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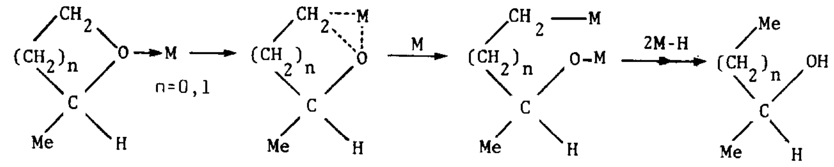
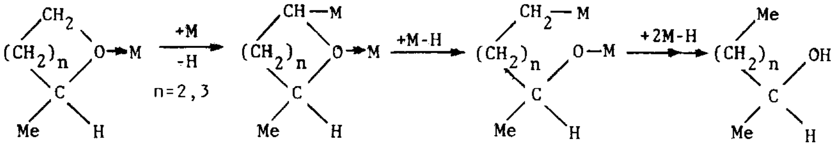
The Mechanism of Hydrogenolysis and Isomerization of Oxacycloalkanes on Metals

VI. The Selectivity-Determining Step on Pt[1]

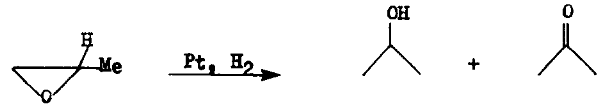
During studies of the hydrogenolysis and isomerization of the 2-Me-oxacycloalkanes (*1, 2*), it was found that the less sterically hindered C—O bond undergoes cleavage on a Pt catalyst. From the observed regioselectivity, it could be concluded that the primary C—O bond is split much more quickly than the secondary C—O bond. To prove this assumption we compared the rates of hydrogenolysis and isomerization of 2-Me-oxacycloalkanes and the corresponding *cis*-diMe-oxacycloalkanes under the same experimental conditions.

Our earlier results (*1*) led us to assume that the 3- and 4-membered cyclic ethers are transformed via an associative mechanism (Scheme 1), while the 5- and 6-membered cyclic ethers via a dissociative mechanism (Scheme 2). This assumption about the reaction routes was supported by the results of deuterium exchange (*3–5*).





Me-oxirane and *cis*-2,3-diMe-oxirane were chosen as model compounds for study of the associative mechanism, and 2-Me-oxolane and *cis*-2,5-diMe-oxolane for study of the dissociative mechanism. Scheme 3 shows the four compounds and the major products.



(1) (2) (3)

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[1] Part V: F. Notheisz, M. Bartók, and Á. G. Zsigmond, *React. Kinet. Katal. Lett.* **29,** 339 (1985).

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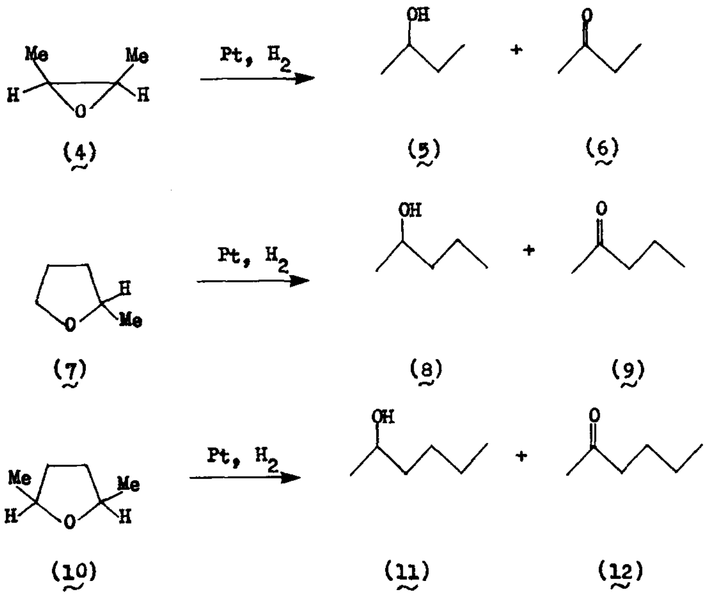

Measurements were performed in a static microreactor (*1*, *6*) or in a circulation reactor (*7*), at hydrogen pressures of 120–130 and 13 kPa, respectively. The 2.9% Pt/Cab-O-Sil catalyst was prepared, pretreated and characterized as described previously (*1*, *7*).

Me-oxirane (**1**), *cis*-2,3-diMe-oxirane (**4**), and 2-Me-oxolane (**7**) were prepared as described previously (*1*), while *cis*-2,5-diMe-oxolane (**10**) was a commerical product from Fluka. The methods of measurement, evaluation, and product identification have been reported elsewhere (*1*, *6*, *8*). The initial rates of transformation of the oxiranes and the oxolanes are given in Tables 1 and 2.

The data clearly reveal that compounds **4** and **10** without primary C—O bonds react faster than compound **1** and **7** with primary and secondary C—O bonds. It may be concluded from this that the secondary C—O bond is cleaved substantially more quickly than the primary C—O bond. Accordingly, it is very surprising that the primary C—O bond is cleaved selectively in the Me derivatives.

From a study on 2-Me-oxolane, it was earlier assumed (*9*) that both C—O bonds undergo cleavage on the most active sites of the Pt, but that the aldehyde formed is decarbonylated and the resulting carbon monoxide disactivates the most active sites. The reaction subsequently proceeds

TABLE 1

Initial Rates of Formation of the Products ($\times 10^5$ mole m^{-2} min^{-1}) in the Transformations of Me-oxirane (**1**) and *cis*-2,3-diMe-oxirane (**4**) on Pt/Cab-O-Sil Catalyst at 373 K in a Static Microreactor

1	**4**	Ratio
$r_0(2) = 38$	$r_0(5) = 72$	$r_0(5)/r_0(2) = 1.9$
$r_0(3) = 1$	$r_0(6) = 4$	$r_0(6)/r_0(3) = 4.0$

TABLE 2

Initial Rates of Formation of the Products ($\times 10^5$ mole m^{-2} min^{-1}) in the Transformations of 2-Me-oxolane (**7**) and *cis*-2,5-diMe-oxolane (**10**) on Pt/Cab-O-Sil Catalyst at 523 K in a Static Microreactor

7	**10**	Ratio
$r_0(8) = 1$	—	—
$r_0(9) = 9$	$r_0(12) = 47$	$r_0(12)/r_0(9) = 5.2$

TABLE 3

The Ratio of Ketone Production Rates $r(\mathbf{12})/r(\mathbf{9})$ in Function of Time for the Transformation of a Mixture of 2-Me-oxolane (**7**) and *cis*-2,5-diMe-oxolane (**10**) (47 and 53 mole%) on Pt/Cab-O-Sil Catalyst at 473 K in a Circulation System

Time (min)	**7**	**10**	$r(\mathbf{12})/r(\mathbf{9})$
	$\times 10^5$ mole		
0	10.2	11.6	5.5
10	9.8	9.4	5.3
20	9.5	7.8	4.8
30	9.25	6.6	5.0
40	9.05	5.6	

TABLE 4

The Ratio of the Alcohol Production Rates $r(\mathbf{5})/r(\mathbf{2})$ for the Transformation of a Mixture of Me-oxirane (**1**) and *cis*-2,3-diMe-oxirane (**4**) (74 and 26 mole%) on Pt/Cab-O-Sil Catalyst at 373 K in a Circulation System

Time (min)	**1**	**4**	$r(\mathbf{5})/r(\mathbf{2})$
	$\times 10^5$ mole		
0	10.9	3.8	2.0
5	9.2	0.4	

only on the less active sites, on which only the primary C—O bond is cleaved. If this assumption is correct, this means that the rate of transformation of the diMe compound must fall to zero on the poisoning action of the carbon monoxide formed in the course of the catalytic transformation of a mixture of the Me and diMe derivatives. In order to check the assumption, we have studied the catalytic transformations of mixtures of **7** and **10** (Table 3) and **1** and **4** (Table 4).

It can be seen from the data that nearly half of **10** underwent transformation during the reaction, but the ratio of the ketone production $r(\mathbf{12})/r(\mathbf{9})$ remained practically unchanged in the function of time and was similar to the ratio of the pure components (see Table 2). In the pressure of **1** compound **2** underwent almost total transformation, and the measured alcohol production ratio $r(\mathbf{5})/r(\mathbf{2})$ was likewise close to that of the pure components (see Table 1). These observations demonstrate that the carbon monoxide formed from **1** and **7** does not selectively poison cleavage of the C—O bond. Accordingly, this cannot be the reason why the primary C—O bond is cleaved with high selectivity in the case of the 2-Me derivatives.

Our experimental results show that the secondary C—O bond is cleaved substantially more quickly than the primary C—O bond. Hence, for the 2-Me derivatives it must be assumed that the selectivity-determining step is not the same as the rate-determining step, but precedes this. Since the rate-determining step is probably the cleavage of the C—O bond (7), the selectivity-determining step may be the adsorption of the C—O bond. The determining factor, therefore, is the preferred adsorption of the primary carbon atom regardless of whether the mechanism is dissociative or associative. We assume that this preferred adsorption of the primary carbon is promoted by the two electron pair adsorption of the oxygen atom (Figs. 1b and 2b) and impeded by the steric hindrance of the Me group in the case of a secondary carbon atom (Figs. 1a and 2a).

We earlier used the expressions "two-point adsorption" and "flat-laying adsorp-

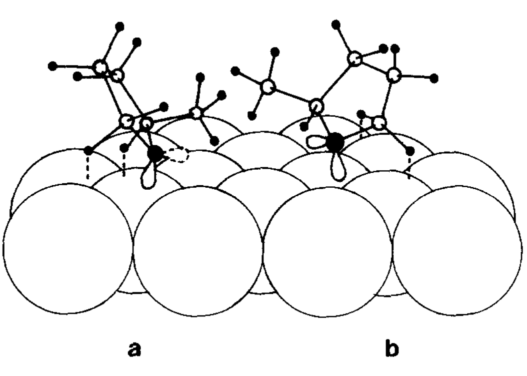

FIGURE 1

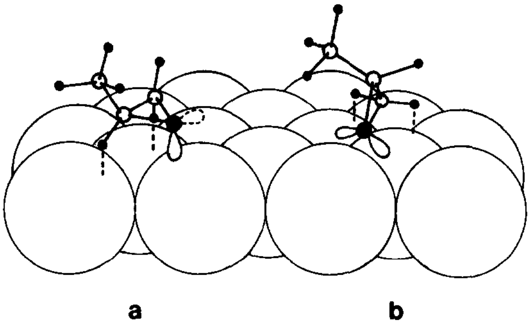

FIGURE 2

tion" to describe the stereochemistry of the adsorption (*6*). The two electron pair adsorption of the oxygen atom corresponds to two-point adsorption for the oxiranes, while the one electron pair adsorption corresponds to flat-laying adsorption. For the oxacycloalkanes with a higher number of ring atoms, one electron pair adsorption does not necessarily mean the flat-laying adsorption of the entire molecule; thus, it appears more correct for the oxacycloalkanes if we speak of one and two electron pair adsorption.

ACKNOWLEDGMENT

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