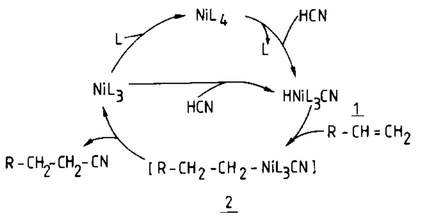

FIG. 1. The alkyl mechanism of the hydrocyanation of monoolefins.

The monohydrocyanation of butadiene yielding pentenenitriles is catalyzed by copper complexes (*14–17*); the twofold hydrocyanation can be achieved by nickel catalysts (*5, 11–13*). The Du Pont de Nemours Company has commercialized this new adiponitrile route applying zerovalent nickel phosphite catalysts. It can be postulated that analogous to other 1,3-diene reactions an "allyl mechanism" shown in Fig. 2 will be applicable.

The nickel-hydrido-cyano species **1** reacts with the diene forming the nickel-allyl-cyano complex **3**. By reductive elimination the nitriles and the complex NiL_3 are formed. The nitriles consisting of 3-pentenenitrile and 2-methyl-3-butenenitrile can be derived via 1,4- and 1,2-addition, respectively. The catalytic cycle will be closed in an analogous way to that discussed in Fig. 1.

Many years ago we became interested in a systematic investigation of the HCN addition to dienes and trienes, which could give rise to new industrial applications. In addition, our interest centered on the validity of the allyl mechanisms. Our experiments focused on the following points:

(1) effect of the methyl group in isoprene and piperylene;

(2) influence of CH_2-spacing groups in α,ω-diolefins;

(3) hydrocyanation of trienes possessing a conjugated diene and an isolated monoene such as 1,3,7-octatriene.

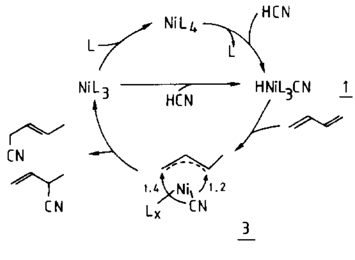

FIG. 2. The allyl mechanism of the hydrocyanation of butadiene.

EXPERIMENTAL

Reagents

The commercial hydrogen cyanide (Degussa,[1] Hanau) contains traces of water and is stabilised by sulfur dioxide. To remove the moisture the liquid HCN is dried over $CaCl_2$ in a cooled vessel. To blow out the SO_2 a stream of dried argon is passed through the liquid HCN at a temperature of 0°C until 5% of the initial volume is evaporated. By heating the vessel to 40°C the hydrogen cyanide is distilled into a storage bottle.

The olefins were obtained as follows:

isoprene	Chemische Werke Hüls[1]
piperylene	Deutsche BP[1]
1,4-pentadiene	synthesized by pyrolysis of 1,5-bis-acetoxypentane
1,5-hexadiene	EGA-Chemie
1,7-octadiene	Erdölchemie[1]
1,3,7-octatriene	synthesized by palladium-catalyzed dimerization of butadiene (*18*)

The phosphites were obtained as follows:

$P(O{-}2{-}Cl{-}Et)_3$	synthesized by ethylene oxide and PCl_3 (*19*)
$P(OBu^n)_3$	EGA-Chemie
$P(OC_{18}{}^n)_3$	synthesized by stearyl alcohol and PCl_3 (*20*)
$P(OPh)_3$	Bayer AG[1]
$P(O{-}p{-}Me{-}Ph)_3$	synthesized by the substituted phenols and PCl_3 (*21*)
$P(O{-}p{-}Bu^t{-}Ph)_3$	
$P(O{-}2{-}naphthyl)_3$	

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[1] We thank these firms for donating these chemicals.

The tetrakistriarylphosphitenickel(0) complexes were prepared according to the methods described in the literature (*22*). Tetrakis(tri-*n*-octadecylphosphite)nickel(0) was synthesized by the reaction of the phosphite with Ni(cod)$_2$ (*23*).

Procedure

All operations, except the workup of the reaction products, were carried out under argon.

The hydrocyanations were accomplished using two methods depending on the boiling points of the olefins.

Experiments with high-boiling olefins have been carried out in a glass vessel. The magnetically stirred reactor was fitted with a dropping funnel, an argon inlet, and a reflux condenser which was cooled by a refrigerant at −20°C. The NiL$_4$ complex, the excess of ligand, and the olefin were added to the flask while the hydrogen cyanide was charged into the funnel. After intensive mixing of the solution and after heating to the reaction temperature (generally 70°C), the HCN was added dropwise at an approximate rate of 50 mmol HCN/h · mmol NiL$_4$.

Deactivation of the catalyst was obvious from an increase in the reflux of hydrogen cyanide.

The excess of hydrogen cyanide was evaporated by switching off the cooler and increasing the argon stream. The reaction mixture obtained was distilled under vacuum and the fractions were analyzed by GLC.

Separation of the individual nitriles was carried out by preparative GLC. The products were characterized by elemental analysis, ir, ^{1}H-NMR, ^{13}C-NMR, and mass spectra.[2]

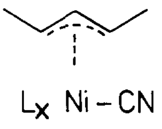
The hydrocyanation of olefins with a low boiling point such as the conjugated dienes isoprene and piperylene was carried out in a glass autoclave provided with a manometer and a magnetic stirrer. The whole amount of hydrogen cyanide was added at the same time by a syringe.

RESULTS AND DISCUSSION

(*a*) *Hydrocyanation of Conjugated Dienes*

Our results on hydrocyanation of isoprene and piperylene are summarized in Table 1, which for reasons of comparison also contains results obtained with butadiene under the same reaction conditions.

The hydrocyanation of piperylene yielded only one product, 2-methyl-3-pentenenitrile. This was to be expected, because the 1,4- and 1,2-adducts are identical. The reaction of hydrogen cyanide and isoprene afforded the 1,4-adduct 3-methyl-3-pentenenitrile and the 1,2-adduct 2,3-dimethyl-3-butenenitrile. By comparing the three 1,3-dienes it can be stated that the 1,4-adducts are always the main products. In addition, the conversion of the diene decreases in the order butadiene > piperylene > isoprene. Obviously, methyl substituents hinder the hydrocyanation of 1,3-dienes, an observation which agrees well with the allyl mechanism giving rise to the formation of **4** for piperylene and **5** for isoprene both possessing different stability.



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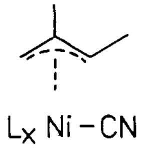

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Co-catalysts, which are effective in the hydrocyanation of monoolefins, disturb the hydrocyanation of 1,3-dienes. For instance, by adding AlEtCl$_2$ the conversion of piperylene decreases from 74 to 28%. Also the addition of solvents like THF, chlorobenzene, or phenol reduces the conversion.

(*b*) *Hydrocyanation of Nonconjugated Dienes*

Conjugated dienes easily form η^3-allyl intermediates. The question arises as to how

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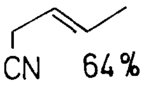
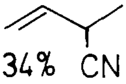
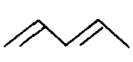
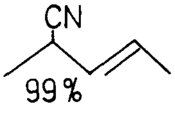
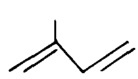
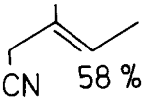
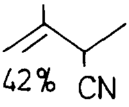
[2] Supplementary information is available upon request.

TABLE 1

Hydrocyanation of Conjugated Dienes[a]

1,3-diene	conversion of diene(%)	product distribution	
		1,4-adduct	1,2-adduct
	98	 64%	 34%
	74	 99%	
	26	 58 %	 42%

[a] Catalyst: 1.3 g (1 mmol) Ni[P(OPh)$_3$]$_4$, 4.96 g (16 mmol) P(OPh)$_3$, 100 mmol diene, 100 mmol HCN. T = 90°C; t = 90° min.

α,ω-dienes react, since here the double bonds are separated by several methylene groups. They can isomerize prior to hydrocyanation forming conjugated systems. It can also be expected that they will form linear α-ω-dinitriles by an isomerization-free HCN addition.

Table 2 lists the nonconjugated dienes which we have investigated.

In the reactions of 1,4-pentadiene and 1,5-hexadiene the nickel-catalyzed isomerization is much faster than hydrocyanation. The conjugated dienes formed react with HCN as discussed in the allyl mechanism. Mononitriles are the products observed.

1,4-Pentadiene, which isomerizes to piperylene, gives only 2-methyl-3-pentenenitrile.

1,5-Hexadiene, which can isomerize to 1,3- or 2,4-hexadiene, thus forming the intermediate allyl complex **6**, yields 2-methyl-3-hexenenitrile and 2-ethyl-3-pentenenitrile as is evident from Fig. 3.

Interestingly, using 1,7-octadiene a twofold anti-Markownikow addition of HCN even in the absence of a Lewis acid was observed. Isomeric mononitriles (57%), sebacic dinitrile (22%), and other nonidentified dinitriles (21%) were obtained. An olefin-to-catalyst ratio of 10 : 1 was applied. To avoid isomerization a minor change of the experimental conditions was carried out: a mixture of 1,7-octadiene and hydrocyanic acid in toluene was added slowly to the catalyst solution during a 90-min period via a dropping funnel.

(*c*) *Hydrocyanation of 1,3,7-Octatriene*

1,3,7-Octatriene is a molecule with two different reaction centers, namely, an isolated double bond and a conjugated diene system. It therefore lends itself to a study of both the presence of a diene and a monoene unit.

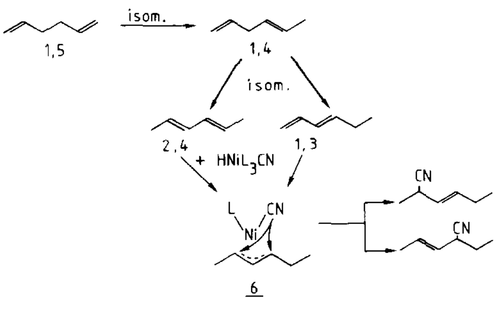
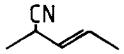
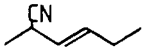
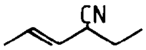


FIG. 3. Hydrocyanation of 1,5-hexadiene.

TABLE 2

Hydrocyanation of Nonconjugated Dienes[a]

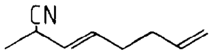
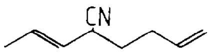
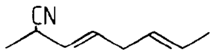
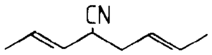
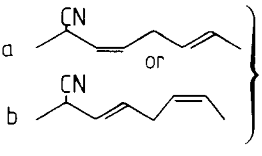
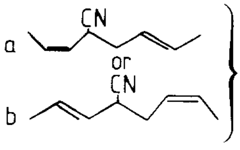
diene	ratio cat./diene	Conversion of diene %	product distribution	%
	1 : 100	82		99
	1 : 100	79		54
				46
	1 : 100	36	sebacic dinitrile	13
			isomeric dinitriles	4
			mononitriles	83
	1 : 10	99	sebacic dinitrile	22
			isomeric dinitriles	21
			mononitriles	57

[a] Catalyst: 1 mmol $Ni[P(OPh)_3]_4$, 16 mmol $P(OPh)_3$. $T = 90°C$; $t = 1.5$ h; diene/HCN ratio = 1 : 1.

The nickel-catalyzed hydrocyanation of 1,3,7-octatriene yielded the six products **7–12** (Table 3), in which the cyano groups are bonded to carbon atom 2 or 4 of the C_8 chain. In a typical experiment 1,3,7-octatriene was hydrocyanated by catalysis with $Ni[P(OPh)_3]_4$ and an excess of ligand, yielding 50 mol nitriles/mol nickel. Nitrile **7** was formed with a 40% selectivity, while 1,4-adduct **8** reached 30%. The residual 30%

TABLE 3

Products of the Hydrocyanation of 1,3,7-Octatriene

CN on C - atom 2	CN on C - atom 4
 7	 8
 9	 10
 11	 12

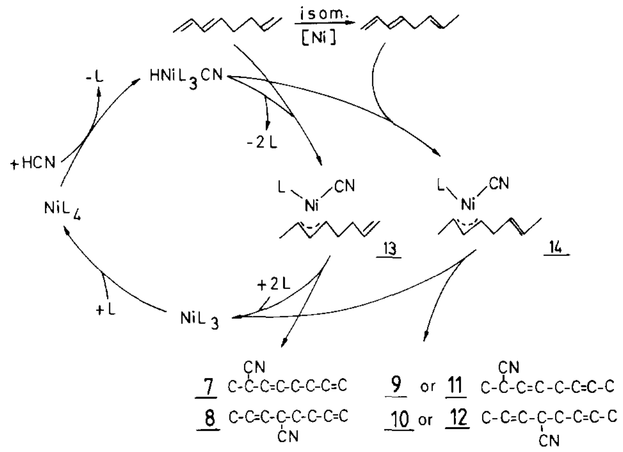


FIG. 4. Mechanism of the hydrocyanation of 1,3,7-octatriene.

consists of the four other isomers **9** to **12**. All products can be explained by the allyl mechanism shown in Fig. 4.

The main products are always the nitriles **7** and **8**, which are formed from the allyl complex **13**. This complex results from a direct reaction of 1,3,7-octatriene and the nickel-hydrido-cyano species as **1**. In a parallel reaction 1,3,7-octatriene can isomerize to 1,3,6-octatriene, which forms an allyl complex **14**, from which the nitriles **9** to **12** can be derived. The compounds **9**, **11** and **10**, **12** differ in the position of the double bonds. Spectroscopically we could not distinguish between the isomers **11a**, **11b** and **12a**, **12b**.

To optimize selectivity and activity, the catalyst has been modified. In Table 4 the influence of the ligand on activity and product distribution is demonstrated. In addition, this table contains two parameters which help to assess the steric and electronic behaviour of the ligands, namely, the cone angle Θ which gives some measurement of the steric hindrance and the ΣX_i values which describe the σ-donor and π-back-bonding ability of the ligands (*24*). The electronic properties of the ligand have

TABLE 4

Influence of the Ligand in Hydrocyanation of 1,3,7-Octatriene

Ligand	ΣX_i (cm^{-1})	Θ (°)	TON[a]	Product distribution (%)		
				7	**8**	**9–12**
P(O-2-Cl-Et)$_3$	27.9	110	0	—	—	—
P(OBu^n)$_3$	19.5	115[b]	9	54	36	10
P(OC$_{18}$^{n})$_3$	19.0[b]	120[b]	63	42	31	27
P(OPh)$_3$	29.2	121	50	40	31	29
P(O-*p*-Me-Ph)$_3$	28.0	128	58	32	32	36
P(O-*p*-Bu^t-Ph)$_3$	28.0[b]	130[b]	50	28	33	39
P(O-*o*-Me-Ph)$_3$	28.0	141	2	—	—	—
P(O-2-naphthyl)$_3$	29.0[b]	145[b]	0	—	—	—

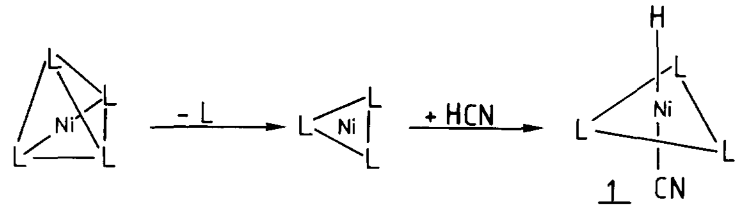
[a] Turnover number (mol nitrile/mol NiL$_4$).

[b] Estimated values.

no substantial influence. For instance, $P(OBu^n)_3$ and $P(OC_{18}{}^n)_3$, two phosphites with approximately equal basicity, show different activities.

A pronounced factor in controlling hydrocyanation seems to be the steric influence of the ligand. Active ligands have cone angles of 115–135°. Optimum activity is reached at 120–130°. The best ligands in our hands have been tri-*n*-octadecylphosphite, triphenylphosphite, and the *para*-substituted triarylphosphites.

This behaviour can be understood by considering the formation of the catalytically active nickel-hydrido-cyanide **1** (Eq. (2)) (*25*).



L = Phosphite

(2)

First, one phosphite ligand L dissociates before the oxidative addition of hydrogen cyanide occurs, forming the trigonal-bipyramidal nickel complex **1**. However, NiL_4 complexes with phosphite ligands which show only small cone angles are very stable and ligand dissociation is limited. On the other hand, the formation of the trigonal-bipyramidal structure is hindered if the three ligands L are too bulky. Therefore, ligands like tris-*o*-tolylphosphite ($\Theta = 141°$) are not able to form the catalytically active species. Only phosphites with a medium cone angle ($\Theta = 120–130°$) possess the best steric conditions to favour the reaction path shown in Eq. (2).

As is also obvious from Table 4, ligands steer the product distribution: phosphites with low cone angles favour the formation of the formal 1,2-adduct **7**, whilst phosphites with high cone angles steer to the isomeric products **9–12**. Only the formation of the 1,4-adduct **8** is not significantly influenced by the steric requirements of the ligands.

Another possibility to effect the reaction path is the addition of co-catalysts. Our results with the co-catalysts $ZnCl_2$ and $AlCl_3$ are shown in Table 5. With $ZnCl_2$ no increase of activity could be obtained. Addition of $AlCl_3$ leads to a loss in catalyst activity with the ligand $P(OC_{18}{}^n)_3$. However, nickel-arylphosphite complexes could be activated with $AlCl_3$.

Regarding the selectivity, adding $AlCl_3$ favours isomerization and the products **9** to **12** prevail.

In our normal experiments with 1,3,7-octatriene the formation of dinitriles could not be observed. However, when the product mixture of monocyanooctadienes was used as the substrate and a twofold excess of hydrocyanic acid was applied, new products were observed by GLC analysis. Elemental analysis showed that the nitrogen content was increased to 15.4%, indicating

TABLE 5

Influence of the Co-catalyst in Hydrocyanation of 1,3,7-Octatriene

Nickel complex	Co-catalyst	TON[a]
$Ni[P(O\text{-}p\text{-}Me\text{-}Ph)_3]_4$	—	51
	$ZnCl_2$	50
$Ni[P(OC_{18}{}^n)_3]_4$	—	63
	$AlCl_3$	35
$Ni[P(O\text{-}p\text{-}Bu^t\text{-}Ph)_3]_4$	—	66
	$AlCl_3$	149

[a] mol nitriles/mol nickel.

a partial twofold hydrocyanation. Because of the complexity of products obtained a characterization was omitted.

ACKNOWLEDGMENTS

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