Isomerization and Hydrogenolysis of 1,3-Dioxacycloalkanes on Metal Catalysts

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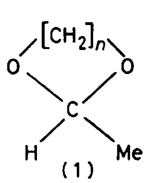
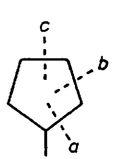
Summary The isomerization of 5-, 6-, and 7-membered 1,3-dioxacycloalkanes to esters on various metal catalysts is reported, the hydrogenolysis pattern for this type of compound is determined, and a new reaction mechanism is proposed to interpret these catalytic processes.

Extensive studies on the hydrogenolysis of 5-, 6-, and 7-membered cycloalkanes have not permitted determination of the variation of the course of the ring-opening reaction with ring size. Although certain regularities have been noted in the hydrogenolysis of hydrocarbons with the cyclopentane skeleton,[1-3] the hydrogenolysis of cyclohexanes and cycloheptanes is difficult to investigate because of the dominance of the concurrent reaction (aromatization).[4]

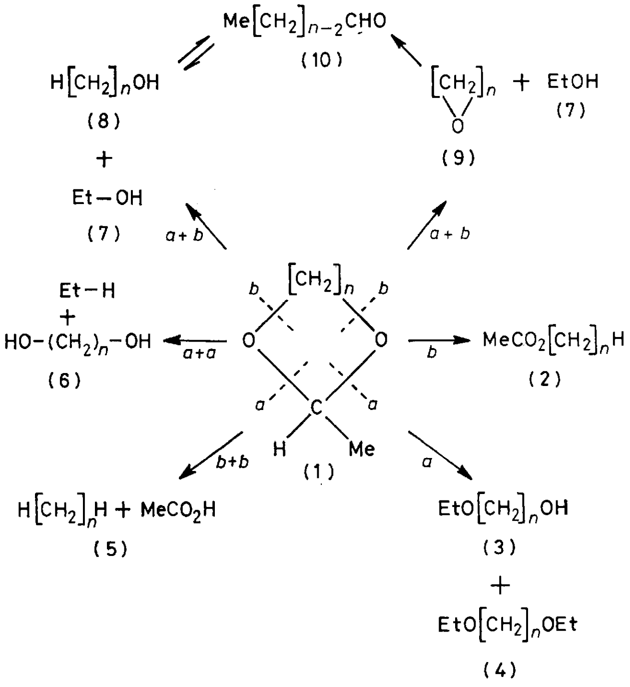
Since the study of hydrogenolysis is one of the central problems in metal catalysis,[5] and 3—5-membered ring compounds have already furnished valuable information we have examined compounds (**1a**), (**1b**), and (**1c**) on M–Cab-O-Sil catalysts (M = Ni, Rh, Pd, or Pt) in the presence of hydrogen (30 ml/min) using a pulse microreactor technique. M–Cab-O-Sil catalysts (0·02 g) containing 5% M were used [specific surface areas: Ni, 40; Rh, 80; Pd, 70; Pt, 40 m²/g M (±10%)]. The compounds formed were identified by g.l.c. comparison with authentic compounds, and experimental data were evaluated with an Autolab System I computing integrator.



(1)
a; n = 2
b; n = 3
c; n = 4



Hydrogenolysis of methylcyclopentane on various metals occurs mainly at the 2,3-bond *b*.[2,3] On Pt–thermolite (a bifunctional catalyst) the 1,3-dioxacycloalkanes (**1a**) and (**1b**) are isomerized to esters.[6] Procedures have been patented for the high-pressure hydrogenolysis of the industrially important 1,3-dioxans to alcohols.[7] It is surprising, however, that there are no reports on the hydrogenolysis of 1,3-dioxacycloalkanes at ordinary pressures.



Scheme 1. *n* = 2—4.

The data in Tables 1 and 2 and Scheme 1 permit the following conclusions to be drawn. (i) As a consequence of adsorption through the ring oxygen atoms (oxacycloalkanes are adsorbed on noble metals *via* oxygen[8]), cleavage of bond *a* may become dominant, in contrast to cycloalkanes. (ii) Bond *b* rupture also occurs because of the presence of the C–O bonds, and this led to the recognition of a new metal-catalysed reaction: the isomerization of 1,3-dioxacycloalkanes to esters. (iii) Bond *a* and *b* cleavages

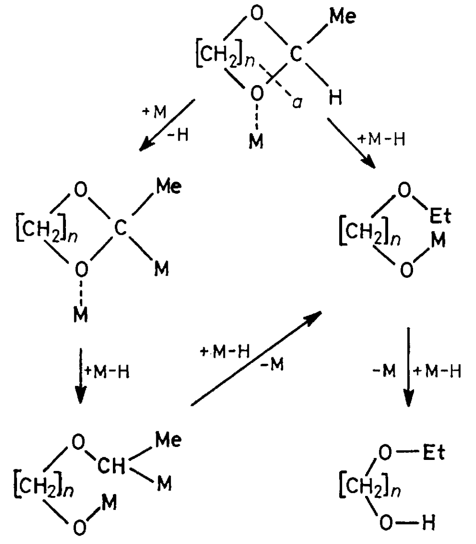
TABLE 1. Transformation of (**1a**), (**1b**), and (**1c**) on various catalysts.

	Catalyst[b]	Temp. /°C	% Conv.	Selectivity (S)/mol %[c]									
				(**2**)	(**3**)	(**4**)	(**5**)	(**7**)	(**8**)	(**9**)	(**10**)	(**11**)	(**12**)
(**1a**)[a]	Ni/CS	200	2	40	[d]	42	0	0	0	0	10	0	0
		300	12	20	[d]	1	0	4	4	0	16	0	54
	Rh/CS	200	31	48	16	13	2	3	3	0	5	0	12
		300	96	38	3	1	23	5	5	0	4	0	35
	Pd/CS	200	40	18	35	33	0	3	3	0	0	0	1
		300	71	54	8	11	[d]	12	12	0	0	0	10
	Pt/CS	200	44	30	30	7	0	2	2	0	0	0	27
		300	94	61	5	1	13	1	1	0	0	0	23
(**1b**)[a]	Ni/CS	200	0	0	0	[d]	0	0	0	0	0	0	0
		300	19	9	0	[d]	0	0	16	0	74	0	38
	Rh/CS	200	45	20	14	13	0	44	18	0	16	0	9
		300	96	12	1	1	0	46	25	0	0	0	40
	Pd/CS	200	60	7	39	37	0	0	8	0	3	0	9
		300	89	23	9	13	0	0	0	0	52	0	14
	Pt/CS	200	51	15	39	11	0	2	18	0	0	0	19
		300	93	50	10	2	0	10	18	0	0	0	21
(**1c**)[a]	Ni/CS	200	16	16	43	27	0	0	0	9	0	[d]	1
		300	43	1	4	3	0	12	1	0	0	53	33
	Rh/CS	200	99	4	0	3	0	15	3	70	0	36	5
		300	99	1	0	0	0	19	3	66	0	11	37
	Pd/CS	200	90	11	24	26	0	3	2	8	0	15	[d]
		300	98	1	1	1	0	36	4	39	0	42	14
	Pt/CS	200	85	3	23	13	0	19	5	8	0	33	10
		300	97	4	2	2	0	23	6	10	0	31	41

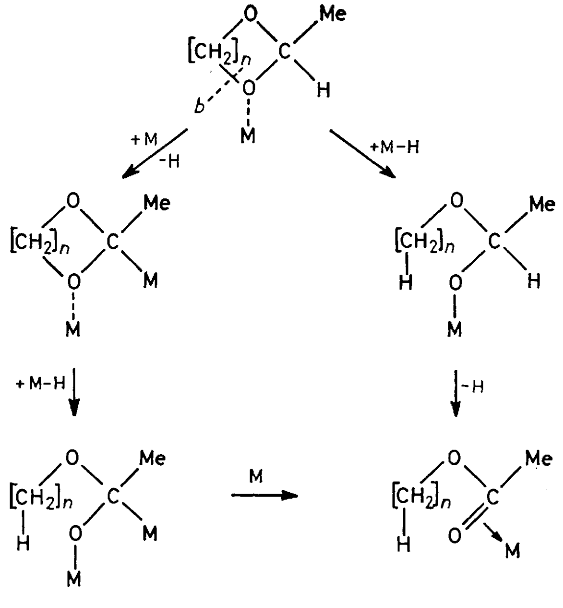
[a] Amount of substance injected: 2 μl. [b] CS = Cab-O-Sil. [c] For (**2**)—(**10**) see Scheme 1. (Chromatography: 2·6 m column of 15% didecyl phthalate on silanized Kieselguhr.) (**11**) represents the amounts of unidentified substances as weight percentages of the product mixture formed; (**12**) represents the amounts of gases, the composition of which will be published elsewhere. [d] Minimal quantity.

are observed for all three compounds on each catalyst, though to different extents. On Rh, *a* rupture is less favoured. The extent of ester formation depends inversely on the number of ring atoms. At higher temperatures, $a+b$ rupture dominates, for which Pt displayed lowest activity. (iv) Ni was the least active in these reactions, and the essential difference between Rh, Pd, and Pt lies not in their activity, but in their selectivity. (v) Temperature has the greatest effect on the ratio of *a* to *b* cleavage. At low temperature *a* rupture predominates, and at high temperature *b* rupture. In this respect too Rh behaves differently.

From a comparison between the reactivities of methylcyclopentane and (**1a**), basic conclusions may also be drawn on the mechanisms of the ring-opening reactions. For methylcyclopentane under similar conditions, the ratio of $a:b:c$ cleavage = 1:4:2, this ratio being dependent on experimental conditions.[2] For (**1a**), adsorption *via* oxygen allows *a* rupture to occur. However, it has been claimed that this plays a subordinate role because of adsorption *via* the tertiary carbon atom.[3]



SCHEME 2. n = 2—4.



SCHEME 3. n = 2—4.

TABLE 2. Distribution (ΣS, %) of products formed by *a*, *b*, and *a*+*b* ruptures in hydrogenolysis of (**1a**), (**1b**), and (**1c**) on various metals.

	Temp. /°C	Ni/CS				Rh/CS				Pd/CS				Pt/CS			
		a	*b*	*a*+*b*	*a*/*b*	*a*	*b*	*a*+*b*	*a*/*b*	*a*	*b*	*a*+*b*	*a*/*b*	*a*	*b*	*a*+*b*	*a*/*b*
(**1a**)	200	42	40	10	1	35	50	8	0·7	68	18	3	3	64	30	2	2
	300	1	20	20	—	17	61	9	0·3	19	54	12	0·3	16	74	1	0·2
(**1b**)	200	0	0	0	—	30	20	44	[b]	76	7	11	7	60	15	18	4
	300	—	9	90	[b]	15	12	46	[b]	25	23	52	[b]	22	50	12	0·3
(**1c**)	200	70	16	9	4	3	4	70	[b]	50	11	8	5	36	3	19	10
	300	7	1	12	[b]	0	1	60	[b]	2	1	40	[b]	4	2	23	[b]

[a] Products of *a* rupture: (**3**), (**4**), and (**6**). Products of *b* rupture: (**2**) and (**5**). [b] The ratio *a*/*b* is not characteristic, for the main transformation results from *a*+*b* rupture.

Schemes 2 and 3 show two examples of the main pathways in the hydrogenolysis of the 1,3-dioxacycloalkanes. Reactions may occur by an associative or a dissociative mechanism, depending on the temperature and other factors. Ester formation too may be regarded as resulting from hydrogenolysis, although the stoicheiometry points to ring opening *via* a C–O σ–π bond shift, *i.e.* intramolecular isomerization.

Schemes 2 and 3 illustrate adsorption *via* one oxygen atom, but adsorption *via* two oxygen atoms is not excluded, as indicated by *a*+*a* and *b*+*b* rupture, yielding (**5**) and (**6**).

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