Regioselective and Stereoselective Oxidation of Steroidal Palladium π-Allyl Complexes to Allylic Alcohols

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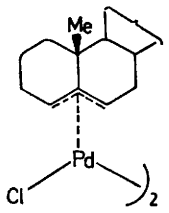
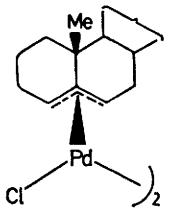
Summary Steroidal palladium π-allyl complexes are oxidised regiospecifically and with high stereoselectivity to allylic alcohols by 3-chloroperbenzoic acid in light petroleum containing pyridine, the hydroxy-group being delivered preferentially to the same diastereotopic face of the π-allyl system as that originally occupied by palladium.

PALLADIUM π-allyl complexes may be oxidised to carbonyl compounds under a variety of conditions,[1a,2] but there are no reports of the preparation of allylic alcohols by oxidation of such complexes. We have found that the α-4—6η-(cholestenyl)palladium chloride dimer (I)[3] on treatment in sequence with pyridine (1 equiv.) and 3-chloroperbenzoic acid in light petroleum gave 4α-hydroxycholest-5-ene (VI) (66%), whilst the β-isomer (II) gave 6β-hydroxycholest-4-ene (X) (61%) and 6α-hydroxycholest-4-ene (XI) (6%). Under the same conditions the α-3—5η-complex (III) afforded 3α-hydroxycholest-4-ene (XII) (67%), whilst the α-5—7η-complex (IV) furnished 7α-hydroxycholest-5-ene (VII) (82%). 3-Chloroperbenzoic acid is soluble only to a limited extent in light petroleum, but use of chloroform, dichloromethane, or benzene, in which it is soluble, led only to gross mixtures of products from all the π-allyl complexes.

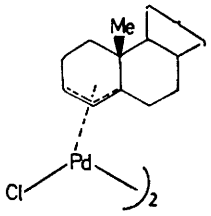
With pyridine and 3-chloroperbenzoic acid in light petroleum–dichloromethane (1 : 1) the β-3—5η-complex (V) (which is almost insoluble in light petroleum) gave a mixture of 3β-hydroxycholest-4-ene (XIII) (32%) and 3α-hydroxycholest-4-ene (XII) (14%), which further suggests that the presence of dichloromethane has an adverse effect upon the efficiency and stereoselectivity of hydroxylation.



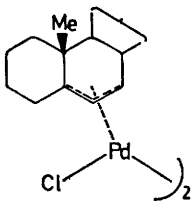
(I)



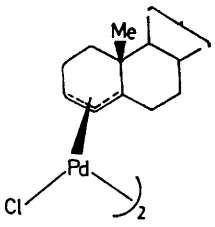
(II)



(III)

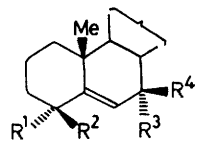


(IV)

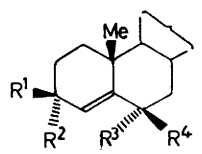


(V)

The presence of pyridine suppresses the formation of carbonyl compounds and enhances the regioselectivity and stereoselectivity of hydroxylation. For example, in the absence of pyridine the α-4—6η-complex (I) with 3-chloroperbenzoic acid in light petroleum gave a mixture of cholest-5-en-4-one (16%), cholest-4-en-6-one (4%), 4α-hydroxycholest-5-ene (VI) (5%), 4β-hydroxycholest-5-ene (VIII) (3%), 6β-hydroxycholest-4-ene (X) (12%), and 6α-hydroxycholest-4-ene (XI) (12%), whilst the α-3—5η-complex (III) gave 3α-hydroxycholest-4-ene (XII) (1%), 3β-hydroxycholest-4-ene (XIII) (12%), cholest-4-en-3-one (45%), and cholest-5-en-3-one (23%). Under the same conditions the α-5—7η-complex (IV) afforded a mixture of 7α-hydroxycholest-5-ene (VII) (29%) and 7β-hydroxycholest-5-ene (IX) (28%). The pyridine presumably breaks the halogen bridges in the steroidal palladium π-allyl chloride dimers and forms asymmetrically bonded π-allyl complexes with pyridine as ligand;[1b] according to t.l.c. the steroidal chloro-bridged complexes were rapidly transformed to other species by pyridine, but we have been unable to isolate the products.



	R^1	R^2	R^3	R^4
(VI)	OH	H	H	H
(VII)	H	H	OH	H
(VIII)	H	OH	H	H
(IX)	H	H	H	OH



	R^1	R^2	R^3	R^4
(X)	H	H	H	OH
(XI)	H	H	OH	H
(XII)	H	OH	H	H
(XIII)	OH	H	H	H

These reactions are significant synthetically, and the high stereoselectivity of hydroxylation provides a potential means of illuminating the stereochemistry of palladium π-allyl complexes.

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