Hydrogenolysis of Unsaturated Alcohols; Hydrocyanation and Hydrogenation of Acetylenes Catalysed by Pentacyanocobaltate(II)

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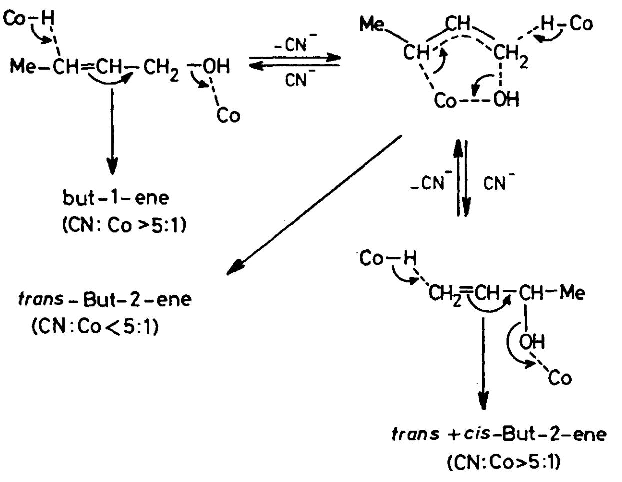
Summary Unsaturated alcohols containing a double or triple bond are catalytically hydrogenolysed to olefins, and terminal acetylenes are hydrocyanated or hydrogenated to saturated secondary nitriles or olefins under mild conditions.

HYDROGENOLYSIS of organic halides by pentacyanocobaltate(II) proceeds by a stepwise free radical mechanism,[1] but the reaction is terminated by the formation of stable halogeno or organocobalt complexes. We now report the catalytic hydrogenolysis of allylic and non-allylic unsaturated alcohols. The striking characteristic of the reaction is the dependence of the reactivity and selectivity on the CN:Co ratio; there is an abrupt change in both at CN:Co = *ca.* 5:1. The reactivity for CN:Co<5:1 was >100 times that for CN:Co>5:1 with a maximum rate at CN:Co = 4·85:1. The selectivity also changes at CN:Co = 5:1, and Table 1 shows the results for C_4-alcohols for ratios of CN:Co below and above 5:1. In contrast to the corresponding halides, in which buta-1,3-diene is a precursor of the products, hydrogenolysis of the alcohols seems to proceed by the concerted mechanism in Scheme 1. We propose this mechanism to explain the selectivity; however, a kinetic study[2] with allyl compounds such as allylamine and allyl alcohol, ether, and sulphide is consistent with the sequence in reactions (1)—(4), in which reaction (4) is the rate-limiting step, and the equilibrium constant for reaction (2) markedly affects the reactivity.

TABLE 1. Hydrogenolysis of C_4-unsaturated alcohols and halides[a]

	Products/mol %					
	CN:Co = 4·8:1			CN:Co = 6·0:1		
Reactants	But-1-ene	*trans*-But-2-ene	*cis*-But-2-ene	But-1-ene	*trans*-But-2-ene	*cis*-But-2-ene
$MeCH{=}CHCH_2OH$	12	78	10	86	12	2
$H_2C{=}CHCH(OH)Me$	10	89	1	8	48	44
$H_2C{=}CH[CH_2]_2OH$	13	84	1		no reaction	
$HOCH_2CH{=}CHCH_2OH$	13	86	1	78	20	2
$MeC{\equiv}CCH_2OH$	10	78	12[b]	93	7	0[b]
$HC{\equiv}CCH(OH)Me$	11	89	1	28	41	31
$HC{\equiv}C[CH_2]_2OH$	11	86	3[b]	90	10	0[b]
$HOCH_2C{\equiv}CCH_2OH$	11	85	3[b]	90	10	1[b]
$MeCH{=}CHCH_2Cl$	11	76	13[c]	64	29	7[c]
$H_2C{=}CHCH(Cl)Me$	17	67	16[c]	81	13	7[c]
$H_2C{=}CH[CH_2]_2Br$	20	70	9[c]	83	14	4[c]

[a] [Co] = 0·15 mol dm^{-3}, [alcohol] = *ca.* 0·2—0·8 mol dm^{-3}, at 20 °C, 1 atm H_2. [b] Buta-1,2-diene was formed. [c] Buta-1,3-diene was formed.



SCHEME 1

$$2\,Co + H_2 \rightleftharpoons 2\,CoH \tag{1}$$

$$Co + ROH \rightleftharpoons Co(ROH) \tag{2}$$

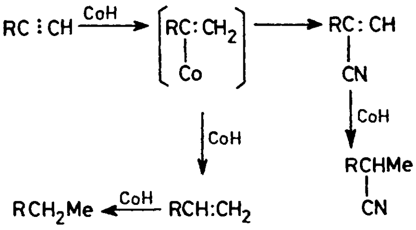
$$CoH + Co(ROH) \rightleftharpoons RH + CoOH + Co \tag{3}$$

$$CoOH + CoH \rightleftharpoons 2\,Co + H_2O \tag{4}$$

$[ROH \equiv \text{unsaturated alcohol};\ Co \equiv Co(CN)_5{}^{3-}]$

The acetylenic alcohols, $MeC{\equiv}CCH_2OH$, $HC{\equiv}C[CH_2]_2OH$, and $HCOCH_2C{\equiv}CCH_2OH$ were initially hydrogenolysed to buta-1,2-diene, but the results for but-1-yn-3-ol can only be explained by an initial hydrogenation to form but-1-en-3-ol. The probability of this hydrogenation occurring has been ascertained as described below. The formation of *trans*-but-2-ene from $H_2C{=}CH[CH_2]_2OH$ and buta-1,2-diene from $HC{\equiv}C[CH_2]_2OH$ suggests a 1,2-H shift, the mechanism of which is not clear at this stage.

1-Ethynylcyclohexanol gave no hydrogenolysed product, but mainly the hydrocyanated and the partly hydrogenated products as shown in Table 2. Although it is known that the hydrocyanation of olefins by addition of HCN is catalysed by some transition metal complexes,[3] hydrocyanation of acetylenes without HCN but with activated H_2 is a new reaction. It is remarkable that the reaction selectively produces secondary nitriles. In addition, the results show that acetylenes can be hydrogenated catalytically under mild conditions.



SCHEME 2

Tertiary alcohols, such as $EtC(Me)(OH)C{\equiv}CH$ and $Me_2C(OH)C{\equiv}CH$, were also hydrocyanated accompanied by hydrogenolysis to form olefins, but olefinic alcohols, such as 3-methylbut-1-en-3-ol, were not hydrocyanated. The

Table 2. Hydrocyanation and hydrogenation of acetylenes RC≡CH[a]

R	[RC≡CH]/[Co]	time h	H_2 cm^3	% yield[b]	Products (%)				
					RCH(CN)Me	RC(CN)=CH_2	RCH=CH_2	REt	RC≡CH
c-C_6H_{10}(OH)-	1	10	186	84	82	0	17	0	0[c]
	2	9	142	72	39	0	7	0	52
	2[d]	12	277	94	58	0	7	0	34
	1[e]	10	180	82	11	0	89	0	0
EtC(Me)(OH)-	1	9	150	54	85[f]	1	13	0	1[g]
	2	9	76	30	21[f]	11	6	0	61[h]
Me_2C(OH)-	1	9	130	35	100	0	0	0	0[i]
Ph	2[e]	9	566	140	39	0	1	59	0

[a] [Co] = 0·2 mol dm^{-3} in 50 cm^3 H_2O at 45 °C, 1 atm H_2, CN/Co = 4·9. [b] Liquid products based on cobalt. [c] 1% cyclohexanone. [d] 0·2 mol dm^{-3} of ethylenediamine was added. [e] 0·22 mol dm^{-3} of 2,2′-bipyridine was added in MeOH–H_2O (1 : 1). [f] Two stereoisomers (2 : 3) by n.m.r. spectroscopy. [g] Composition of pentenes in gaseous phase (%): H_2C=CH(Me)Et (4), *trans-* and *cis*-MeCH=C(Me)Et (45 and 51), HC≡CH(Me)Et (1). [h] Pentenes (%): H_2C=CHCH(Me)Et (20), *trans-* and *cis*-MeCH=C(Me)Et (19 and 29), HC≡CCH(Me)Et (22). [i] Butenes (%): H_2C=CHCH(Me) (2), MeC(Me)=CHMe (98).

secondary alcohol HC≡CCH(OH)Me gave a trace of the hydrocyanation product. Since phenylacetylene was also hydrocyanated, the presence of the OH group is not essential for this reaction.

Since pentacyanocobaltate(II) forms stable complexes with acetylenes,[4] the addition of excess of acetylenic compounds suppresses the reaction and gives the intermediate RC(CN)=CH_2; the reaction requires the presence of both organocobalt and hydridocobalt complexes. The addition of amines, such as ethylenediamine and 2,2′-bipyridine, promotes the reaction even in the presence of excess of acetylenic compounds. Phenylacetylene was almost completely unreactive in the absence of these amines. This promotion effect is probably due to the formation of a $[Co(CN)_3(amine)H]^-$ species which is more active than $[Co(CN)_5]^{3-}$.[5] It is remarkable that hydrogenation rather than hydrocyanation is greatly promoted in the presence of 2,2′-bipyridine.

This reaction is shown in Scheme 2, which includes a postulated intermediate complex and the insertion of the CN ligand into the C–Co bond.

We thank the Ministry of Education for a grant.

(*Received*, 11*th July* 1977; *Com.* 698.

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