Stereoselective Vinyl Transfer from Palladium to Carbon

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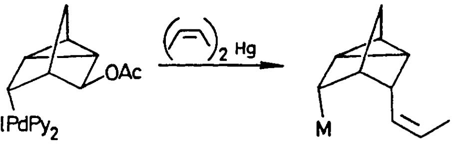
Summary Reaction of chloro(*exo*-5-acetoxy-*endo*-3-nortricyclyl)dipyridinepalladium (**1**) with bis(*cis*-propenyl)-mercury results in displacement of acetate by the *cis*-propenyl group with 98% retention of double-bond geometry.

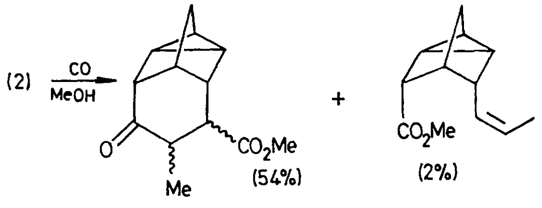
Treatment of the palladium complex (**1**)[1] with bis(*cis*-propenyl)mercury[2] in methanol, followed by borohydride reduction[3] affords *cis*-3-propenylnortricyclene (**4**) (75%, 98:2 *cis*:*trans*)†. Using acetonitrile in place of methanol causes a drastic decrease in reaction rate and considerable loss of olefin geometry (13%, 2:1 *cis*:*trans*). The intermediate organopalladium species from reaction in methanol can be isolated as the chlorine-bridged dimer (**2**) (m.p. 180° decomp.) by chromatography, and reduction of (**2**) as before affords (**4**) (95:5 *cis*:*trans*). A small amount of the mercurial (**3**) (m.p. 82°) is also isolated due to metal exchange of the organopalladium intermediates with mercuric chloride.[1]



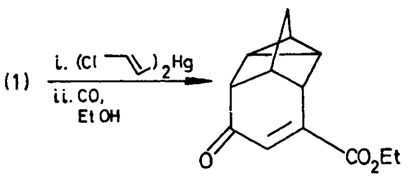
(1)

(2) M = ClPd/2
(3) M = ClHg
(4) M = H

In support of the *endo,cis* geometry of (**2**), treatment with carbon monoxide–methanol gives a keto-ester(**5**) (ν_{CO} 5·79 µm) resulting from internal acylpalladium addition to the double bond[4] followed by carbonylation. Reaction of (**1**) with bis(2-chlorovinyl)mercury followed by carbonylation in ethanol affords the corresponding unsaturated keto-ester (**6**) due to elimination of hydrogen chloride from the initially formed product.



(5)



(6)

A possible mechanism for the vinyl transfer process is based on backside displacement of acetate by olefinic carbon in an intermediate such as (**7**) in the Scheme.[5] Retention of olefin stereochemistry indicates that the hypothetical cation (**8**) is not free to rotate due to carbon 2*p*-palladium 4*d* overlap. Alternately, acetate departure prior to vinyl transfer may convert (**7**) into a π-olefin complex of norbornadiene and a propenylpalladium salt (path b) Subsequent addition of palladium and carbon to the *endo* face of one of the norbornadiene double bonds would be analogous to the mechanism proposed for the Heck reaction[6] (arylation of alkenes with "ArPdX"). Since norbornenyl- and nortricyclyl-palladium complexes are

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† N.m.r. spectra, and in some cases i.r., mass, or u.v. spectra and elemental analyses were used to confirm structures. The geometry of (**4**) was confirmed by independent synthesis from nortricyclylcarbaldehyde and ethylidenetriphenylphosphorane.

readily interconverted,[1] the two mechanisms cannot be distinguished by available data.

A small amount of hexa-2,4-diene is formed in addition to the nortricyclyl products from reaction of (**1**) and bis(*cis*-propenyl)mercury. Vinylmercurial coupling to diene is also induced by other palladium salts, and is stereoselective. Bis(acetonitrile)palladium dichloride at —40° converts the mercurial into *cis,cis*-, *cis,trans*-, and *trans,trans*- hexa-2,4-diene (78 : 17 : 5, 15—20%). This reaction is analogous to the palladium-induced conversion of diphenylmercury into biphenyl.[7]

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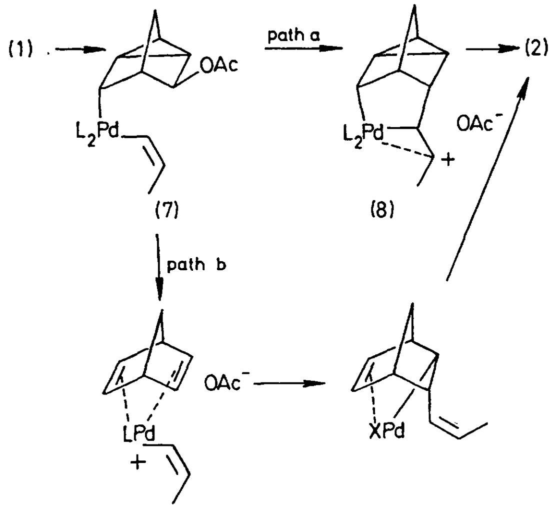
Subsequent to submission of our manuscript, similar conclusions were published regarding the reaction of diphenylmercury and norbornadienepalladium chloride.[8]



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