Stereochemistry of the Hydroxypalladation Step in the Wacker Process

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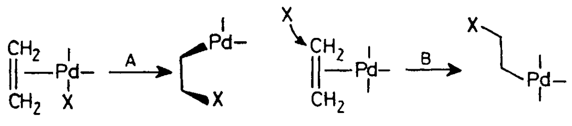
Summary Stereospecific formation of *threo*-1,2-dideuterio-2-chloroethanol [*threo*-(**3**)] in the Wacker reaction of *trans*-1,2-dideuterioethene (**2**) indicates that the hydroxypalladation step is a *trans*-process.

IN recent years, the mechanism of the Wacker oxidation of ethene to acetaldehyde has attracted considerable interest.[1-8] Although it is now reasonably clear that an unstable β-hydroxyethylpalladium complex (**1**; X = OH) (Scheme 1) is an intermediate in the oxidation, there is still disagreement about the steric course of the hydroxypalladation step (path A or B, Scheme 1). Kinetic studies suggest that a *cis*-addition of Pd^{II} and co-ordinated OH takes place[2-6] (path A). A few palladium-promoted nucleophilic additions (X = Cl, alkyl, or aryl) have in fact been shown[5] to occur in this manner, but a number of reactions related to Wacker hydroxylation, *e.g.* acetoxylation,[5] methoxylation,[7] and amination[8] of mono-olefins proceed *trans*. In one case, with the chelating olefin cyclo-octa-1,5-diene under alkaline conditions, even hydroxylation has recently been shown to proceed *trans*.[7a] Since the chelating diene most certainly prevents co-ordination of water to palladium and this might inhibit[6,9] a competing *cis*-attack (path A), further studies seemed desirable. We report here results that provide conclusive evidence that the Wacker hydroxypalladation is a *trans* process.

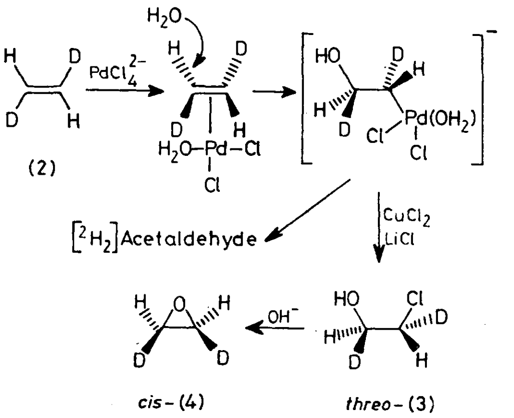


(**1a**) (**1b**)

SCHEME 1

In the Wacker oxidation of ethene the formation of chlorohydrin has been observed[1,10] which can be obtained as the main product by increasing the copper(II) and chloride ion concentrations.[10] We have studied the stereochemistry of this hydroxychlorination using *trans*-dideuterioethene (**2**) (Scheme 2), prepared by chromium(II) chloride reduction of dideuterioacetylene.[11] The steric course of the hydroxypalladation step can then be derived from the configuration of (**3**).

The compound (**2**) was hydroxychlorinated using the catalytic system $PdCl_2$–$CuCl_2$–LiCl (Scheme 2) to give (**3**) whose configuration was determined by microwave spectroscopy. By treatment with hydroxide ion, (**3**) was converted into the corresponding epoxide (**4**), which was also analysed by microwave spectroscopy. This conversion, which results in one inversion, was carried out in order to improve the accuracy of the intensity measurements, the rotational transitions of (**4**) being much stronger than those of (**3**). The chlorohydrin formed from (**2**) was found to be *threo*-(**3**) and the corresponding epoxide was *cis*-(**4**) (Table).



SCHEME 2

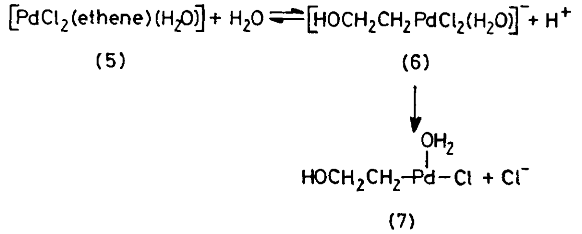
For quantitative analysis of (**4**), the following transitions were used: $3_{21} \leftarrow 3_{12}$ 19252·85 MHz [*cis*-(**4**)], 19742·83 MHz [*trans*-(**4**)] and $4_{31} \leftarrow 4_{22}$ 24407·89 MHz [*cis*-(**4**)], 25859·55 MHz [*trans*-(**4**)]. The extent of *cis–trans* isomerisation of (**2**) was <1% during the reaction, as shown by conversion[12] of the recovered ethene into *trans*-(**4**) and subsequent microwave analysis.

TABLE. Hydroxypalladation of (**2**).[a]

Reaction time/h	Initial pressure of (**2**) (kg/cm²)[b]	Product (**3**)	Conversion product *cis*-(**4**)	*trans*-(**4**)[d]
32	5·0	*threo*[c]	—	—
28	5·5	—	97[e]	3[e]
36	4·7	—	97·5[e]	2·5[e]

[a] Performed in water at 20 °C with the following concentrations: $PdCl_2$ 0·033 M, $CuCl_2$ 2·7 M, LiCl 3·3 M. [b] 500—600 ml of (**2**) (20 °C, 1 atm) was condensed into a glass autoclave containing 20 ml of a frozen (−196 °C) water solution (*cf.* a). [c] Only *threo*-(**3**) (>90%) could be detected in the microwave spectrum. [d] Also prepared independently by a known method (ref. 12). [e] Relative yield estimated from the intensities of the rotational transitions in the microwave spectrum.

The copper(II) chloride cleavage of a palladium–primary carbon bond in a closely related system, where palladium is replaced by chloride, has recently been shown[13] to take place with inversion of configuration at carbon. The conversion of (**2**) into *threo*-(**3**) therefore shows that the hydroxypalladation of ethene under Wacker conditions must be a *trans*-process.



$$\underset{(5)}{[PdCl_2(ethene)(H_2O)]} + H_2O \rightleftharpoons \underset{(6)}{[HOCH_2CH_2PdCl_2(H_2O)]^-} + H^+$$

$$\downarrow$$

$$\underset{(7)}{HOCH_2CH_2\text{–}\overset{\overset{OH_2}{|}}{Pd}\text{–}Cl} + Cl^-$$

The steric course of the hydroxypalladation step found here appears to be at variance with kinetic data.[5,6] However, this can be resolved by modifying the mechanism proposed earlier.[3–6] Thus we suggest that *exo*-attack of water on the neutral complex (**5**) takes place with reversible formation of the σ-complex (**6**), followed by a rate-determining transformation of (**6**) to (**7**). Complex (**7**) then undergoes rapid β-elimination. This mechanism is compatible with kinetic data,[5,6] isotope effects,[3a,14] and the stereochemistry (present work) of the hydroxylation step.

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