Hydrogenation, Hydrogenolysis, or Isomerization of Dienes and Monoenes Catalyzed by the Nickel Cyanide Complex

Taiichi MIZUTA, Hiroshi SAMEJIMA and Takao KWAN
Faculty of Pharmaceutical Sciences, The University of Tokyo, Hongo, Tokyo

(Received June 28, 1967)

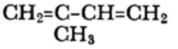
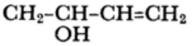
The hydrogenation, hydrogenolysis, and isomerization of allene, butadiene, isoprene, butene, and some of their derivatives were studied in an aqueous solution containing the nickel cyanide complex and excess sodium borohydride. The catalytic behavior of the nickel cyanide complex appeared to be somewhat different from that of the cobalt cyanide complex reported on in previous works.[1-5]

The catalyst formation was as follows. A tetracyanonickelate(II) complex, $Ni(CN)_4{}^{2-}$, dissolved in an aqueous solution gave a homogeneous red solution, accompanied by the evolution of hydrogen

---

[1] J. Kwiatek, I. L. Mader and J. K. Seylor, "Advances in Chemistry Series, Reaction of Coordinated Ligands and Homogeneous Catalysis," A. C. S. (1963).
[2] T. Mizuta and T. Kwan, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **86**, 1010 (1965).
[3] T. Suzuki and T. Kwan, *ibid.*, **86**, 713 (1965).
[4] T. Suzuki and T. Kwan, *ibid.*, **86**, 1342 (1965).
[5] T. Mizuta and T. Kwan, *ibid.*, to be published.

TABLE 1. THE REACTION OF DIENES AND MONOENES WITH SODIUM BOROHYDRIDE IN THE PRESENCE OF THE NICKEL CYANIDE COMPLEX $T=0°C$

Substrate	Product, %			
	Isopentane	2-Me-1-Butene	2-Me-2-Butene	3-Me-1-Butene
 $CH_2=C(CH_3)-CH=CH_2$	0	21	79	trace
	Butane	1-Butene	*trans*-2-Butene	*cis*-2-Butene
$CH_2=CH-CH=CH_2$	trace	14	65	21
$CH_3CH=CH-CH_2Cl$	6	18	59	17
$CH_3-CH=CH-CH_2OH$	6	70	17	7
 $CH_2-CH(OH)-CH=CH_2$	trace	1	65	34
		Propane	Propylene	
$CH_2=C=CH_2$		20	80	
$CH_2=CH-CH_2Cl$		21	79	
$CH_2=CH-CH_2Br$		21	79	
$CH_2=CH-CH_2I$		23	77	
$CH_2=CH-CH_2NCS$		25	75	
$CH_2=CH-CH_2OCOCH_3$		27	73	
$(CH_2=CH-CH_2)_2S$		23	77	
$CH_2=CH-CH_2OH$		4	96	
$CH_2=CH-CH_2NH_2$		6	94	
$(CH_2=CH-CH_2)_2O$		3	97	

gas when excess sodium borohydride was added. The UV absorption peaks shifted from 268 and 285 mμ to 318 and 475 mμ. A red crystalline compound was isolated and subjected to the IR absorption measurement. The spectra appeared to agree entirely with that reported by El-Sayed and Sheline,⁶⁾ who studied the IR spectrum and the structure of the hexacyanodinickelate (I) complex, $K_4[Ni_2(CN)_6]$. The addition of allene, butadiene, or isoprene made the color of the solution change from red to yellow. The UV absorption measurements showed maxima at 303 mμ (allene), 315 mμ (butadiene), and 302 mμ (isoprene).

The apparatus and procedure for the measurement of the reaction were almost the same as those reported previously.³,⁵⁾ The reaction took place rapidly and was completed within ten to thirty minutes, depending on the kind of substrates at 0°C, when the amount of the substrate was not greater than that of the complex. The products were usually collected after thirty minutes' contact and were analyzed by gas chromatography. Their compositions are shown in Table 1, where the substrates investigated are listed in the first column.

As is shown in Table 1, isoprene gave three olefins, with no paraffin, just as in the case of the cobalt cyanide complex with a CN/Co molar ratio of less than five.⁴⁾ Butadiene and butenyl derivatives also gave rise to three olefin isomers. Table 1 shows also that the reductive elimination of a substituted group, such as halogen or hydroxyl, takes place. In this connection it is of interest to note that the distribution of the three isomers produced is sensitive to the kind and the position of the substituted group.

Allene and allyl derivatives gave both propane and propylene, proving that the nickel cyanide complex is active in both hydrogenation and hydrogenolysis. As has already been reported,³⁾ the cobalt cyanide complex yielded propylene exclusively from allyl halides. Again, the selective formation of propane and propylene appeared to depend on the kind of substituted group; that is, both allyl alcohol and allyl amine gave more propylene than allyl halides. It should be mentioned that the rate of the reaction is faster with allyl halides than with allyl alcohol or amine.

When 1-butene or *cis*-2-butene was introduced,

TABLE 2. THE ISOMERIZATION OF 1-BUTENE IN THE PRESENCE OF $Ni(CN)_4^{2-}$-$NaBH_4$ $T=0°C$
4 mmol of $Na_2Ni(CN)_4 \cdot 3H_2O$
36 mmol of $NaBH_4$
1 mmol of 1-butene in 100 m*l* of H_2O

Time min	1-Butene	*trans*-2-Butene	*cis*-2-Butene	Butane
0	100	0	0	0
10	50	27	14	9
20	45	30	15	10
40	40	34	16	10
120	28	44	17	11
Equilibrium	3	75	22	—

---

6) M. F. El-Sayed and R. K. Sheline, *J. Am. Chem. Soc.*, **72**, 702 (1956).

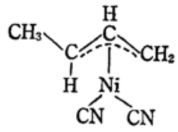
Table 3. The isomerization of *cis*-2-butene in the presence of $Ni(CN)_4^{2-}$–$NaBH_4$, $T=0°C$
The composition of the reacting solution is the same as that of Table 2.

Time min	*cis*- 2-Butene	1-Butene	*trans*- 2-Butene	Butane
0	100	0	0	0
10	65	trace	35	trace
60	60	1	38	1
120	55	2	41	2
180	53	2	43	2

the isomerization of the butene took place, and a small amount of *n*-butane was formed. The results are shown in Tables 2 and 3. The isomerization of butenes was not detectable with the cobalt cyanide complex.³⁾ It can be seen from Tables 2 and 3 that *trans*-2-butene, thermodynamically most stable, surpasses the other isomer during the course of the reaction. The rate of the isomerization seems much slower than that of the hydrogenation of butadiene, but faster than the rate of formation of butane.

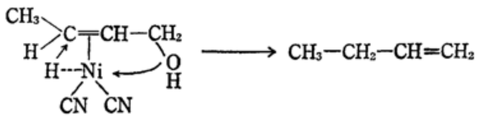
Let us now discuss some of the results. The hydrogenation of acetylene or butadiene in the presence of the nickel cyanide complex and sodium amalgam has been reported briefly.[7,8] Little is known, however, about the mechanism of the reaction. We have already shown[4] that isoprene is hydrogenated almost exclusively to 2-methyl-2-butene by the cobalt cyanide complex only when the CN/Co molar ratio is kept below five. In other words, two-site coordination[9] is necessary for isoprene to be hydrogenated to 2-methyl-2-butene.

The hydrogenation of isoprene and butadiene by sodium borohydride in the present case yielded 2-methyl-2-butene and *trans*-2-butene, respectively, as the major products. Therefore, it seems reasonable to assume that the same sort of interaction is operative between dienes and the nickel cyanide complex. Thus, it is tentatively suggested that the nickel cyanide complex forms a π-allyl type of intermediate, such as:



The addition of a hydrogen atom to the less hindered terminal methylene may produce *trans*-2-butene, although it is not certain whether the hydrogen atom comes directly from sodium borohydride or from nickel hydride.

It is of interest to note that butenyl chloride and butenyl alcohol react at different rates and give different distributions of the butene isomers produced. The difference can probably be explained as follows. Butenyl chloride loses its chlorine atom easily and gives a π-allyl type intermediate, for it gave almost the same distribution of the olefins formed as did butadiene. On the other hand, butenyl alcohol may form a π-type intermediate complex without losing its hydroxyl group.



If the hydrogen atom attacks the γ-carbon of the intermediate, followed by the elimination of the hydroxyl group, 1-butene may be expected to form mainly, as was the case. The dominant formation of *trans*-2-butene from $CH_3{-}CH(OH){-}CH{=}CH_2$ can also be explained if a similar sort of mechanism is assumed.

---

7) M. S. Spencer and D. A. Dowden, U. S. Pat. 2966534 (1960).

8) M. G. Burnett, *Chem. Commn.*, 507 (1965).

9) T. Suzuki and T. Kwan, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **87**, 395 (1966).