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OLEFIN INTERMEDIATES IN THE HYDROGENOLYSIS OF POLYALKYLCYCLOPROPANES

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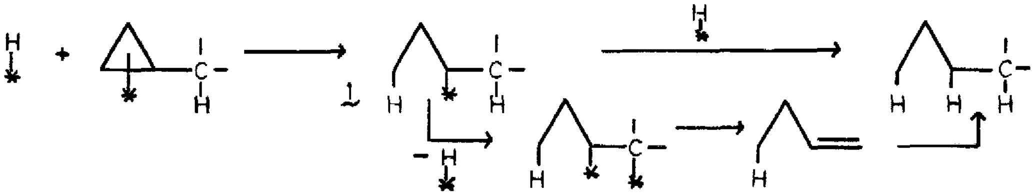
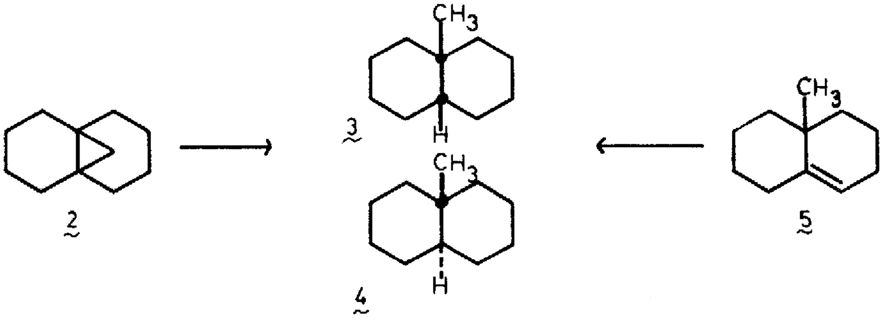
Early work on the hydrogenolysis of cyclopropane led to the mechanistic proposal[1] shown in the top line of the Figure below. On the basis of this proposal *cis* addition of the two added hydrogens would be expected. In recent years, though, a number of reports have been published which show that *cis* addition is not always observed.[2-7] To account for the exclusive formation of the 5α product (apparent *trans* addition) on hydrogenolysis of lumitestosterone the formation of an olefinic intermediate was proposed with the product formed from the hydrogenation of this olefin.[7] The presence of olefinic intermediates can also be used to account for most of the reported anomolous stereochemistry results.[8]



There are, however, some discrepancies in this area which need clarification. In the first place the mechanistic conclusions shown above were based primarily on data obtained from the vapor phase deuterolysis of cyclopropane and its simpler monosubstituted derivatives[1] while all of those hydrogenolyses which gave anomolous stereochemical results were run in solution. Since deuterium exchange is more extensive in vapor phase reactions than it is in those run in solution[9] it is also conceivable that the stereochemical course of the reaction could also be different. Secondly, the presence of an olefin intermediate, while a viable generality, has only been established with reasonable certainty in the hydrogenolysis of lumitestosterone.[7] Since the expected *cis* addition product from this reaction is highly strained and the reaction conditions used were quite severe, the generality of any conclusions arrived at from this study could be questioned.

The first of these discrepancies was recently resolved when it was shown[10] that the product stereochemistry observed on vapor phase hydrogenolysis of some propellanes was the same as that reported[3] for the solution reaction. It was further found that the products obtained from vapor phase deuterolyses were consistent with the presence of a double bonded intermediate in the reaction.[10] The following data is presented to show that such an intermediate can also be generally considered in the solution hydrogenolyses of polysubstituted cyclopropanes.

The hydrogenolysis of the propellane, tricyclo [4.4.1.0] undecane (2), over PtO_2 in acetic acid has been reported[3] to give nearly equal amounts of the *cis*-(3), and *trans*-9-methyldecalins (4). Since these reaction conditions were quite mild and it was shown[8] that the solvent was not involved in the ring opening process, these conditions were considered to be compatible with any generalized mechanistic study. In our hands the cleavage of 2 gave a 48:52 ratio of 3 and 4. Hydrogenation of the olefin (5) expected to be the intermediate in this hydrogenolysis gave a 43-57 ratio of these products under the same reaction conditions. An exact correspondence was not expected since the olefin:catalyst ratio can be influential in determining product stereochemistry[11] but, even with this factor the observed correlation is quite good.



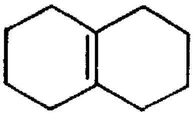
Deuterolysis of 2 in d_4-acetic acid gave 3 and 4 having the deuterium composition shown in the Table. There is no deuterium exchange with either products or starting materials under these reaction conditions. These data parallel those results obtained from the deuteration of $\Delta^{9,10}$-octalin (6)[9], a reaction from which both the *cis* and *trans* decalins are obtained and in which product formation is preceded by isomerization to 7 with concomitant incorporation of one deuterium.

The d_{Ave} of nearly 3 found for both 3 and 4 indicates that on cleavage of the cyclopropane ring one deuterium is placed on the methyl group thus formed and two more, on the average, add to the double bond produced on ring opening as in the sequence 2 → 5 → 3 + 4. This process can be verified by consideration of the direct correlation between the intensities of the variously deuterated molecular ion peaks and their corresponding M-CH_2D peak, also shown in the Table. From this correlation it appears that almost every product molecule contained a-CH_2D group.

Table

	3		4	
	%	M-CH_2D%	%	M-CH_2D%
d_o	—		7.38	
d_1	8.73	5.77	5.17	8.01
d_2	42.45	42.25	22.05	18.95
d_3	30.51	30.51	36.07	42.99
d_4	12.39	15.08	20.85	22.31
d_5	4.66	4.77	5.44	5.66
d_6	1.70	1.61	2.95	2.08
d_{Ave}	2.67		2.86	

The available data, therefore, supports the premise that the hydrogenolysis of polysubstituted cyclopropanes occurs through the intermediacy of an olefinic species in both vapor[10] and solution reactions. The deuteration of the methyl group on 3 and 4 (Table) rules out any concerted catalytic transfer of an α hydrogen to the methyl group during ring opening and olefin formation. Whether this double bond is formed as the ring is opened as previously proposed[7] or it arises from the half-hydrogenated species, 1, formed via a classical ring opening as shown in the Figure still remains to be established.



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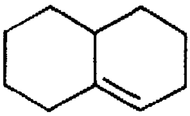

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