

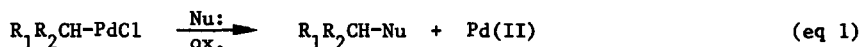
STEREOCHEMISTRY OF THE OXIDATIVE CLEAVAGE OF PALLADIUM-CARBON BONDS BY CUPRIC CHLORIDE

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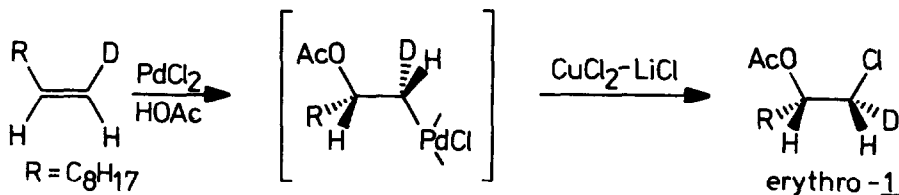
Oxidative cleavage of palladium-carbon bonds where a nucleophile replaces palladium (eq 1) occurs in catalytic systems utilizing palladium^{2,3} and has recently been used to achieve oxy-



amination⁴ and diamination^{4,5} of olefins. The stereochemistry of such cleavages is of interest and has been studied by several workers.^{2,4,6,7,8} In systems where acetate is the replacing nucleophile the cleavage occurs with inversion of configuration at carbon^{2,4} but replacement with halide as in halogen cleavage^{6,7} or cupric chloride cleavage² may occur with either retention or inversion.

In connection with other studies involving oxidative cleavage of palladium-carbon bonds^{4,5} it was of interest to determine the stereochemistry of the cupric chloride cleavage of the palladium-carbon bond. We chose to study acetoxychlorination of *Z*-1-deuterio-1-decene. The result shows that chloride replaces palladium mainly with inversion.

Z-1-Deuterio-1-decene⁹ was acetoxychlorinated at high chloride concentration using^{10a} conditions similar to those described by Henry^{2a} for 2-butenes. The isolated^{10b} 1-chloro-1-deuterio-2-decylacetate 1 was analysed by NMR¹¹ (Table I). From the NMR spectrum the ratio of *erythro*-



to *threo*-1 was determined to be 4:1. The configurational assignment was verified by independent synthesis of *threo*-1 (Table I note b, cf. ref. 11).

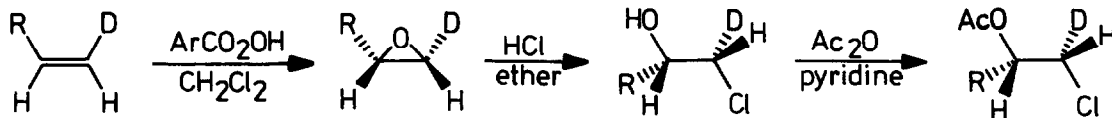
Some isomerization of the olefin during the reaction might be expected. The NMR spectrum on unreacted 1-deuterated 1-decene isolated at the end of the reaction shows that some isomerization of *Z*-1-deuterio-1-decene to *E*-1-deuterio-1-decene had taken place, the ratio being *Z*:*E* = 5:1. Thus some of the *threo* isomer formed can be accounted for by isomerization of *Z*-1-deuterio-1-decene during the reaction.

TABLE I. NMR data^a on 1 in CCl₄

| | <i>erythro</i> -1 | <i>threo</i> -1 ^b |
|---------------------------------|-------------------|------------------------------|
| δ ₁ (ppm) | 3.63 | 3.57 |
| J ₁₂ | 4.4 | 5.9 |
| rel. yield as determined by NMR | 80 | 20 |

a) Deuterium decoupled NMR spectra were run on a Hitachi-Perkin Elmer R22 (90 MHz).

b) Independently prepared from Z-1-deuterio-1-decene according to the sequence:



Acetoxypalladation of double bonds is known to be a *trans*-process.¹² Consequently, the cleavage of the palladium-carbon bond by cupric chloride at high chloride concentration takes place with inversion. This is in contrast to recent results that indicate a radical mechanism in the copper(II) cleavage of a palladium-carbon bond but is consistent with the idea^{2c} that oxidative cleavage occurs with predominant inversion in the presence of excess of free nucleophile.

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- (a) The following concentrations were used: (LiCl, PdCl₂, LiOAc, CuCl₂) = (4.0, 0.03, 0.9, 2.0) moles per litre of acetic acid. Reaction time 60 h at 25°C. (b) Isolated by preparative TLC (silica gel) using ethyl acetate: hexane = 1:20 as eluent. The ratio 1-chloroisomer: 2-chloroisomer = 6:1 (from GLC before purification).
- This has recently been used successfully for configurational assignment of similar compounds: K.B. Sharpless, A.Y. Teranishi and J.E. Bäckvall, submitted for publication.
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