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Isomerization of Olefins and Substituted Olefins Catalyzed by Nickel Complexes*

B. CORAIN* AND G. PUOSI†

Centro per lo Studio della Stabilità e Reattività dei Composti di Coordinazione del C.N.R., Università di Padova, Italy

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The catalytic activity of several Ni(diphosphine)$_2$/acid homogeneous systems (acid = HCN, CF_3COOH, CCl_3COOH, and H_2SO_4) in the double bond and *cis-trans* isomerizations of olefins has been tested with the following compounds: pentene-1, *cis*-pentene-2, *trans*-pentene-2, allyl benzene, allyl cyanide, allyl alcohol. The catalytic efficiency of the Ni(diphosphine)$_2$/acid systems depends markedly on the nature both of the diphosphine and of the acid employed. When the diphosphine is 1,4-bis(diphenylphosphino)butane and acid = HCN a particularly efficient catalytic system is formed *in situ* and only in the case of the allyl cyanide is the isomerization limited. During the isomerization of pentene-1, the stereoselectivity in the formation of the *cis*-2 and *trans*-2 isomers is quite dependent on the nature of the cocatalyst. It is proposed that a σ-alkyl mechanism is operating in the Ni(O)/CF_3COOH system and a π-allyl one in the case of Ni(O)/HCN.

The complex Ni(dpb)$_2$ [dpb = 1,4-bis(diphenylphosphino)butane] displays a remarkable reactivity towards a series of reagents both in substitution and in oxidative addition reactions (*1*). In particular, it undergoes a rather peculiar oxidative addition reaction with HCN in benzene, which occurs in two discrete steps: the first one produces the complex $Ni_2(I)(CN)_2(dpb)_3$ and the second leads to the stable square planar complex *trans*-[Ni(CN)$_2$(dpb)]$_2$ (ld). Moreover, the complex can activate the HCN molecule and promote its catalytic addition to butadiene to give 3-pentenenitrile with appreciable number of cycles and very limited production of branched isomers (*2*). It was also briefly reported that the system Ni(dpb)$_2$/HCN can catalyze double bond migration in pentene-1 and under very mild conditions (*3*). Finally it has been recently reported that the complex $Ni_2(I)(CN)_2(dpb)_3$ is an efficient catalyst for double bond migration in a variety of olefins in methylene chloride at 20°C (*4*).

We wish to describe here the catalytic activity of a variety of Ni(O)/acid systems on pentene-1 and substituted olefins and to point out how the nature of the acid cocatalyst affects the stereoselectivity of double bond migration and the catalytic activity of this system.

EXPERIMENTAL

Materials

Ni(dpb)$_2$, Ni(dpp)$_2$ (dpp = 1,3-bis(diphenylphosphino) propane), $Ni_2(CN)_2(dpb)_3$ and $Ni_2(CN)_4(dpb)_2$ were prepared by published methods (1c) (*4*, *5*). $NiCl_2(dpb)$ was prepared by adding a benzene solution (40 ml) of dpb (1 mmole) to $NiCl_2 \cdot 6H_2O$ (C. Erba reagent with low cobalt content) (1 mmole) in methanol (30 ml) under vigorous stirring at room temperature. The mauve precipitate was fil-

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† Centro Ricerche di Chimica Organica, Montedison (Novara).

tered off and washed with methanol (20 ml) and benzene (20 ml). *Anal.* Calcd for $NiCl_2P(C_6H_5)_2\text{-}(CH_2)_4\text{-}P(C_6H_5)_2$:C, 60.48; H, 5.04. Found: C, 59.57; H, 4.67. Benzene was a C. Erba RS solvent. The olefins were high-purity products (Fluka and Schuchardt) and were used as received. CF_3COOH (Schuchardt) was distilled before use and CCl_3COOH and H_2SO_4 (98%) were C. Erba reagents used as received. Hydrogen cyanide (Montedison) was purified by distillation at reduced pressure and room temperature, followed by degassing with argon.

Isomerization and Product Analysis

Double bond migration has been attempted on the following organic molecules: pentene-1, *cis*-pentene-2, *trans*-pentene-2, allyl alcohol, allyl cyanide and allyl benzene. The catalytic systems tested were the following: $Ni(dpb)_2/HCN$; $Ni(dpb)_2/CF_3COOH$; $Ni(dpb)_2/CCl_3COOH$; $Ni(dpp)_2/HCN$; $Ni(dpp)_2/CF_3COOH$. The solvent was benzene and concentrations are given in Table 1. The reactions, which were conducted under UPP argon (SIO), were followed by a combination of ir and g.l.c. analysis for the C_5H_{10} isomers and by ir spectra alone for the substituted olefins.

Infrared spectra were recorded on a Perkin Elmer 457. Gas–liquid chromatographic analysis was performed on a Hewlett-Packard research instrument employing stainless steel columns 4 m long filled with dimethylsulfolane on chromosorb (20%) at 30°C. Calibration graphs were used to determine the concentrations of C_5H_{10} isomers both with ir and GLC experiments.

The disappearance of pentene-1 can be followed at 1645 cm^{-1} ($\nu_{C=C}$) and the formation of the *cis*-2 isomer at ca 1660 cm^{-1}. However, the majority of the results in this case were obtained by GLC. In the conditions employed, the only products from isomerization of pentene-1 were the *cis*-2 and *trans*-2 isomers.

The reaction products of the isomerization of substituted olefins were identified by comparing the ir spectra of the reaction mixtures with those of standard solutions containing the expected reaction products. The solvent was benzene and the temperature 20°C ± 0.1. The isomerization reactions were performed in an argon atmosphere and the reaction vessel was a four-necked flask (50 ml), one neck of which bore a special valve for the addition of the solid catalyst. This equipment enables the apparatus (with the solid catalyst) to be filled with argon and the addition of the solvent, the olefins and the cocatalyst previously saturated with argon) is possible without oxygen contamination. Another neck was closed with a gas-tight rubber cap and samples for the ir or GLC analysis could be withdrawn easily by means of micro or ordinary syringes. The reactions of the C_5H_{10} isomers could be followed by GLC spectra for 90 min and change of isomer distribution with time could be determined accurately and reproducibly.

The isomerization of the substituted olefins was followed very easily by the decrease of characteristic ir bands of the reactants and the development of significant bands of the products. The ir or GLC spectrum of the olefin solution containing the cocatalyst was always taken as reference spectrum. An ir cell with sodium chloride windows and a 0.5 mm pathlength was

TABLE 1

Olefin	*M*	cat *M*	cocat *M*
pentene-1	1.5–0.4	1×10^{-2}–1×10^{-3}	7×10^{-2}–1×10^{-2}
cis-pentene-2	0.4	3×10^{-3}	1.3×10^{-2}
trans-pentene-2	0.4	3×10^{-3}	1.3×10^{-2}
allyl benzene	0.47	3.9×10^{-3}	1.5×10^{-2}
allyl cyanide	0.76	5.7×10^{-3}	13×10^{-2}
allyl alcohol	0.49	3.9×10^{-3}	1.5×10^{-2}

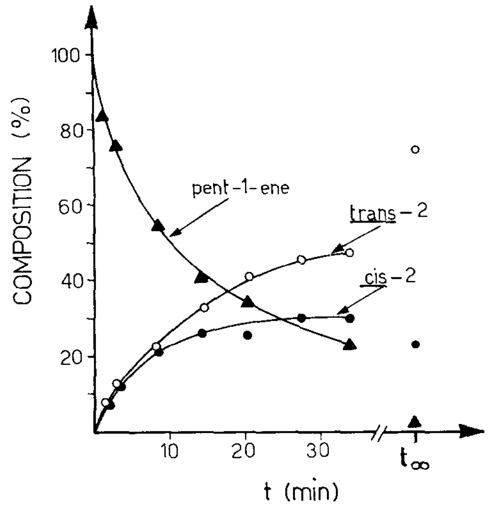

FIG. 1. Profile for the $Ni(dpb)_2/HCN$ catalyzed isomerization of pentene-1. $Ni(dpb)_2 = 1.1 \times 10^{-3}$ *M*; HCN = 1.3×10^{-2} *M*; pentene-1 = 0.39 *M*.

found most convenient for recording the spectra of the reacting solutions.

RESULTS

Behavior of $Ni(dpb)_2$

a. Pentene-1. Addition of the catalyst to the olefin solution containing HCN leads to clear golden-yellow solutions which are stable for several hours. After 10–15 hr, a yellow microcrystalline product begins to precipitate which has been identified as *trans*-$[Ni(CN)_2(dpb)]_2$ on the basis of ir and visible spectra (5). The profile of the isomers distribution vs. time for a typical experiment is given in Fig. 1. It is noteworthy that neither $Ni(dpb)_2$, in the absence of HCN, nor the complex $Ni(CN)_2$-(dpb) in the presence of HCN are capable of promoting the isomerization reaction under the conditions employed for the Ni(O)/HCN system.

When trifluoroacetic acid is the cocatalyst, a stable clear yellow solution is obtained and the isomer distribution vs. time graph is shown in Fig. 2. The t_∞ figures are relatively far from the equilibrium values. Good equilibrium figures can be obtained by using a Ni(O) concentration of 3.2×10^{-3} *M*.

b. *cis*-Pentene-2 and *trans*-pentene-2. When the cocatalyst is HCN, the visual pattern is identical with that observed for pentene-1. The isomerization reaction appears, however, to be much slower especially for the *trans* isomer in which the first changes were observed after ca 100 min (conditions of Table 1). Even for the *cis* isomer, only 22% had been converted into pentene-1 and *trans*-2 after 42 min.

When the cocatalyst is trifluoroacetic acid, the visible changes during the reaction are still identical with those observed for pentene-1 but the decrease in the rate of disappearance of the *cis*-2 isomer compared with that of the pentene-1 is even more

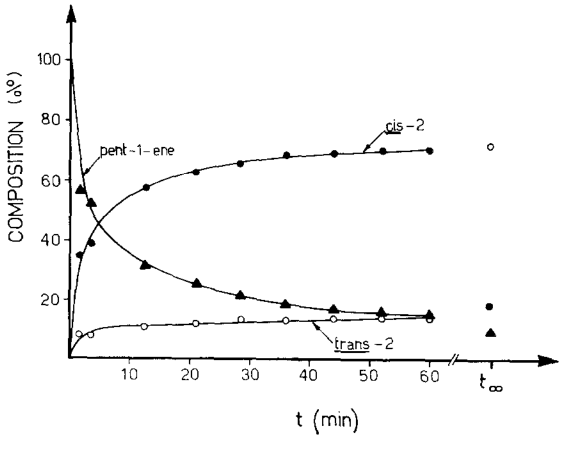

FIG. 2. Profile for the $Ni(dpb)_2/CF_3COOH$ catalyzed isomerization of pentene-1. $Ni(dpb)_2 = 1.1 \times 01^{-3}$ *M*; $CF_3COOH = 1.3 \times 10^{-2}$ *M*; pentene-1 = 0.39 *M*.

pronounced than that observed with HCN and *trans*-pentene-2 had not isomerized at all after 20 hr (conditions of Fig. 1).

c. Allyl benzene. The isomerization to *trans*-propenyl benzene occurs rapidly and quantitatively with both HCN and CF_3COOH as cocatalysts. The reaction is complete within ca. 40 min. The reaction mixture is homogeneous throughout during the isomerization.

d. Allyl alcohol. The isomerization occurs rapidly when the cocatalyst is HCN ($t_\infty \sim 25$ min). The disappearance of the bands due to the C=C and O—H stretches of the reagent and the appearance of a very strong band due to the C=O stretch attributable to an aldehyde reveal that the direct conversion of allyl alcohol to propionaldehyde occurs. In fact, the final ir spectrum is identical with that of an equimolar propionaldehyde benzene solution.

CF_3COOH is completely unable to cocatalyze the same isomerization in the conditions employed for HCN.

e. Allyl cyanide. The isomerization occurs only partially when either HCN or CF_3COOH are employed as cocatalysts. The C≡N stretching band of the reacting olefin decreases in intensity and a band at 2220 cm^{-1} develops. Comparison with a standard crotononitrile solution shows that a 5–10% conversion has occurred. The isomerization stops after ca 15 min at 20°C.

Behavior of Other Ni Complexes

The ability of the complex $Ni(dpp)_2$ to catalyze the isomerization of pentene-1 in the standard conditions employed was investigated in the presence of both HCN and CF_3COOH. With HCN the reaction proceeds much more slowly than with $Ni(dpb)_2$ and after 90 min only 20% of pentene-1 had isomerized ($Ni = 3.1 \times 10^{-3}$ M; $HCN = 7.4 \times 10^{-2}$ M; pentene-1 = 0.38 M). The solution initially appears clear and golden yellow, then slowly becomes dark red.

With CF_3COOH no catalysis at all was observed.

The Ni(II) complex, $Ni(CN)_2(dpb)$, which is the final oxidation product of $Ni(dpb)_2$ (1d), in the presence of free dpb (0.5 mole) and HCN, is unable to catalyze the isomerization of pentene-1 in the standard conditions employed for the complex $Ni(dpb)_2$.

Behavior of H_2SO_4 and CCl_3COOH as Cocatalysts

Sulfuric acid and trichloroacetic acid have been used as cocatalysts with $Ni(dpb)_2$ to isomerize pentene-1 under conditions similar to those employed for HCN and CF_3COOH. While H_2SO_4 is an efficient cocatalyst and the profile of the isomer distribution with time closely resembles that observed with CF_3COOH, the trichloro analogue is completely inactive. Addition of $Ni(dpb)_2$ to a benzene solution of CCl_3COOH leads to immediate precipitation of a mauve product, whose color and ir spectrum in the region 250–4000 cm^{-1} are identical to those of $NiCl_2(dpb)$ prepared from $NiCl_2$ and dpb in a mixture of ethyl alcohol and benzene.

The presence of free dpb slows down the isomerization of pentene-1 considerably when $Ni(dpb)_2$ is used. When the dpb concentration is ten times that of the catalyst, isomerization is almost undetectable after 20 min at 20°C and after 24 hr the isomer mixture is still far from the equilibrium one.

The results obtained in the present work are summarized in Table 2.

DISCUSSION

The compound $Ni(dpb)_2$ appears to be a versatile and efficient catalyst for the isomerization of different olefins under very mild conditions and the choice of the acid cocatalyst has a marked influence on the ratio of stereoisomers in the early stages of the isomerization. Hydrogen cyanide appears to be a more efficient cocatalyst than CF_3COOH and isomerization of the pentenes, allyl alcohol and allyl benzene can be achieved. The yield is limited only with allyl cyanide (Table 2).

H_2SO_4 also appears to be an effective cocatalyst in the isomerization of pentene-1, while CCl_3COOH fails completely. In the isomerization of pentene-1 the stereoselectivity is quite dependent on the nature

TABLE 2

BEHAVIOR OF Ni SYSTEMS IN THE CATALYTIC ISOMERIZATION OF VARIOUS OLEFINS

Catalyst	Cocatalyst	Olefin	Products %[a]	
$Ni(dpb)_2$	HCN	pentene-1	*cis*-2	(22.7)
			trans-2	(75.1)
$Ni(dpb)_2$	CF_3COOH	pentene-1	*cis*-2	(23.4)
			trans-2	(74.4)
$Ni(dpb)_2$	H_2SO_4	pentene-1	*cis*-2	(29.8)
			trans-2	(67.4)
$Ni(dpb)_2$	CCl_3COOH	pentene-1	none	
$Ni(dpp)_2$	HCN	pentene-1	*cis*-2	(43.4)[b]
			trans-2	(45.9)
$Ni(dpp)_2$	CF_3COOH	pentene-1	none	
$Ni(dpb)_2$	HCN	*cis*-pentene-2	pentene-1	(2.5)
			trans-2	(76.4)
$Ni(dpb)_2$	CF_3COOH	*cis*-pentene-2	pentene-1	(2.9)
			trans-2	(50.7)
$Ni(dpb)_2$	HCN	*trans*-pentene-2	pentene-1	(2.2)
			cis-2	(ca. 23.0)
$Ni(dpb)_2$	HCN	allyl benzene	*trans*-propenyl benzene	(100)
$Ni(dpb)_2$	CF_3COOH	allyl benzene	*trans*-propenyl benzene	(100)
$Ni(dpb)_2$	HCN	allyl alcohol	propionaldehyde	(100)
$Ni(dpb)_2$	CF_3COOH	allyl alcohol	none	
$Ni(dpb)_2$	HCN	allyl cyanide	crotononitrile	(5)
$Ni(dpb)_2$	CF_3COOH	allyl cyanide	crotononitrile	(10)
$Ni(CN)_2(dpb) + 0.5$ dpb	HCN	pentene-1	none	
$Ni(dpb)_2$	no	pentene-1	none	
$Ni_2(CN)_2(dpb)_3$	HCN	pentene-1	*cis*-2	(22.1)
			trans-2	(75.3)

[a] The composition of the C_5H_{10} isomers in the equilibrium mixture in benzene at 70°C is reported to be: pentene-1:3.3%; *cis*-2:20.2%; *trans*-2:76.5% (6).

[b] Composition after 120 hr.

of the cocatalyst. Inspection of figs. 1 and 2 reveals that in the early stages of the isomerization reaction the *cis/trans* ratio is larger then 1 when CF_3COOH is used (at 80% of pentene-1 the ratio is about 6), while when HCN is used (at 80% of pentene-1) the ratio is very nearly 1. For the H_2SO_4 cocatalyzed isomerization, the ratio is ca. 10 (at 80% of pentene-1).

The occurrence of kinetically controlled *cis*-2/*trans*-2 ratios during the early stages of the reaction, is a rather common feature of base or metal complex catalyzed double bond migration in terminal olefins. Thus ratios significantly larger than one were observed with Ni (*7*), Rh (*8*), Pd (*6*), Co (*9*) catalysts and organic bases (*10*) at low 1-olefin conversion. On the other hand, a very large *trans*-2/*cis*-2 ratio was observed for a Pt(II) catalyst (*11*).

Analysis of the literature indicates a substantial lack of correlation between stereoselectivity and type of catalytic mechanism and this discourages any attempt to deduce the detailed mechanism of the reactions involved from the data presented here.

What is certain is that in the system $Ni(P(O\text{-}Et)_3)_4/H_2SO_4$ the *cis/trans* ratio at zero conversion is 2.5 (*7*) for the isomerization of butene-1 and the catalytic species in this case is known to be a Ni(II) hydrido complex (*12*).

We believe that in the $Ni(dpb)_2/CF_3COOH$ system, the catalytic species is also a hydride complex, $Ni(dpb)(H)(CF_3COO)$, analogous to that prepared by Jonas and Wilke through the oxidative addition of CH_3COOH to $Ni(PCy_3)_2$ in toluene (*12*) and that the catalytic mechanism is a π-olefin/σ-alkyl type (intermolecular hydrogen exchange) based on the mentioned hydride complex.

The relatively limited efficiency of this system in interconverting the C_5H_{10} isomers can be due to further reaction of the hydride complex formed *in situ* with CF_3COOH leading to slow decomposition of the catalyst.

The inefficiency of CCl_3COOH is very probably due to the preferential breaking of the C–Cl bond which leads to the overall formation of a dichloro Ni(II) complex which is expected to be totally inactive, at least in the present conditions.

In the case of the $Ni(dpb)_2$/HCN system, the active species is thought to be the Ni(I) cyano complex $Ni_2(CN)_2(dpb)_3$ or a closely related species. It is known that the slow oxidation of $Ni(dpb)_2$ to *trans*-$Ni(CN)_2(dpb)_2$ occurs through the rapid formation of the isolable intermediate $Ni_2(CN)_2(dpb)_3$ and that hydride complexes are not formed in appreciable concentration during the reaction (1d). Moreover, we found here that a benzene solution of $Ni_2(CN)_2(dpb)_3$ (1d)(*4*) can catalyze the isomerization of pentene-1 displaying, in the presence of HCN (conditions as those reported in Fig. 1), stereoselectivity and efficiency very similar to those observed with the $Ni(dpb)_2$/HCN system. As it has been ascertained that the reaction of $Ni(dpb)_2$ or $Ni_2(CN)_2(dpb)_3$ with HCN in benzene does not lead to detectable amounts of Ni-hydride complexes (1d), it is tentatively proposed that a π-olefinic/π-allylic mechanism based on a Ni(I) complex is operative in the present case (intramolecular hydrogen exchange).

The marked decrease in the catalytic efficiency observed on passing from $Ni(dpb)_2$ to $Ni(dpp)_2$ is significant. In fact the reactivity of both complexes with HCN and $(CN)_2$ (*14*)(1a) for instance, is rather similar and preliminary data suggest that $Ni(dpb)_2$ and $Ni(dpp)_2$ react with CF_3COOH in benzene in a similar way. No simple explanation is proposed for this behaviour.

The complete inability of the $Ni(dpb)_2$/CF_3COOH system to isomerize allyl alcohol in contrast to $Ni(dpb)_2$/HCN again suggests that the mechanism is quite different on changing cocatalyst (it has been ascertained that CF_3COOH and allyl alcohol do not react appreciably in the experimental conditions employed).

Finally, the reduced ability of $Ni(dpb)_2$ in the presence of either HCN or CF_3COOH to isomerize allyl cyanide is again a remarkable feature of the catalytic systems described in the present work. We believe that a much more intensive study of the mechanism will be necessary to explain this last experimental result.

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