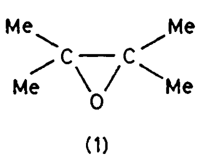
1,2-Bond Shift Isomerization of Oxirans on Noble Metals

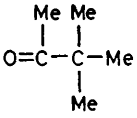
By Mihály Bartók and Ferenc Notheisz
(*Department of Organic Chemistry, József Attila University, Szeged, Hungary*)

Summary On a platinum catalyst in the presence of hydrogen, besides yielding 3,3-dimethylbutan-2-ol (**5**) as the main hydrogenolysis product, 2,2,3,3-tetramethyloxiran (**1**) undergoes isomerization to t-butyl methyl ketone, *via* 1,2-methyl migration, this being the first experimental observation of 1,2-bond shift isomerization of a compound containing a C–O bond on a noble metal.

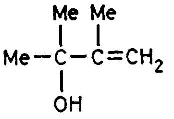
Isomerization of alkanes *via* a 1,2-bond shift mechanism is catalysed by noble metals.[1] The study of the isomerization of heteroatom-containing carbon compounds in the presence of metals, in the course of which C–C bonds undergo cleavage, is of theoretical importance, as it permits the investigation of processes involving a bond shift mechanism in the case of compounds where the reactant is adsorbed at the heteroatom. (It has already been proved experimentally that the adsorption of oxa-cycloalkanes, for example, on noble metals takes place *via* the oxygen atom.[2])

We recently reported studies providing the first evidence of isomerization *via* a 1,3-bond shift mechanism on noble metals.[3] We were surprised to discover that experimental observations have apparently not been described that confirm the occurrence of a 1,2-bond shift isomerization in the case of carbon compounds containing C–O bonds.

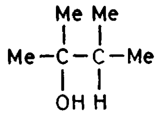

(1)


$O{=}C(Me){-}C(Me)_2{-}Me$

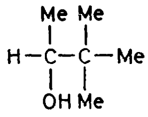
(2)


$Me{-}C(Me)(OH){-}C(Me){=}CH_2$

(3)


$Me{-}C(Me)(OH){-}C(Me)(H){-}Me$

(4)

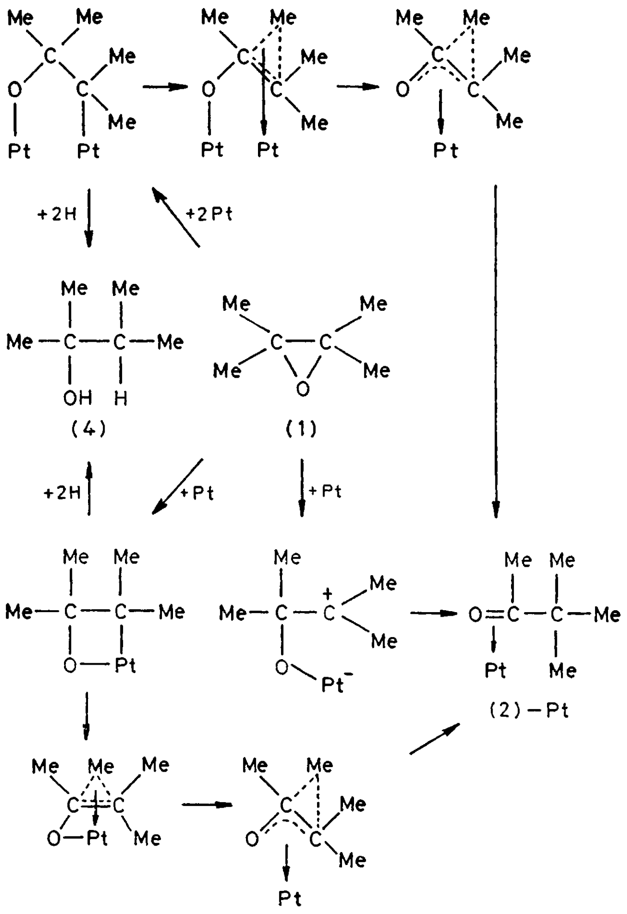

$H{-}C(Me)(OH){-}C(Me)_2{-}Me$

(5)

We have accordingly studied transformations of 2,2,3,3-tetramethyloxiran (**1**) on Pt/T, Rh/T, Pd/T, Pt/C, and Pt catalysts (T = thermolite, a support of the diatomaceous earth type) and on the T support alone in the presence of hydrogen using a pulse microreactor technique (see Table).

Literature results indicate that in the presence of acids compound (**1**) is isomerized to t-butyl methyl ketone (**2**).[4,5] Under different conditions it can isomerize to 2,3-dimethylbut-3-en-2-ol (**3**).[6] Depending upon the experimental conditions, ring-opening of (**1**) by the action of $LiAlH_4$ yields 2,3-dimethylbutan-2-ol (**4**) and 3,3-dimethylbutan-2-ol (**5**).[4,7] The transformation of (**1**) has not been examined in the presence of metals.

On the Pt/T, Pd/T, Rh/T, and Pt/C catalysts, two parallel reactions occur: isomerization to yield (**2**), and hydrogenolysis resulting in the formation of (**4**). The simultaneity of the two processes is proved, amongst other evidence, by the fact that the reactions (**2**) + $H_2 \rightleftharpoons$ (**4**) cannot be observed. The primary nature of the isomeriza-



SCHEME

TABLE. Transformation of (**1**), (**2**), (**4**), and (**5**) on various catalysts.

Substrate	Catalyst	Temp./°C	Conversion, %	Selectivity, mole % A[d]	(2)[e]	(4)[e]	(5)[e]
(**1**)	Pt/T[a]	100	100	0	25	75	0
(**1**)	Pt/T[a]	200	100	20	70	0	10
(**1**)	Rh/T[a]	100	100	0	30	70	0
(**1**)	Rh/T[a]	200	100	20	73	7	0
(**1**)	Pd/T[a]	100	20	0	55	45	0
(**1**)	Pd/T[a]	200	100	10	80	10	0
(**1**)	T[a]	150	100	35	65	0	0
(**2**)	Pt/T[a]	100	77	4	—	0	96
(**4**)	Pt/T[a]	100	6	100	0	—	0
(**4**)	Pt/T[a]	200	100	100	0	—	0
(**5**)	Pt/T[a]	150	10	2	98	0	—
(**1**)	Pt/C[b]	150	84	36	57	7	0
(**1**)	Pt[c]	150	48	8	20	72	0

[a] 0·5 g catalyst containing 10% metal was used, prepared as described by M. Bartók, J. Apjok, R. A. Karakhanov, and K. Kovács, *Acta Chim. Hung.*, 1969, **61**, 315; specific surfaces: Pt/T 16, Pd/T 4, Rh/T 8 m^2/g metal (±10%). A Rasotherm glass microreactor was used in conjunction with a Carlo Erba ATC/f chromatograph. Carrier gas: 40 ml H_2/min. Amount of substance injected: 5 μl. Chromatography: column 1 m containing 15% Carbowax 20 M on thermolite + 1 m containing 15% Fractonitril III on thermolite; thermostat: 60 °C. [b] 0·0127 g catalyst containing 18·5% Pt (0·23 m^2) was used, prepared as described by M. Bartók and S. Fényi, *Acta Phys. et Chem. Szeged*, 1966, **12**, 157. [c] 0·144 g catalyst (0·23 m^2) was used, prepared from H_2PtCl_6 by reduction with alkaline formaldehyde (P. Tétényi and K. Schächter, *Acta Chim. Hung.*, 1966, **50**, 128). [d] A = unidentified decomposition products, with substantially lower retention times than that of (**1**). [e] The compounds formed were identified on the basis of the g.l.c. retentions of authentic compounds synthesized independently. [Retention time/min: (**1**), 4·39; (**2**), 7·35; (**4**), 12·28; (**5**), 13·65]. The experimental data were evaluated with a Perkin-Elmer Sigma 10 integrator.

tion process is confirmed, therefore, by the experimental observation that isomerization of the carbon skeleton could not be observed in the transformations of (**2**), (**4**), and (**5**). Since the transformation (**1**) $\rightarrow$ (**2**) also proceeds on the thermolite support, on its Brönsted acid centres, it appears probable that on the thermolite-supported catalysts in question the reaction (**1**) $\rightarrow$ (**2**) likewise takes place on the acid centres of the catalysts, while the transformation (**1**) + H_2 $\rightarrow$ (**4**) can be attributed to the effect of the metal. The isomerization activity of Pt/C can similarly be ascribed to the acid centres.

Since the experiments on the supported catalysts did not provide proof that the heteroatom-containing compounds undergo a 1,2-bond shift rearrangement as a result of the action of the metals, investigations were also carried out on support-free platinum prepared under alkaline conditions. These experiments showed that 1,2-alkyl migration may be observed in the case of C–O bonded systems, *i.e.*, when the adsorption of the substrate commences at the oxygen atom.

On the basis of the 1,2-bond shift mechanism accepted for the metal-catalysed isomerization of alkanes,[8] or by analogy with the transformation of cyclopropanes on transition metal complexes,[9] the isomerization process experimentally observed may be explained by the mechanisms in the Scheme.

(*Received*, 30*th March* 1979; *Com.* 330.)

[1] J. R. Anderson, *Adv. Catalysis*, 1973, **23**, 1; J. K. A. Clarke and J. J. Rooney, *ibid.*, 1976, **25**, 125.

[2] D. Cornet, Y. Gault, and F. G. Gault, Proceedings of the Third International Congress on Catalysis, Amsterdam, 1965, p. 1184; J. C. Duchet and D. Cornet, *J. Catalysis*, 1976, 57; J. Apjok, L. I. Lafer, M. Bartók, and V. I. Yakerson, *Izvest. Akad. Nauk S.S.S.R., Ser. Khim.*, 1977, 24.

[3] M. Bartók, *J.C.S. Chem. Comm.*, 1979, 139.

[4] W. J. Hickinbottom and D. R. Hogg, *J. Chem. Soc.*, 1954, 4200.

[5] Y. Pocker, *Chem. and Ind.*, 1959, 332; Y. Pocker and B. P. Ronald, *J. Amer. Chem. Soc.*, 1978, **100**, 3122.

[6] C. C. Price and D. D. Carmelite, *J. Amer. Chem. Soc.*, 1966, **88**, 4039; S. S. Srednev, S. I. Kryukov, and M. I. Farberov, *Zhur. Org. Khim.*, 1974, **10**, 1608.

[7] E. L. Eliel and M. N. Rerick, *J. Amer. Chem. Soc.*, 1960, **82**, 1362.

[8] M. A. McKervey, J. J. Rooney, and N. C. Samman, *J. Catalysis*, 1973, **30**, 330.

[9] (A referee's suggestion): K. C. Bishop, III, *Chem. Rev.*, 1976, **76**, 461; M. N. Akhtar, W. R. Jackson, and J. J. Rooney, *J. Amer. Chem. Soc.*, 1976, **96**, 276.