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THE MECHANISM OF HYDROGENOLYSIS OF CYCLOPROPANES AT PLATINUM AND PALLADIUM

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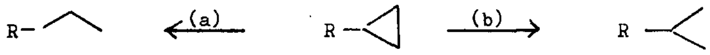
In the hydrogenolysis of substituted cyclopropanes [1] the predominant direction of ring fission (1,2) is evidently related to the electronic nature of the substituent R:



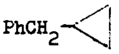
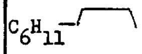
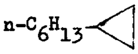
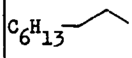
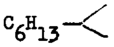
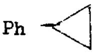
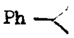
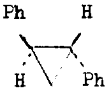
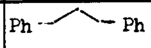
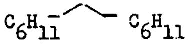
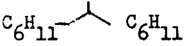
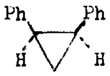
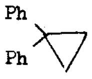
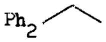
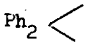
R = Ph, Vinyl, COMe [1] R = Alkyl, aralkyl

A comparative study of further examples (cf. Table) confirms this conclusion, and indicates that the ratio of fission: (a)/(b) falls: R = Ph $>$ PhCH$_2$ $>$ n-hexyl, and that the rates of hydrogenolysis fall in the same order. Hydrogenolysis is found to be generally much faster at palladium than at platinum which commonly requires an added acid catalyst, e.g. HCl to achieve a satisfactory rate. The proportion of fission (a) is also significantly greater at palladium.

Benzyl cyclopropane was found, in competition experiments, to retard the hydrogenolysis of phenyl cyclopropane, and 1,1-diphenylcyclopropane of both cis- and trans- 1,2- diphenyl cyclopropanes, all at palladium. This is taken to indicate generally strong adsorption with hydrogenolysis as the rate limiting step.

Hydrogenolysis is known (1) to involve a chemisorbed cyclopropane, and there is no evidence of isomerisation or hydrogen/deuterium exchange (1), i.e. on adsorption the ring remains intact. This is in agreement with the

Table: Products of hydrogenolysis in ethyl alcohol (g.l.c. analysis).

Cyclopropane	Catalyst	Products,%		
	Pt			
		25	75	
	Pd			
		75	25	
	Pd*			
		5	95	
				$C_6H_{11}Pr$
	Pt	90	3	7
	Pd	100	-	-
				
	Pt	-	42	58
	Pd	100	-	-
	Pt	-	35	65
	Pd	100	-	-
				
	Pt	35	65	
	Pd	100	-	

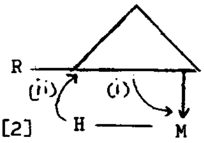
* At platinum hydrogenolysis in this case is inconveniently slow.

observed (3) reversible formation of cyclopropane $PtCl_2$ complexes.

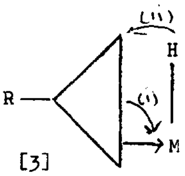
From the correlation of heterogeneous hydrogenation and homogeneous hydrogenation with hydrido-metal complexes (4), the hydrogen, in both systems, may, with some probability, be identified as a nucleophilically polarised reagent. Further, the effect of the nature of R on the proportions of (a) and (b) fission of [1] is consistant with preferential hydrogen transfer to the most electrophilic carbon i.e. to the centre of lowest electron density.

Phenyl, vinyl and COMe are strongly electrophilic groups, $PhCH_2$ is less electrophilic, and n-hexyl, as an alkyl group, will act as an electron donor.

These considerations lead to a rational mechanism for hydrogenolysis as in [2] or [3], based on an electrophilic polarisation step (i), consequent on chemisorption, and hydrogen transfer (ii). The electronic nature of the R-group will discriminate between the alternatives[2] and [3], an electrophilic R-group clearly assisting [2], and a relatively fast reaction, whilst electron donor groups will lead to a slower reaction as in [3]. The substituent must, however, also exert a steric effect. A process dependent on bond formation will be sensitive to steric hinderance which will favour reaction at the less hindered position as in [3]. A process dependent on bond rupture, on the other hand, will be subject to steric acceleration by substitution, thus assisting [2]. The diphenyl cyclopropanes, at platinum, exhibit more type (b) fission than phenyl cyclopropane which reacts almost entirely by route (a). This difference we attribute to the greater steric hinderance in the diphenyl derivatives, and we infer that, at platinum, hydrogenolysis may be dependent on a bond forming step. Hydrogenolysis at palladium on the other hand, appears to depend more on bond rupture since all the phenyl cyclopropanes give exclusively type (a) fission. This is consistent with the known greater electron acceptor capacity of palladium (5). The possible intervention of a chemisorbed palladium π-allyl intermediate seemed unlikely in view of the lack of catalysed isomerisation of cyclopropanes under mild conditions. However, a π-allyl intermediate should give on deuterolysis a significant amount of a trideuterated product. The molar percentages of di- and tri- deuterated material from deuterolysis at palladium in

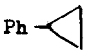
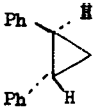
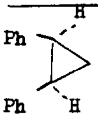
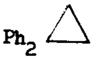


[2]



[3]

deuteromethanol:

	$C_9H_{11}D$ 11.8	$C_9H_{10}D_2$ 64.8	$C_9H_9D_3$ 19.5
	$C_{15}H_{15}D$ 5.2	$C_{15}H_{14}D_2$ 81.8	$C_{15}H_{13}D_2$ 11.5
	8.2	76.8	12.7
	16.4	69.9	11.8

appear to indicate that direct hydrogenolysis of the cyclopropane is the major route of reaction.

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