Hydroisomerization of 1,3-Dioxacycloalkanes to Esters on Platinum. The Role of Hydrogen in the Isomerization.

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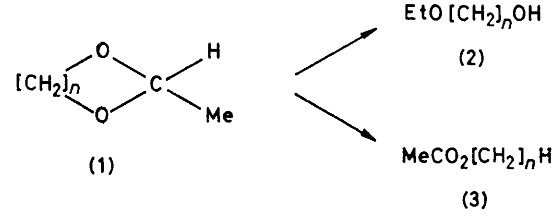
Summary Experiments show that the isomerization of 1,3-dioxacycloalkanes to esters proceeds only in the presence of hydrogen, and the selectivity for ester formation can be $>90\%$ with optimum hydrogen coverage; new data are reported relevant to the mechanism of ester formation and the generalization of the hydroisomerization.

It has been demonstrated and is now accepted that the very varied isomerization reactions of the hydrocarbons on platinum are hydroisomerization processes.[1,2] A number of experimental observations led to the assumption of the catalytic role of chemisorbed hydrogen,[3] and the general nature of the hydroisomerization.[4] On the basis of this assumption, we studied the isomerization of various cyclic carbon compounds containing C–O bonds with the aim of determining the optimum hydrogen coverage for the hydroisomerization.[5] It has been shown that oxacycloalkanes undergo hydroisomerization to ketones,[6] and this has been confirmed in the case of oxirans.[7]

We reported earlier the transformations of 1,3-dioxacycloalkanes on some transition metals in the presence of hydrogen;[8] two main processes occur in parallel (hydrogenolysis and isomerization), their extents depending on the experimental conditions (Scheme 1).

We now report on the transformations of 2-methyl-1,3-dioxolan (**1a**) and 2-methyl-1,3-dioxan (**1b**) on a 5% Pt on



Scheme 1

a; $n = 2$
b; $n = 3$

Table 1. Reactions of (**1a**) and (**1b**) on 5% Pt on Cab-O-Sil as catalyst.

	(**1a**)				(**1b**)			
	%	Selectivity, mol %			%	Selectivity, mol %		
Wt./g of catalyst	Conv.	(**2a**)	(**3a**)	X[a]	Conv.	(**2b**)	(**3b**)	X[a]
20 mg (with H_2)	82	25	48	27	86	28	38	34
100 mg (no H_2)	5	0	20	80	6	0	17	83

[a] Selectivity for formation of various cracking products; details will be published elsewhere.

TABLE 2. Variation in extent of ester formation with hydrogen content; details as in Table 1.

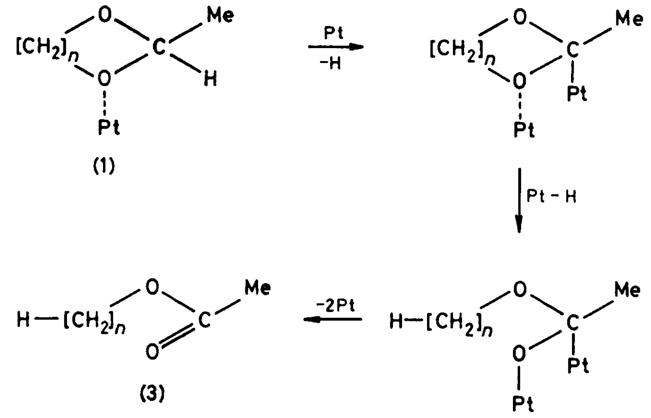
	(1a)				**(1b)**			
	%	Selectivity, mol %			%	Selectivity, mol %		
% H_2 in N_2	Conv.	**(2a)**	**(3a)**	X	Conv.	**(2b)**	**(3b)**	X
0	0	0	0	0	0	0	0	0
7	2	0	72	28	3	0	52	48
20	4	0	91	9	5	8	80	12
50	6	14	61	23	10	25	62	13
100	8	45	31	24	18	55	27	18

Cab–O–Sil catalyst in the absence of H_2 and in the presence of H_2–N_2 mixtures of various compositions. Some of our experiments were performed in a static microreactor at 250 °C, with a reaction time of 1 min, in the way described previously.[6] Product analysis and identification, and the processing of the experimental data have also been described before.[8] Experiments were carried out on a prehydrogenated catalyst, and also on a catalyst freed from hydrogen with high-purity helium (hydrogen was removed in a gas flow of 50 ml He/min at 300 °C for 3 days, the extent of hydrogen removal being checked continuously with propene). The overall experimental results are given in Table 1.

The characteristic data for experiments to establish the optimum hydrogen coverage for ester formation are given in Table 2. These measurements were made in a flow microreactor [20 mg of 5% Pt on Cab–O–Sil; 200 °C; $H_2 + N_2$ 30 ml/min; 0·74 g of (**1a**) or 0·36 g of (**1b**) per hour]. Sinter-glass vapour saturators were used for addition of (**1a**) and (**1b**), and the carrier gases were purified.

The results show clearly the following. (i) In the absence of hydrogen no conversion of 1,3-dioxacycloalkanes occurs. (ii) Isomerization to esters can be optimized by variation of the hydrogen coverage of the catalyst. (iii) With an appropriate hydrogen : reactant ratio, the selectivity for ester formation can be increased to >90%.

Our experimental data indicate that the role of hydrogen is the determining factor in the isomerization of 1,3-dioxacycloalkanes to esters, which therefore provides a new example of hydroisomerization. The data further suggest that under hydrogen-poor conditions, at higher temperature, the mechanism of the reaction is of a dissociative type: H-abstraction in the course of the σ–π bond shift accompanies ring opening, with subsequent H-addition (Scheme 2).



SCHEME 2

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[1] G. C. Bond and P. B. Wells, *Adv. Catal.*, 1964, **15**, 92; J. R. Anderson, *ibid.*, 1973, **23**, 1; J. K. A. Clarke and J. J. Rooney, *ibid.*, 1976, **25**, 125.

[2] D. I. Hagen and G. A. Somorjai, *J. Catal.*, 1976, **41**, 466; J. H. B. Haining, C. Kemball, and D. A. Whan, *J. Chem. Research* (*S*), 1978, **364**; D. A. Dowden, in 'Catalysis' (Specialist Periodical Report), vol. 2, eds D. A. Dowden and C. Kemball, The Chemical Society, London, 1978, p. 1.

[3] M. Bartók, *Acta Phys. et Chem. Szeged*, 1975, **21**, 79.

[4] M. Bartók, *React. Kinet. Catal. Lett.*, 1975, **3**, 115.

[5] Z. Paál and P. Tétényi, *J. Catal.*, 1973, **29**, 176.

[6] M. Bartók and F. Notheisz, *J. Catal.*, in the press.

[7] H. Davidová and M. Kraus, *J. Catal.*, 1980, **61**, 1.

[8] M. Bartók and J. Czombos, *J. Chem. Soc., Chem. Commun.*, 1981, 106.