1,3-Bond Shift Isomerization of 2,2,4,4-Tetramethyloxetan on Noble Metals

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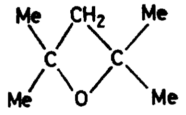
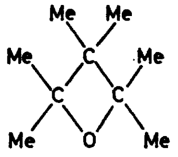
Summary In the presence of hydrogen on platinum, palladium, and rhodium catalysts, 2,2,4,4-tetramethyloxetan undergoes isomerization to neopentyl methyl ketone *via* a 1,3-methyl migration; this is the first experimental observation of a 1,3-bond shift isomerization on noble metals.

Isomerization of alkanes *via* a 1,2-bond shift mechanism is catalysed by noble metals.[1,2] We have found no reports of experimental observations on metal-induced 1,3-bond shifts, however. Since the isomerization of oxetans to ketones is catalysed by noble metals,[3] 2,2,4,4-tetramethyloxetan (I) and 2,2,3,3,4,4-hexamethyloxetan (II) were chosen for a study of the 1,3-bond shift,[4,5] since they do not contain C–H bonds on C-2 and C-4.

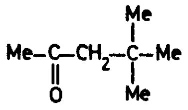
Transformation of the oxetan (I) on Pt–T, Rh–T, and Pd–T catalysts (T = thermolite, a support of the diatomaceous earth type) and the oxetan (II) on a Pt–T catalyst in the presence of hydrogen was studied using a pulse microreactor technique (see Table). Compounds (III), (IV), and (VI) were also studied under the same conditions.



(I)

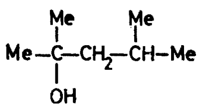


(II)



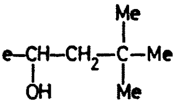
$\mathrm{Me-\underset{\underset{O}{\|}}{C}-CH_2-\overset{\overset{Me}{|}}{\underset{\underset{Me}{|}}{C}}-Me}$

(III)



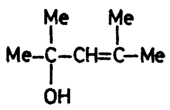
$\mathrm{Me-\overset{\overset{Me}{|}}{\underset{\underset{OH}{|}}{C}}-CH_2-\overset{\overset{Me}{|}}{CH}-Me}$

(IV)



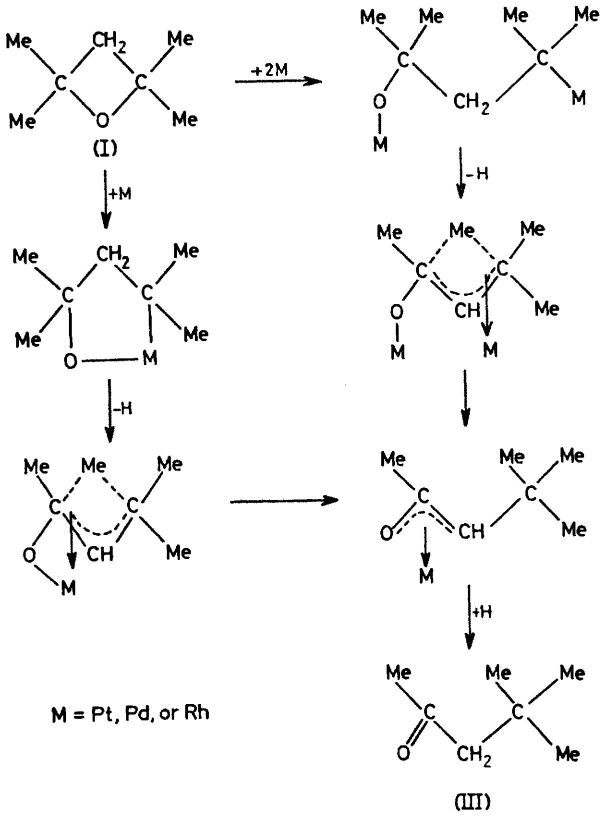
$\mathrm{Me-\underset{\underset{OH}{|}}{CH}-CH_2-\overset{\overset{Me}{|}}{\underset{\underset{Me}{|}}{C}}-Me}$

(V)



$\mathrm{Me-\overset{\overset{Me}{|}}{\underset{\underset{OH}{|}}{C}}-CH=\overset{\overset{Me}{|}}{C}-Me}$

(VI)



Scheme

Comparison of the results for (I) with those for (III), (IV), and (VI), together with the results for ketones of various types[7] unambiguously prove that the isomerization takes place by a 1,3-methyl migration.

Table

Substrate	Catalyst[a]	Temp/°C	Conversion %	Selectivity/mole %			
				Pyrolysis	(III)[b]	(IV)[b]	(V)[b]
(I)	Pt–T	100	5	0	100	0	0
(I)	Pt–T	150	47	57	22	21	0
(I)	Pd–T	100	10	0	90	10	0
(I)	Pd–T	150	25	34	45	21	0
(I)	Rh–T	100	8	0	100	0	0
(I)	Rh–T	150	24	50	38	12	0
(II)	Pt–T	150	50	100	—	—	—
(IV)	Pt–T	100	8	100	0	—	0
(IV)	Pt–T	150	40	100	0	—	0
(III)	Pt–T	100	85	6	—	0	94
(VI)	Pt–T	100	100	40	0	50	0

[a] T = thermolite. 0·5 g of catalyst containing 10% metal was used [prepared as in ref. 6; specific surfaces: Pt–T 16, Pd–T 4, and Rh–T 8 m^2 g of metal (±10%)]. A Rasotherm glass microreactor was incorporated with a Carlo Erba GV g.l.c. instrument. Carrier gas: 60 ml H_2 min^{-1}; amount of substance injected: 5 μl; chromatography: column 1 m 15% Carbowax 20 M–thermolite + 1 m 15% Fractonitrile III–thermolite; thermostat 120 °C. [b] Compounds were identified on the basis of their i.r. (Unicam SP 1000) and ^1H n.m.r. spectra (JEOL C-60-HL) after separation and recovery (with a Carlo Erba Fractovap automatic preparative g.l.c.) of several 20 μl pulses. Quantitative evaluation was performed on the basis of calibration employing compounds (III) and (IV) synthesized independently.

The Table shows that although reaction i may occur for the processes $(I) + H_2 \xrightarrow{i} (IV) \xrightarrow{ii} (III)$ and $(I) \xrightarrow{i} (VI) \xrightarrow{ii} (III)$, reaction ii cannot be observed under the given experimental conditions. Since isomerization of the ketones with rearrangement of the carbon skeleton does not take place either, the occurrence of the complex process (I) ⟶ intermediate ⟶ (III) may be excluded.

On the basis of the 1,2-bond shift mechanism recently accepted for the metal-catalysed isomerization of alkanes,[8] and also the mechanism of isomerization of oxirans to ketones,[9] the mechanism in the Scheme is proposed for the observed isomerization process, involving the participation of one or two metal atoms.

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