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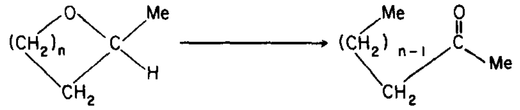
Hydroisomerization of Oxacycloalkanes on Platinum

According to the definition accepted in the literature, hydroisomerization is the isomerization of hydrocarbons that occurs only in the presence of hydrogen (*1–3*).

The role of hydrogen in the isomerization processes of the most varied types of hydrocarbons (saturated, unsaturated, alicyclic, aromatic) on metal-containing catalysts has long been recognized and has been investigated comprehensively. In addition to its industrial importance, such research work has been justified by the striving toward an understanding of the regularities in metal-catalyzed reactions. The hydroisomerization of hydrocarbons has aroused the interest of a number of research groups.

Significant results have been achieved in clarifying the skeletal hydroisomerization of saturated and alicyclic hydrocarbons (*4–11*), the racemization of saturated hydrocarbons (*12*), the configurational isomerization of alicyclic hydrocarbons (*13, 14*), the geometrical isomerization of olefins (*15*), the migration of the double bond of olefins (*16–18*), and the hydroisomerization of alkyl aromatic hydrocarbons (*2*). It has been proved that the role of hydrogen is of determining importance in these isomerization processes. The results of the wide-ranging investigations have been subjected to detailed reviews (*19–26*). Naturally, as a consequence of the elaboration of new types of metal catalysts and the introduction of new methods of examination, further impetus has been given to the study of the hydroisomerization of hydrocarbons (*27–30*).

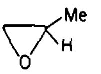
Many experimental observations have been reported on the isomerization on platinum metals of oxacycloalkanes containing different numbers of ring atoms (3, 4, 5, or 6). Such investigations have demonstrated the general nature of isomerizations in which carbonyl compounds are formed, the starting compounds ranging from oxiranes to oxanes (*31–36*); the mechanisms of these reactions have likewise been examined.



$n = 0, 1, 2, 3.$

In spite of the fact that the studies were carried out in the presence of hydrogen, very few observations have been made with regard to the hydroisomerization character of the isomerization, i.e., very few references have been made to the determining role of hydrogen (*33, 35*). The reason for this is that the object of the study of the reactions of the oxacycloalkanes in the presence of hydrogen was not the isomerization itself, but the hydrogenolysis of these compounds to yield alcohols. Isomerization, as a side-reaction accompanying hydrogenolysis, was therefore not at the focus of interest.

The aim of our experiments reported here was to establish whether isomerization can be observed for oxacycloalkanes containing different numbers of ring atoms on Pt in the absence of hydrogen. Compounds **1–4** were selected as models; **1** was a commercial product of BDH, **3** was a product of Aldrich-Europe, and **2** and **4** were prepared on the basis of (*37*) and (*38*), respectively.



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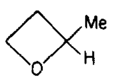

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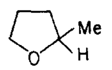

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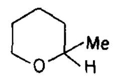

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Experiments were performed in a static microreactor (*39*). Preparation of the Pt/CS

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(Cab-O-Sil with a Pt content of 3%): 10 g CS was moistened with ion-free water, and an aqueous solution (0.3 g Pt/20 ml) of H_2PtCl_6 was added under intensive stirring. After the mixture had stood for 1 day, the water was removed by film evaporation and the mass was then dried for 16 h at 130°C. Reduction was carried out in a current of hydrogen, for 1 h at 210°C, and subsequently for 2 h at 350°C. Specific surface of Pt/CS: 38 m^2/g Pt ($\pm 10\%$). Experimental conditions: 118 mg catalyst; 250°C; reaction time, 1 min; sample taken, 2 μl. Chromatography: Carlo Erba model C ATC/f chromatograph, 1.5-m column containing 15% Carbowax, 20 *M* on kieselguhr (Merck); thermostated at 50°C. The ketones formed were identified on the basis of the glc retentions of authentic compounds. Retention times (min): acetone, 0.88; 2-butanone, 1.94; 2-pentanone, 2.34; 2-hexanone, 3.84; **1**, 0.44; **2**, 1.16; **3**, 1.43; **4**, 1.88. The CO and hydrocarbons formed were separated on a 1.5-m silica gel BDH column at 60°C (retention times (min): CO, 2.9; ethane, 4.8; ethene, 6.9; propane, 9.1; propene, 19). Since the CO does not separate from the methane under these gc conditions, the analysis was also carried out on a 2-m column containing a Carlo Erba 5A molecular sieve. The experimental data were evaluated with a Perkin-Elmer Sigma 10 integrator. Experiments were carried out on a prehydrogenated catalyst, and also on a catalyst freed from hydrogen with a high-purity helium stream of 50 ml/min for 3 days, the extent of hydrogen removal being checked continuously with propene; as revealed by the tabulated data, complete removal of hydrogen could not be achieved under the given conditions. Some characteristic experimental data relating to the transformation of **1** are given in Table 1, and the overall experimental results in Table 2.

The experimental data clearly show that both the conversion and the ketone selectivity are considerably lower in the absence of hydrogen.

Thus, our experimental data demonstrate that the role of hydrogen is of determining importance in the isomerization of oxacycloalkanes to yield ketones; i.e., hydroisomerization occurs. The data also indicate the complete suppression of alcohol formation from compounds **1–3** in the absence of H_2. This appears to be consistent with the role of H_2 in alcohol formation via hydrogenolysis reactions according to the literature. The data in Table 1 reveal that the formation of C_3 hydrocarbons is likwise strongly suppressed in the absence of H_2. (Since the main product of the transformation of 2,3-dimethyloxirane in D_2 is d_0-butene (*33*), it may be assumed that in the absence of H_2 the chemisorbed oxygen blocks the centers responsible for deoxygenation.) At the same time, the formation of CO is not influenced by the absence of H_2. It is very probable that propionaldehyde is formed on the electrophilic centers of the Pt/CS (*40*), but undergoes decarbonylation at the given temperature. On this basis the isomerization is not an intramolecular process. The H abstraction accompanying the ring opening and σ–π bond shift (the C–O σ bond

TABLE 1

Product Compositions (mole%) in the Transformations of 1 on Pt/CS Catalyst in the Presence of H_2 or He Carrier Gas at 250°C

	CO	CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	1	Acetone	2-Propanol	1-Propanol	H_2O
H_2	20	0	21	0	12	0	0	30	4	3	10
He	19	0	9	12	0	1	58	1	0	0	0

TABLE 2

Conversions and Selectivities of Transformations of Compounds **1–4** in the Presence and Absence of H_2

	1			**2**			**3**			**4**		
	a	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*
Pt/CS + H_2	100	30	63	85	22	76	68	57	35	53	49	51
Pt/CS − H_2	42	2	98	33	8	92	16	6	94	10	10	90

Note. a = conversion%; *b* = ketone selectivity (mole%) acetone, 2-butanone, 2-pentanone, and 2-hexanone for **1**, **2**, **3**, and **4**, respectively; *c* = selectivity of formation of hydrocarbons (mole%). These are hydrogenolysis or decomposition products, which were not the object of study here. Their presence indicates that the catalyst was not deactivated during the removal of hydrogen. The value 100 − (*b* + *c*) means 1-propanol + 2-propanol in the case of **1**, 2-butanol in the case of **2**, and 2-pentanol in the case of **3**.

gives rise to a π bond) and the subsequent H addition take place by different pathways probably depending on the number of ring atoms. One of our future aims is to study what types of hydrogen species play roles in the hydroisomerization of C–O-containing compounds.

To summarize, it may be stated that the isomerization to ketones of oxacycloalkanes containing 3–6 ring atoms occurs on a platinum catalyst only in the presence of hydrogen. The process is therefore one of hydroisomerization.

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