1,2-Bond Shift Isomerization of Oxiranes on Copper-Graphimet

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2,2,3,3-Tetramethyloxirane (**1**) undergoes isomerization on copper intercalated graphite (graphimet) to t-butyl methyl ketone (**4**) *via* a 1,2-methyl migration and to 2,3-dimethylbut-3-en-2-ol (**5**) *via* a 1,3-hydrogen shift, as well as deoxygenation and dehydration products.

We previously reported isomerizations, *via* a 1,2-bond shift mechanism, of compounds containing a C–O bond on noble metals[1] and on copper.[2] Whereas earlier findings suggested that copper was inactive for the transformation of hydrocarbons,[3,4] more recent investigations revealed the copper-catalysed hydrogenolysis of 3-methylpentane[5] and substituted cyclopropanes.[6] However, it is somewhat surprising that, apart from our own results,[1,2] there have been no reports of experimently confirmed bond shift isomerizations of oxygen-containing organic compounds on metal catalysts. Combined with our interest in the unique properties of metal intercalated graphite catalysts,[7—9] this prompted us to study copper intercalated graphite (copper-graphimet, CuGm). In catalytic studies, CuGm has exhibited activity in the dehydrogenation of alcohols,[10] while it proved inactive in the hydrogenation of alkenes.[11] To our knowledge, no other catalytic application has been reported. We now report that 2,2,3,3-tetramethyloxirane (**1**) undergoes isomerization to t-butyl methyl ketone (**4**) and 2,3-dimethylbut-3-en-2-ol (**5**) over CuGm.

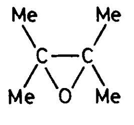
Experiments were carried out using a commercial CuGm (Alfa Chemical Company) with a 2.4% nominal copper loading. For comparison, a Raney-type copper (Cu/Al, prepared as in ref. 12) and a 6.8% copper on Cab-O-Sil catalyst (Cu/CS, prepared as in ref. 13) were also used. The catalysts were characterized by pulse titration with N_2O at 90 °C. Measurements were made in the vapour phase with the pulse technique in a microreactor connected directly to a g.c.

The data (Table 1) suggest the following conclusions.

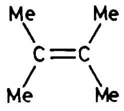
Table 1. Transformations of (**1**) on various copper catalysts.[a]

Catalyst, mg (surface area /$m^2 g^{-1}$)	Temp. /°C	Sample /μl	Conv. /%	Selectivity/mol % (**2**)	(**3**)	(**4**)	(**5**)	TON[d]
CuGm,[b] 10 (0.78)	66	1	73	7	10	63	20	31.6
	150	1	100	5	30	60	5	
	250	1	100	7	28	60	5	
Cu/Al,[b] 230 (18.2)	100	5	60	0	0	55	45	0.24
	150	5	100	10	15	65	10	
	200	5	100	5	20	75	0	
Cu/CS,[c] 10 (4.15)	200	1	15	30	0	37	33	1.22
Cab-O-Sil,[b] 10	200	1	3	0	0	90	10	

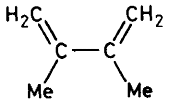
[a] Chromatography: 3.6 m CWAX 20M on Kieselguhr column, 100 °C, hydrogen carrier gas (30 ml min^{-1}). The compounds formed were identified on the basis of g.l.c. retention times of authentic compounds synthesized independently and i.r. spectroscopy. [b] Pretreated at 200 °C for 1 h in flowing hydrogen (30 ml min^{-1}) before use. [c] Pretreated at 200 and 250 °C for 30 min each then at 300 °C for 1 h in flowing hydrogen (30 ml min^{-1}) before use. [d] Turnover number = molecules transformed per surface copper atom per pulse.



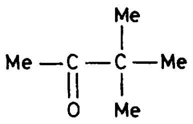
(**1**)



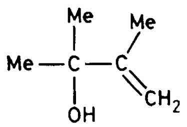
(**2**)



(**3**)



(**4**)

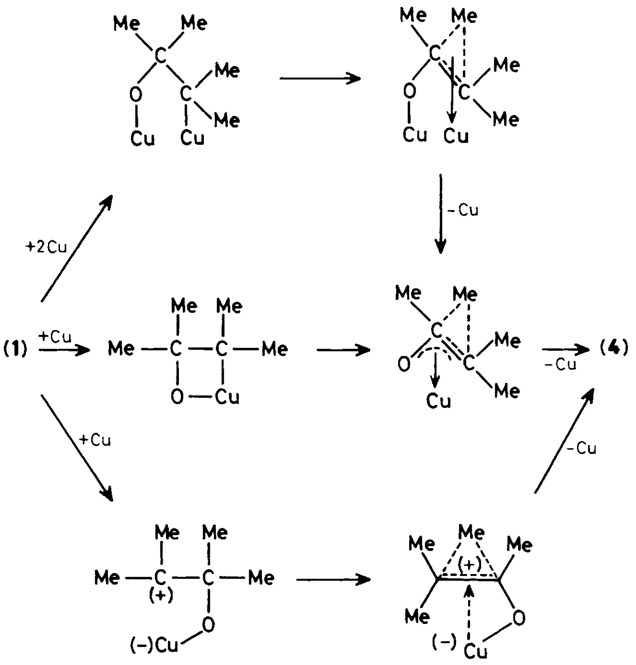


(**5**)

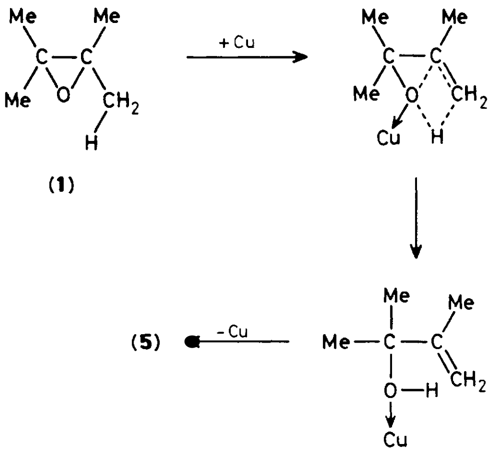
(i) The two main transformation directions of (**1**) are isomerization to (**4**) *via* a 1,2-methyl shift and formation of (**5**) by a 1,3-H shift. (ii) Minor products are 2,3-dimethylbut-2-ene (**2**), resulting from deoxygenation, and 2,3-dimethylbuta-1,3-diene (**3**), formed by the dehydration of (**5**). (iii) The turnover numbers indicate an exceptionally high activity of CuGm. It follows from a comparison of the activities of the Cab-O-Sil support, the Cu/CS catalyst, and the support-free Cu/Al that the isomerizations [formation of (**4**) and (**5**)] are catalysed by the metal atoms. These observations provide confirmation of earlier findings that isomerizations involving a bond shift mechanism can take place on copper if a heteroatom ensures adsorption on the surface copper atoms.

The surprisingly high activity of CuGm can be interpreted in terms of the special structural and electronic features of the metal intercalated graphite catalysts. The layered structure of metal-graphimets may ensure the formation of highly dispersed metal particles in a more homogeneous distribution than in the traditional supported catalysts. A change in the metallic properties, resulting from interaction of the metal with the graphite, may also influence the catalytic properties.

Schemes 1 and 2 outline the reaction pathways proposed to interpret the experimental observations. The mechanism for the 1,2-methyl shift [formation of (**4**), Scheme 1] is based on findings for the metal-catalysed isomerization of alkanes,[14—16] and was formulated assuming the participation of one or two copper atoms. Mechanistic considerations relating to the 1,3-H shift, which take into account literature data concerning alkene isomerization on transition metals,[17—19] suggest the mechanism of Scheme 2 for the formation of (**5**).



Scheme 1



Scheme 2

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