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OXIDATIONS CATALYSED BY TRISTRIPHENYLPHOSPHINERHODIUM CHLORIDE

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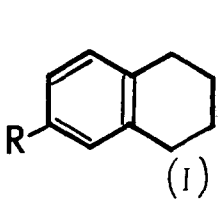
Tristriphenylphosphinerhodium chloride acts as a soluble catalyst for hydrogenation[1], for double-bond isomerisation[2] and for some benzylic oxidations involving oxygen gas[3]. Tetralin (I,R=H) gave tetralone (II,R=H) in 48-60% yield, or more than 90% conversion. Only ketones were observed as products in such oxidations[3].

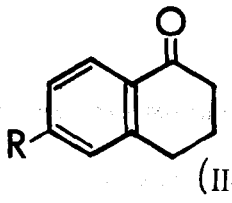
The ketone (II,R=OMe) is a key intermediate in the industrial total synthesis of oestrone and analogues, e.g.[4], and although readily obtained by chromic acid oxidation of (I,R=OMe)[5] the process has some practical disadvantages. A catalytic method might be superior.

Oxidation of (I,R=OMe) by passing air through a refluxing benzene solution in presence of about 5% by weight of tristriphenylphosphinerhodium chloride gave (III) in 48% yield with 40% recovery of (I,R=OMe). In no experiment involving the use of a solvent was formation of ketone observed. However, omission of solvent and heating on the steam-bath led to (II,R=OMe) in 40% yield with substantial recovery of unchanged material. Further oxidation of (III) to (II,R=OMe) together with spectral data supported its structure.

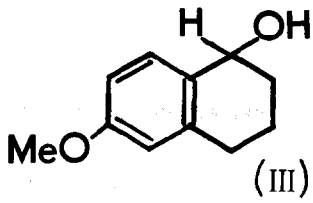
To see whether a tertiary alcohol could be produced, the process was carried out in benzene on oestrone methyl ether 17-ethylene ketal. The product in 10-15% yield with recovery of most of the unchanged starting-material, gave after removal of the ketal 9α(?)-hydroxyoestrone methyl ether (IV). It is a tertiary alcohol since reaction with chromic acid gave only 9(11)-dehydrooestrone, also readily produced by other acids. The stereochemistry has not been proved, but is likely to be α- because of preferred attack by the bulky reagent from this side.



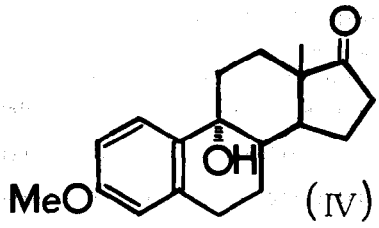
(I)



(II)



(III)



(IV)

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