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CONVERSION OF ACRYLONITRILE INTO 1,4-DICYANOBUTA-1,3-DIENE AND PROPIONITRILE CATALYSED BY GROUP VIII METAL SPECIES

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Summary

At 150°C the conversion of acrylonitrile into nearly equimolar quantities of propionitrile and a mixture of 1,4-dicyanobuta-1,3-dienes is catalysed homogeneously by certain platinum and ruthenium species.

Introduction

A recent account [1] of the catalytic disproportionative coupling of ethylene into ethane and butadiene prompts us to report the analogous conversion of acrylonitrile into propionitrile and 1,4-dicyanobuta-1,3-diene, a potential precursor of nylon-6,6.

During studies of olefin amination, treatment of ethylene in acetone with *trans*-$(C_2H_4)PtCl_2(Et_3NH)$ [2] was found to give traces of butadiene. Since group additivity tables [3] show that conversion of ethylene into butadiene and ethane is very favourable thermodynamically (ΔH°_{298} —32 kcal mol^{-1}, ΔS^0_{298} —34 Gibb mol^{-1}) * and that the energetics of the overall reaction are rather insensitive to the presence of substituents on the olefin, effort was directed at the commercially more attractive disproportionative coupling of acrylonitrile. This study provides the first unambiguous evidence for a functionalised olefin reacting in this way.

Experimental

Materials

Acrylonitrile (BDH) was freshly distilled under nitrogen. Catalysts and standards of 1,4-dicyanobuta-1,3-diene were prepared by literature methods [4].

General procedure

Typically, acrylonitrile (15.2 mmol) and catalyst (0.1 mgatom of metal) were

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* Gibb ≡ cal °C^{-1}.

degassed and sealed in a Carius tube. Reactions were performed at 150°C for 4 h. Products were analysed by GLC (FID) using a 2 m column of 5% LAC-2R-446 at 50°C for monomers and at 160°C for dimers. Products were identified on the basis of their retention times and their GLC mass spectra.

Results and discussion

As shown in Table 1, *trans*-$(C_2H_4)Pt(Et_2NH)Cl_2$ and $Et_2NHCH_2CH_2PtCl_2(Et_2NH)$ promote the conversion of acrylonitrile into propionitrile and 1,4-dicyanobuta-1,3-diene. Other platinum complexes closely related to these active species, but lacking the diethylamine ligand, do not support the reaction. We believe that this is the first example of acrylonitrile dimerisation in solution catalysed at a metal centre other than ruthenium [5].

Dimerisation of acrylonitrile mainly into 1,4-dicyanobut-1-ene is catalysed rapidly by $RuCl_3 \cdot 3H_2O$ in the presence of hydrogen [6]. In the absence of hydrogen, but with an electron-donating ligand present, the slow formation of 1,4-dicyanobuta-1,3-diene promoted by $RuCl_3 \cdot 3H_2O$ has been reported [7]. The fate of the hydrogen lost in this condensation was not determined. As with the platinum-catalysed reaction, we find the co-product of this Ru reaction is propionitrile (eq. 1).

$$3\ CH_2{=}CHCN \rightarrow CH_3CH_2CN + NCCH{=}CHCH{=}CHCN \qquad (1)$$

The stoichiometry of reaction 1 is not always followed exactly and an excess of propionitrile is sometimes formed (Table 1). In the reactions catalysed by $(C_2H_4)Pt(Et_2NH)Cl_2$ and by $RuCl_3 \cdot 3H_2O/KOAc$, propionitrile and 1,4-dicyanobuta-1,3-diene are formed nearly linearly with time up to 4 h, so they are probably primary products *.

At longer reactions times, the yield of 1,4-dicyanobuta-1,3-diene approaches a maximum of ca. 0.6 mmol after 8 h, but propionitrile formation continues unabated. Thus, in these two reactions, the slight excess of propionitrile probably results from the instability of the diene, and this instability is confirmed by observation of the degradation of 1,4-dicyanobuta-1,3-diene added to the reaction mixture. However, the large excess of propionitrile resulting from the $RuCl_3 \cdot 3H_2O/Et_3N$ reaction presumably results from a concurrent hydrogenation. Consumption of acrylonitrile in excess of the volatile products measured is attributed to polymerisation.

The distribution of geometrical isomers of 1,4-dicyanobuta-1,3-diene is approximately that expected if there was no preference between *cis*- and *trans*-geometry about the olefinic bonds. This is in marked contrast to the observation [8] that the related disproportionation of hex-1-ene into hexane and hexa-2,4-diene yields the diene isomers in nearly equilibrium ratio ** (it is estimated [3] that *cis*-substituted olefins are about 1 kcal mol^{-1} less stable than their *trans*-isomers).

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* Although 1,4-dicyanobut-1-ene is also formed in the presence of most of the ruthenium catalysts in yield 0.2 that of 1,4-dicyanobuta-1,3-diene, this olefin is stable towards the conditions of both the Pt and Ru reactions, and so it is not a precursor of 1,4-dicyanobuta-1,3diene.

** In this energetically less favourable reaction ($\Delta H^0 = -9.60$ kcal mol^{-1}, $\Delta S^0 = -0.24$ Gibb mol^{-1} [3]), apparently the transition states resemble the product isomers much more closely than is the case in disproportionative coupling [9].

TABLE 1

REACTIONS OF ACRYLONTRILE (15.2 mmol) AT 150°C FOR 4 h

Complex (0.1 mg-atom)	Addtivie (mmol)	Acrylonitrile consumed (mmol)	Products (mmol)			
			Propionitrile	1,4-Dicyanobuta-1,3-diene		
				cis, cis	*cis, trans*	*trans. trans*
None	0	0.4	0	0	0	0
$(C_2H_4)Pt(Et_2NH)Cl_2$	0	2.3	0.40	0.07	0.16[a]	0.11
$Et_2NHCH_2CH_2Pt(Et_2NH)Cl_2$	0	2.6	0.46	0.04	0.10[a]	0.07
$(C_2H_4)Pt(Et_2NH)Cl_2$	KOAc (0.6)	1.7	0.07	0	0	0
$(C_2H_4)(Ph_3P)PtCl_2$	0	1.5	0	0	0	0
$[(C_2H_4)PtCl_2]_2$	0	0.4	0	0	0	0
$RuCl_3 \cdot 3H_2O$	0	2.4	0	0	0	0
$RuCl_2 \cdot 3H_2O$	KOAc (0.6)	1.2	0.35	0.05	0.20[b]	0.05
$RuCl_3 \cdot 3H_2O$	Et_3N (0.6)	4.3	0.83	0.14	0.26[b]	0.15
$RuCl_3 \cdot 3H_2O$	KOAc (0.6) Et_3N (0.6)	3.1	0.29	0.05	0.17[b]	0.06
$[Ru_3O(AcO)_6(H_2O)_3]OAc$	0	2.1	0.28	0.06	0.18[a]	0.06
$[Ru_3O(EtCOO)_6(H_2O)_3]OOCEt$	0	1.4	0.17	0.04	0.11[b]	0.02

[a] Essentially no 1,4-dicyanobut-1-ene formed. [b] 1,4-Dicyano-but-1-ene appears as a shoulder on the GLC peak but it is not included in the determination.

Both the platinum and ruthenium catalysed reactions follow Arrhenius temperature dependence between 120 and 160°C with activation energies of ca. 16 kcal mol^{-1}. We note with interest that the 1/1 ratio of dimer/propionitrile is strikingly similar to that of the highest such ratio obtained with the $RuCl_3 \cdot 3H_2O/H_2$ system [6].

Pez implies [1] that ethylene disproportionative coupling is a rare example of a novel transformation which requires a polymetallic catalyst. Our work indicates that this class of reaction can also be catalysed by monometallic species.

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