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THE STEREOCHEMISTRY OF THE PALLADIUM-CATALYSED HYDROGENATION OF ALLENES

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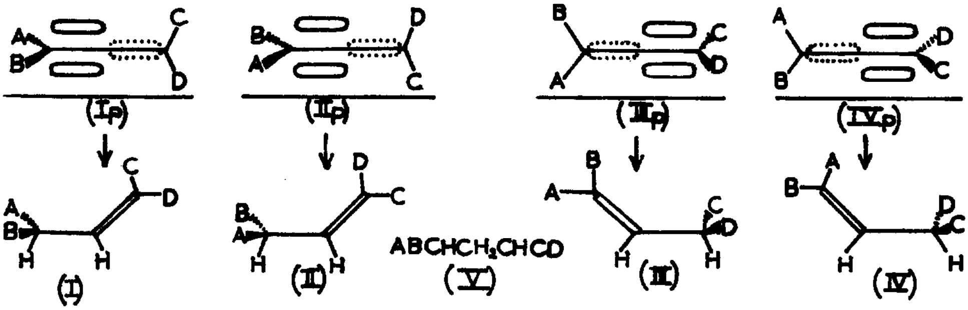
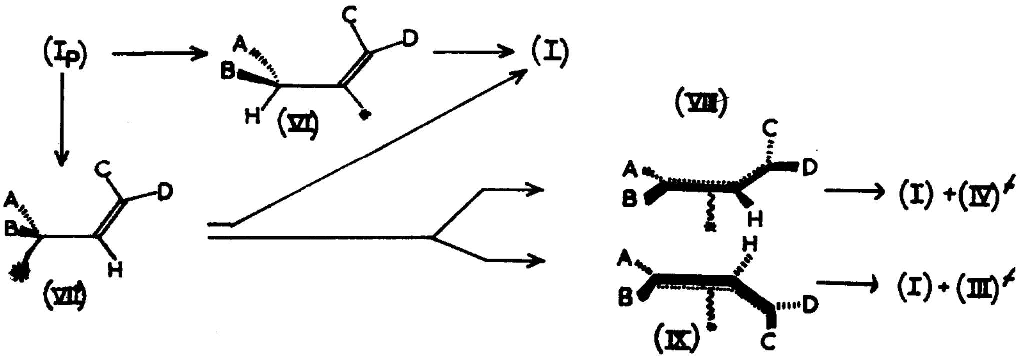
An allene of appropriate substitution has four distinguishable attitudes of presentation to a solid catalyst (Ip - IVp) leading by 1,2-cis-addition to four different olefins (I-IV).



Steric effects occurring on approach of the oriented allene to the catalyst might be expected to be important whether transition states for forming a re-hybridised σ-intermediate[1] or forming, or 'half hydrogenating', a π-complexed intermediate[1-4] are considered. Addition of hydrogen to give the 'half-hydrogenated' species (VI) leads to (I). However, addition to give the alternative (VII), in which the hydrogen addition occurred initially at the central



*Produced as enantiomorph of species illustrated.

carbon could lead, by flattening of the double bond on to the catalyst surface, to the two π-allylic species (VIII) and (IX).[3,4] Addition of the second hydrogen can then lead to (I) and the isomeric olefins (IV) and (III) respectively.[*][≠]

Little qualitative or quantitative information[5-9] is available on the semi-hydrogenation of allenes and we now report data for a number of examples in Table 1. These data (liquid phase) are mostly derived from a study of complete product analyses (g.l.c.) over the range 0.0 - 2.0 mol. of added hydrogen. Such build up/decline curves are necessary to obtain proper perspective on events at the 1 mol.

Table 1. Product Analyses at the Semihydrogenation Point of Allenes

Allene:	R.A.[a] %	Olefins % (I)	(II)	(III)	(IV)	% Satd. (V)	Sel.[e]	% $t_{max.}$[b] (VI)
Ex. 1. A = Pr^i; B,C,D. = H	4	⟵ 25 ⟶		0	69	2	0.94	26
Ex. 2. A = CH_2OH; B,C,D. = H	2	⟵ 26 ⟶		8	63	0	0.98	40
Ex. 3. A = CH_2OAc; B,C,D. = H	0	⟵ 24 ⟶		3	69	4	0.96	-
Ex. 4. A,B = Bu^i; C,D = H	0	⟵ 17 ⟶		⟵ 80 ⟶		3	0.97	-
Ex. 5. A = Et, B = Me, C,D = H	1	⟵ 18 ⟶		28	52	0	0.99	41[c]
Ex. 6. A = Pr^i, B = Me, C,D = H	1	⟵ 29 ⟶		12	58	0	0.99	28[c]
Ex. 7. A = Bu^t, B = Me, C,D = H	12	⟵ 15 ⟶		9	54	11	0.77	44[c]
Ex. 8. A = Et; B,C = Me, D = H	3	31	2	⟵ 62 ⟶		1	0.94	33[d]
Ex. 9. A = CO_2H; B,C,D = H	5	⟵ 0 ⟶		2	89	4	0.91	33
Ex. 10. A = CO_2Me; B,C,D = H	1	⟵ 0 ⟶		3	95	1	0.98	32
Ex. 11. A = CO_2H; B = Me; C,D = H	4	⟵ 4 ⟶		6	85	1	0.95	40[c]
Ex. 12. A = CO_2Me, B = Me; C,D = H	0	⟵ 4 ⟶		7	87	2	0.98	51[c]

[a] R.A. = residual allene; [b] $t_{max.}$ = maximum amount of trans-material developed during absorption of the second mol. of hydrogen; [c] max. of III; [d] max. of II; [e] Sel. = selectivity.

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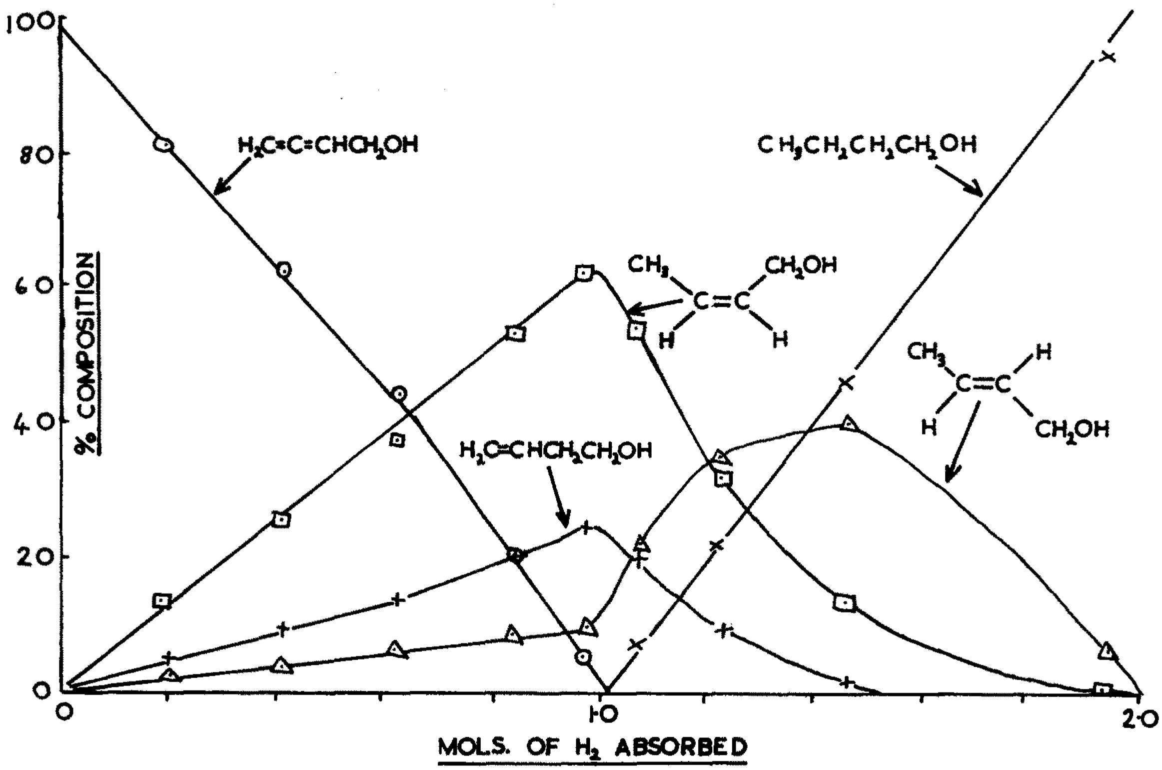
[*] An intermediate which may alternatively be written as a π-allyl intermediate[1] has been invoked in the interesting work of Moore,[10] to explain the products of semi-hydrogenation of the constrained allene cyclo-1,2-decadiene.

[≠] Only one enantiomer for each racemate is illustrated.



GRAPH 1. Product Analysis for Hydrogenation of Buta-2,3-dienol

absorption point (cf. Graph 1). The ratio of % olefinic products to total % composition is shown in column Sel. and indicates the selectivity of the catalyst (5% Pd/BaSO$_4$) for completing semi-hydrogenation of the allene before producing saturated products. Column (VI) shows the maximum concentration of *trans*-material produced by stereomutation between the absorption of 1 and 2 mols. of hydrogen.

In all cases, selectivity is good (with the possible exception of Ex. 7) and products of *cis*-addition are predominant. There is a general correlation between steric accessibility of a double bond from a particular direction and its ability to hydrogenate. As a rough guide the values x and y are collected in Table 2 to indicate the accessibility of

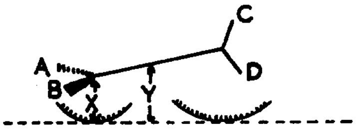
Table 2. Distance of Termini, from a Plane Surface, of Allene Double Bond Undergoing Hydrogenation[a,d]

Allene[c]	Allene Orientation			
	I	II	III	IV
Ex. 1,2,3	x 1.55 y 1.75 1.65[b]	1.55 1.75 1.65	1.50 2.05 1.78	1.35 1.60 1.48
Ex. 4,5,	x 1.80 y 1.90 1.85	1.80 1.90 1.85	1.45 1.90 1.68	1.45 1.90 1.68
Ex. 6.	x 1.95 y 1.95 1.95	1.95 1.95 1.95	1.50 2.20 1.85	1.45 1.90 1.68
Ex. 7.	x 2.05 y 2.10 2.08	2.05 2.10 2.08	1.65 2.50 2.08	1.45 1.90 1.68
Ex. 8.	x 1.80 y 1.90 1.85	2.05 2.40 2.23	1.60 2.05 1.83	1.60 2.05 1.83
Ex. 9.10	x 1.45 y 1.60 1.53	1.45 1.60 1.53	1.65 2.45 2.05	1.35 1.60 1.48
Ex. 11,12	x 1.60 y 1.80 1.70	1.60 1.80 1.70	1.65 2.45 2.05	1.45 1.90 1.68

[a] Measurements (Å) using Crystal Structure models (allene double bond 1.31 Å) with van der Waals spokes (hydrogen 1.2 Å, methyl and methylene 2.0 Å, oxygen 1.4 Å).

[b] Mean distance. [c] See Table 1.

[d]



the two correctly oriented carbon atoms in the least hindered approach of the allene.

The three monosubstituted allenes Ex. 1 - 3 hydrogenate predominantly in the least hindered orientation (IVp) with the substituent pointing away from the catalyst, and only to a very minor extent are the products expected from least favourable orientations (IIIp) obtained [the (III) obtained is probably a stereomutation product]. A moderate amount of product comes from orientations (Ip) and (IIp) with the substituent parallel to the catalyst, or else from orientation (IVp) followed by π-allyl isomerisation. These results resemble data for methyl allene.[7,8] In the case of 1,1-di-isobutyl allene (Ex. 4.) only two products are possible and both form, that from the least hindered orientation predominating. With the 1,1-di-substituted examples (Ex. 5,6 and 7), three products are formed. The situation is similar to that of Ex. 4 except that these indicate that the orientation (IVp) with Me pointing into the catalyst is preferred to (IIIp) with the other substituent pointing downwards. When Et is replaced by Pr^i and Bu^t the distribution of products shifts further in favour of (IVp).

The tri-substituted allene Ex. 8 is of interest. Hydrogenation with the geminal Me and Et parallel to the catalyst proceeds with marked preference for the orientation (Ip), in which the hydrogen points into the catalyst, over (IIp) in which the methyl points down. However, hydrogenation appears to proceed equally easily to (Ip) when the geminal H and Me are parallel to the catalyst. The very small amount of trans-olefin (II) formed in this case also indicates little π-allyl formation in the approaches (IIIp) and (IVp) inasmuch as the double bond migration would give this product. However, the converse possibility in which approach via orientation (Ip) followed by π-allyl formation which leads to (III) and (IV) by isomerisation, is not ruled out.

The monosubstituted allene acid and ester (Ex. 9,10) contrast with Ex. 1 - 3 in that no product (I = II) expected from the orientation with the acid group parallel to the catalyst occurs. It is possible that the steric effect in Table 2 is an underestimate, or that polarity is an important factor here. The cis-acid and ester in Ex. 9 and 10 contain little trans material. 1-Methylallene carboxylic acid and ester (Ex. 11,12) again give predominantly α-unsaturated material and the orientation with methyl pointing into the catalyst is heavily preferred to the orientation with an acid or ester pointing downwards: such preference may prove useful in stereospecific synthesis of tri-substituted olefins.

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