Evidence for a Ruthenium Insertion Reaction into a Vinylic Carbon–Hydrogen Bond

By E. BILLIG,* C. B. STROW, and R. L. PRUETT

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

THERE have been reports[1] concerning the conversion of acrylonitrile into a mixture of 1,4-dicyanobut-1-ene (DCB) and propionitrile (PN) *via* ruthenium chloride catalysis. This reaction requires hydrogen pressures of 200—600 lb. in.$^{-2}$ at 100—150° for a suitably high reaction rate. No significant catalytic reaction occurs in the absence of hydrogen.

We report the effect on the reaction of adding $SnCl_2$ (or Et_4NSnCl_3) together with bifunctional amines such as *N*-methylmorpholine, and/or bifunctional alcohols such as Methylcellosolve. The net result of inclusion of these ligands is a lowering of the minimum hydrogen pressure requirement by a factor of *ca.* 4 (under the same temperature conditions as the analogous "high-pressure" dimerization). A typical "low-pressure" run carried out at 85 lb. in.$^{-2}$ H_2 and 150° is given in Table 1, example 1. In analogy to the "high-pressure" dimerization, no catalytic reaction was observed in the absence of hydrogen.

In order to elucidate the role of hydrogen in the

TABLE 1

No.	Pressure lb. in.$^{-2}$	Time (hr.)	$RuCl_3,3H_2O$ (moles × 10^{-3})	Et_4NSnCl_3 (moles × 10^{-3})	Amine[a] (moles × 10^{-2})	Solvent[b] (g.)	AN (g) initial	AN (g) final	Products (g.) *cis*-DCB	Products (g.) ADN[c]	Products (g.) *trans*-DCB	Products (g.) PN	Efficiency to dimer (%)	Efficiency to PN (%)
1	$85/H_2$	3	1·5	1·5 × 10^{-3}	2·5 × 10^{-2}	100	30·5	1·00	6·28	2·97	7·21	11·2	55·8	38·1
2	$85/{}^2H_2$	,,	,,	,,	,,	,,	,,	2·35	5·99	2·35	7·00	9·32	54·5	33·1

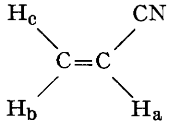
[a] Amine = *N*-methylmorpholine.
[b] Solvent = Methylcellosolve
[c] ADN = adiponitrile.

TABLE 2

	% Deuteriation $[^2H_0]$	$[^2H_1]$	$[^2H_2]$	$[^2H_3]$	$[^2H_4]$
Acrylonitrile	67·2	25·6	7·2		
Propionitrile	77·5	20·3	2·2		
cis-1,4-Dicyanobut-1-ene ..	31·1	41·1	21·2	5·7	0·9
trans-1,4-Dicyanobut-1-ene ..	40·2	38·8	16·1	4·0	1·0
Methylcellosolve	100·0				
$^2H_2$			100·0		

"low-pressure" reaction, a series of dimerizations were carried out under a deuterium atmosphere (see Table 1, example 2). Per cent deuterium incorporation into products and unreacted acrylonitrile (AN), determined by mass spectral analysis, is given in Table 2.

The 100 MHz n.m.r. spectrum of the recovered partially deuteriated acrylonitrile indicated that deuterium was incorporated, with a high degree of specificity, *trans* and β to the cyano-group. The chemical shifts of the various protons of perprotioacrylonitrile, expressed in p.p.m. (δ) from tetramethylsilane are:



H_a 5·72, H_b 6·08, and H_c 6·22 p.p.m. The coupling constants are J_{ac} 18, J_{ab} 11·5, and J_{bc} 1·6 Hz. The spectrum of the recovered, partially deuteriated acrylonitrile contained the expected absorption lines from the perprotioacrylonitrile, and an additional pair of multiplets separated by 18 Hz, representing H_a in the partially deuteriated molecules. The absence of the *cis*-coupling constant in the resonance multiplets of H_a, places the deuterium *trans* to the cyano-group. Fine splitting (1—2 Hz) was observed due to deuteron–proton interactions. The propionitrile formed in the reaction was largely perprotio (77·5%) and contained only 20·3% of monodeuteriopropionitrile.

Because of the type and extent of deuterium incorporation into acrylonitrile and propionitrile one can rule out a mechanism involving formation of a ruthenium deuteride (or hydride) *via* reaction (a). Such a process would lead to α-deuterioacrylonitrile *via* (b) and (c_1), as well as predicting

(a) $Ru^{II} + D_2 + B \longrightarrow Ru^{IV}D + BD^+$

(b) $Ru^{IV}D + CH_2{=}CH{\cdot}CN \longrightarrow Ru{-}CH_2{\cdot}CH(D){\cdot}CN$*

(c) $Ru{-}CH_2{\cdot}CH(D){\cdot}CN \xrightarrow[(c_1)]{-H} CH_2{=}CH(D){\cdot}CN$

$Ru{-}CH_2{\cdot}CH(D){\cdot}CN \xrightarrow[+D_2]{(c_2)} CH_2(D){\cdot}CH(D){\cdot}CN$

the formation of predominantly 1,2-dideuteriopropionitrile *via* (b) and (c_2).

Alternatively, formation of a ruthenium hydride

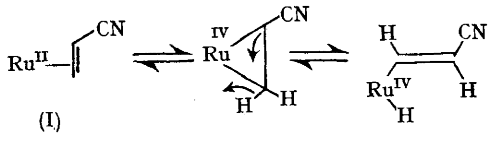
---

* The alternative addition intermediate, $Ru{-}CH(CN){-}CH_2D$ would give rise to non-linear dimers.

via a reaction with Methylcellosolve is unlikely since no incorporation of deuterium into the solvent was observed. Moreover, the reaction proceeded, albeit at a slower rate, in the absence of hydroxylic solvents. A mechanism that is consistent with the accumulated ^{1}H and ^{2}H n.m.r. data for the "low-pressure" reaction is presented in reactions (d)–(i).

Catalyst generation

(d)



(I) (II) (III)

Dimerization

(e) $(III) + CH_2{=}CH{-}CN \longrightarrow NC{\cdot}CH_2{\cdot}CH_2{-}Ru^{IV}{-}CH{=}CH{\cdot}CN$

(IV)

(f) $NC{\cdot}CH_2{\cdot}CH_2{-}Ru^{IV}{-}CH{=}CH{\cdot}CN \xrightarrow{CH_2=CH\cdot CN} (I) + NC{\cdot}CH{=}CH{-}CH_2{\cdot}CH_2{\cdot}CN$†

† Equilibration of the dimers occurs under the reaction conditions giving an equilibrium mixture of 1·2—1·0 *trans*—*cis*-1,4-dicyanobut-1-ene (DCB).

Reduction

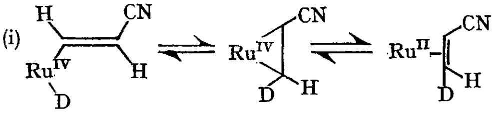
(g) $(IV) + (III) \longrightarrow MeCH_2{\cdot}CN + NC{\cdot}CH{=}CH{-}Ru{-}Ru{-}CH{=}CH{\cdot}CN$

(V)

(h) $NC{\cdot}CH{=}CH{-}Ru{-}Ru{-}CH{=}CH{\cdot}CN + D_2 \longrightarrow 2D{-}Ru{-}CH{=}CH{\cdot}CN$

(VI)

(i)



A catalytic species such as (III), formed *via* reaction (d), would account for the relatively small amount of deuteriopropionitrile formed. Reactions (d)–(i) also describe a possible stereospecific route for *trans*-β-deuterium incorporation into unchanged acrylonitrile. Deuterium incorporation into 1,4-dicyanobut-1-ene would occur from insertion of acrylonitrile into (VI) followed by reaction (f). Vinylic protium–deuterium exchange in dicyanobutene could also occur through reactions analogous to (d) and (i) *via* a π-co-ordinated dicyanobutene.

The primary role of deuterium (or hydrogen) in the proposed scheme is for the regeneration of the active catalyst (VI or III). The promotional effect of $SnCl_2$, co-ordinated $SnCl_3^-$, may be due in part to the dissociation of $SnCl_3^-$ from (V), providing a vacant site for the attack of deuterium or hydrogen. In support of this, optimum conditions were realized by use of one equivalent of $SnCl_2$ or Et_4NSnCl_3 per mole of ruthenium. The "low-pressure" reaction was totally inhibited at ten equivalents of $SnCl_2$ per mole of ruthenium. The role of *N*-methylmorpholine and/or Methylcellosolve in promoting the "low-pressure" dimerization is less clear. However, in examining other solvent systems, it was found that the "low-pressure" reaction did not proceed in propan-2-ol, aqueous or anhydrous 1,2-dimethoxyethane, or ethylene glycol but did occur in propane-1,3- or -1,4-diol. This suggests that the solvent is functioning as a bridging ligand and a possible "inner-sphere" oxidative addition mechanism may be operative.

Related to the proposed cyanovinyl hydride oxidative addition, reaction (d), analogous insertions of metals into alkyl[2] and aryl[3] carbon–hydrogen bonds have been reported. To our knowledge, the present work represents the first evidence for transition-metal insertion into a vinylic carbon–hydrogen bond.

(*Received, August* **15*th*, 1968**; ***Com.*** **1129**.)

---

[1] A. Misono, Y. Uchida, M. Hidai, and H. Kanai, *Chem. Comm.*, 1967, 357; A. Misono, Y. Uchida, T. Saito, and M. Hidai, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1967, **20** (11), 1890; J. D. McClure, R. Owyang, and L. H. Slaugh, *J. Organometallic Chem.*, 1968, **12**, P8.

[2] J. Chatt and J. M. Davidson, *J. Chem. Soc.*, 1965, 843.

[3] M. A. Bennett and D. L. Milner, *Chem. Comm.*, 1967, 581.