1,2-Bond Shift Isomerization on Copper

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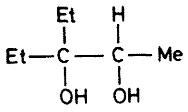
Summary Besides yielding 3-ethyl-3-hydroxypentan-2-one (**2**) and 3-ethylpentan-2-one (**4**), 3-ethylpentane-2,3-diol (**1**) is transformed on copper catalysts into 4-methyl-4-hydroxyhexan-3-one (**3**) and 4-methylhexan-3-one (**5**), *via* 1,2-ethyl migration, this being the first experimental observation of 1,2-bond shift isomerization on copper.

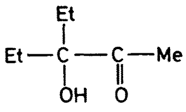
ALKANES are known to undergo isomerization by a 1,2-bond shift mechanism on noble metals.[1] The study of the reactions of heteroatom-containing carbon compounds in the presence of metals, in the course of which C–C bonds are cleaved, is of theoretical importance as it permits the investigation of processes involving a bond shift mechanism in the case of compounds where the reactant is adsorbed at the hetero-atom.

We recently reported studies providing the first evidence of 1,2-bond shift isomerization of compounds containing a C–O bond on a noble metal.[2]



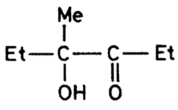
$Et{-}C(Et)(OH){-}CH(OH){-}Me$

(1)



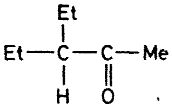
$Et{-}C(Et)(OH){-}C(=O){-}Me$

(2)



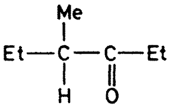
$Et{-}C(Me)(OH){-}C(=O){-}Et$

(3)



$Et{-}CH(Et){-}C(=O){-}Me$

(4)



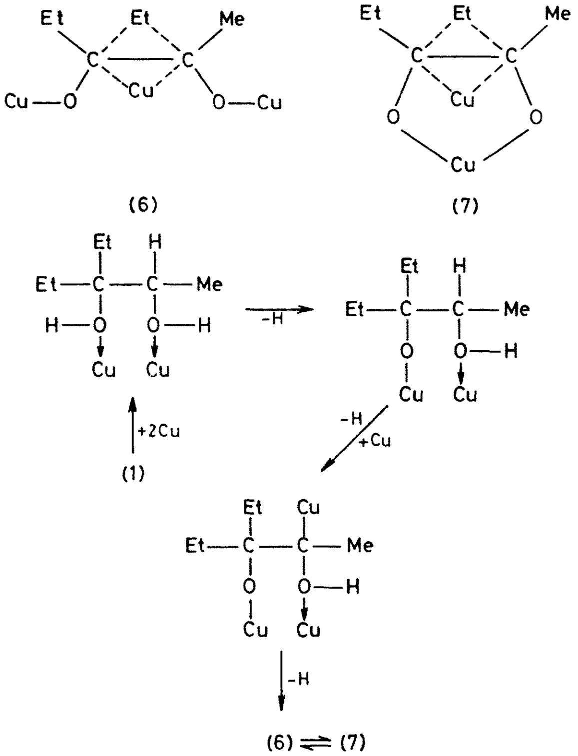
$Et{-}CH(Me){-}C(=O){-}Et$

(5)

Earlier examinations suggested that copper was inactive both in the hydrogenolysis of C–C bonds,[3] and in the isomerization of alkanes.[4] More recent investigations[5] confirmed the latter finding, but revealed a certain degree of activity of copper in the hydrogenolysis of some hydrocarbons.

Studies of the chemical transformations of alcohols and diols have demonstrated that copper catalysts prepared in various ways are active in the dehydration of certain alcohols,[6,7] and 1,3-, 1,4- and 1,5-diols.[8,9] (These processes took place *via* the action of the electrophilic centres of the catalysts.) It seemed reasonable to examine the reactions of 1,2-diols on copper catalysts, and accordingly, we have studied the transformations of 3-ethylpentane-2,3-diol (**1**) on copper catalysts (Cu/Al and other catalysts, prepared by reduction of different precursors, see Table). 'Cu (2)' did not contain acidic centres titrable with butylamine. 'Cu/CS' contained electrophilic centres, but it was found that this catalyst is not capable of pyridinium ion formation, determined by i.r. spectroscopy.[10]

Measurements were made in the vapour phase with a flow technique (catalyst volume 7.5 ml, grain size 0·63—1 mm). The compounds formed, after isolation, were identified on the basis of the g.l.c. retention times of authentic compounds synthesized independently, and i.r., n.m.r., and mass spectroscopy.



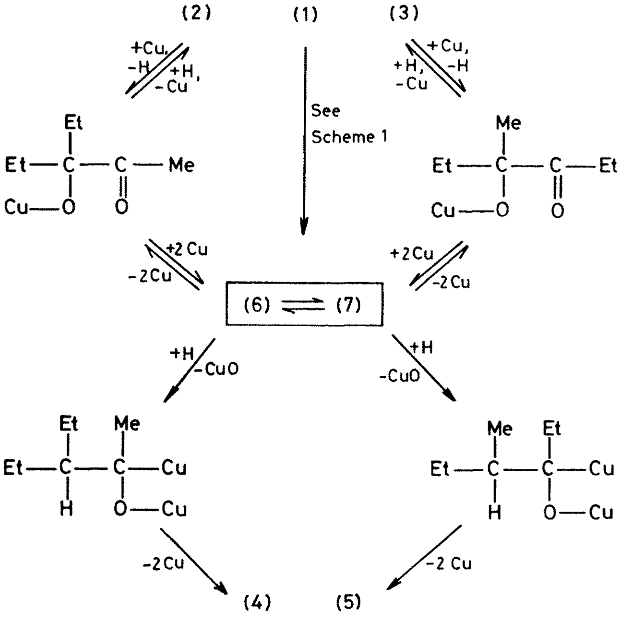
Scheme 1.

The following main conclusions may be drawn from the tabulated data: (i) (**3**) and (**5**) are formed by 1,2-ethyl migrations even on the catalysts 'Cu/Cs' and 'Cu (2),' which do not contain acidic centres; (ii) (**2**) and (**3**) are intermediates in the formation of (**4**) and (**5**); note that this does not exclude the possibility of the formation of (**4**) and (**5**) directly from (**1**) (see Schemes 1 and 2).

Table. Transformations of (**1**) and (**2**) on various copper catalysts.

Substrate	Catalyst (% copper, precursor)	Space velocity[a]	Temp. /°C	Conversion/%	Selectivity/mole %				
					(**2**)	(**3**)	(**4**)	(**5**)	A[b]
(**1**)	Cu/Al (70, Cu–Al alloy)[9]	0·16	225	100	8	20	29	26	17(3)
(**1**)		0·16	260	100	4	10	54	14	18(3)
(**1**)	'Cu (1)' (40, CuO)[9]	0·16	225	95	21	56	12	2	9(1)
(**1**)		0·16	250	100	15	40	17	25	3(1)
(**1**)		0·16	270	100	1	1	25	73	0
(**1**)	'Cu/KG' (40, CuO/Kieselguhr)[11]	0·16	225	98	22	58	7	4	9(1)
(**1**)		0·16	250	100	5	22	23	46	4(1)
(**2**)		0·16	200	40	0	58	24	18	0
(**1**)	'Cu (2)' {100, $[Cu(NH_3)_4](OH)_2$}[12]	0·25	230	98	17	52	8	21	2(2)
(**1**)		0·50	230	95	26	58	6	9	1(2)
(**1**)	'Cu/CS' (40, CuO/Cab-O-Sil)[11]	0·16	205	90	22	33	22	19	4(2)
(**2**)		0·16	200	60	0	65	17	13	5(2)
(**2**)		0·16	290	91	0	26	20	52	2(2)

[a] Dimension = (ml liquid/ml catalyst) h^{-1}. [b] A = unidentified products; the numbers in parentheses are the numbers of compounds not identified.



SCHEME 2

The reaction mechanisms outlined in Schemes 1 and 2 are proposed to allow interpretation of the above experimental data on the 'Cu (2)' and 'Cu/CS' catalysts The mechanisms in the schemes are similar to those introduced[13,14] for the dehydrogenation of alcohols

On the catalysts containing acidic centres ['Cu/Al,' 'Cu (1),' and 'Cu/KG'], (**4**) and (**5**) may also be formed from (**1**) by other routes (pinacol rearrangement, elimination of water and subsequent tautomerization, *etc*) The reason for the investigations with the other types of catalysts was to obtain unambiguous evidence of the role of the copper Transformation of (**1**) into (**2**) may occur in three ways by direct dehydrogenation, by hydrogen transfer, and by the action of CuO formed in the decomposition of surface species [CuO + (**1**) $\rightarrow$ Cu + H_2O + (**2**)]

Our experimental results clearly prove that reactions involving a 1,2-bond shift mechanism [(**1**) $\rightarrow$ (**3**), (**1**) $\rightarrow$ (**5**), (**2**) $\rightarrow$ (**3**), and (**2**) $\rightarrow$ (**5**)] can also occur on the copper, if the reactant contains a heteroatom which ensures its binding to some surface atom of the copper Common di- or tri-adsorbed surface species have been assumed in the mechanisms of these processes The Schemes suggested herein further show that copper is not generally able to effect the direct dehydration of compounds containing the HC–C–OH grouping

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