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Pd°-CATALYZED MERCURY EXTRUSION: STEREOSELECTIVE CONVERSION OF BIS(PROPENYL)-MERCURY INTO 2,4-HEXADIENE

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In a previous paper we noted that bis(cis-propenyl)mercury is converted into isomeric 2,4-hexadienes by palladium chloride complexes[1]. Reasonable stereoselectivity in favor of the cis,cis isomer can be achieved by careful temperature control, but the yield of dienes is poor. Since vinylic mercurials are now readily available from alkynes by a hydroboration; mercuration procedure[2], an efficient method for mercury extrusion would have synthetic potential for preparation of conjugated dienes.

We have found that tetrakis(triphenylphosphine)palladium[3] is a superior catalyst for the formation of 2,4-hexadiene. This complex induces extrusion of metallic mercury from bis(cis-propenyl)mercury[4] or bis(trans-propenyl)mercury with high stereoselectivity. Yields of 2,4-hexadienes in excess of 1000% based on the palladium complex are easily obtained at room temperature in acetonitrile solution. Methanol is also suitable, but the reaction fails in tetrahydrofuran or hydrocarbon solvents (Table 1).

A variety of palladium(II) complexes are capable of inducing diene formation (Table 2) but mercury is no longer extruded as the metal. Instead, an insoluble (uncharacterized) black precipitate appears during the reaction. The Pd(II) reactions tend to require stoichiometric amounts of palladium reagent[5], the yields are variable, and the stereoselectivity is generally low. These reactions are also more complex, and side products have been characterized in some cases. For example, norbornadienepalladium dichloride gives 3-propenylnortricyclyl-5-palladium chloride[1] (60% isolated), the product of "propenylpalladium" addition to the norbornadiene ligand, as well as hexadienes. Similarly, a "propenylpalladium" moiety apparently adds to styrene upon treatment of bis(styrene)-

palladium dichoride with bis(cis-propenyl)mercury, as evidenced by isolation of 1-phenylbutadiene (5%) and 1-benzyl-3-methyl-π-allylpalladium chloride dimer (5%). These products probably arise by the Heck reaction[6,7] as shown in Fig. 1. Although no attempt was made to detect hexadienes in this case, some further indication of the fate of bis(cis-propenyl)mercury in the presence of Pd(II) salts is provided by isolation of 1-methyl-3-ethyl-π-allylpalladium dimer (5%). A plausible source of the latter involves addition of a chloropalladium hydride species to 2,4-hexadiene.

The Heck reaction of vinylic palladium derivatives has been observed in several other systems[7] and the process appears to be fairly general. However, we observed no products resulting from addition of propenylpalladium to 1,5-cyclooctadiene using the corresponding palladium dichloride complex although propenylpalladium species must have been present as evidenced by formation of hexadienes.

Figure 1

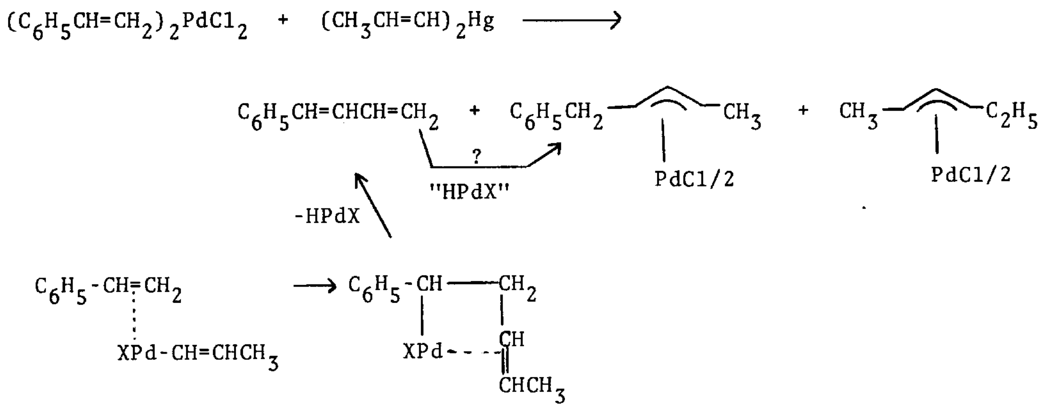

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Table 1. $[(C_6H_5)_3P]_4Pd$ Catalyst; Excess mercurial

				2,4 hexadiene		
Starting Material	Solvent	Time	Yield based on Pd(%)	cis,cis	cis,trans	trans,trans
bis(cis-propenyl)mercury	CH_3CN	12 hr	1300	86	12	2
" "	CH_3OH	7 hr	510	92	8	--
" "	" "	17 hr	920	91	9	--
" "	THF	12 hr	trace	--	--	--
bis(trans-propenyl)mercury	CH_3OH	" "	485	--	4	96

Table 2. Palladium(II) Reagents[a]

Mercurial	Pd Complex	Solvent temp	Time	Diene Yield From Pd	cis, cis	cis, trans	trans, trans
bis(cis-propenyl)-mercury	1,5-COD·$PdCl_2$	CH_3OH(20°)	12 hr	76%	35	24	41
" " "	$(CH_3CN)_2PdCl_2$[a]	CH_3CN(-44°)	3 hr	11%	78	17	5
" " "	" "	" (20°)	5 hr	14%	48	25	27
bis(trans-propenyl)-mercury	1,5-COD·$PdCl_2$	CH_3CN(-22°)	0.5 hr	92%	--	65	35
" " "	norbornadiene-$PdCl_2$	CH_3CN-CH_2Cl_2 (-78°)	12 hr	34%	--	33	67

a) Excess mercurial unless noted otherwise.

b) Equimolar amounts of palladium complex and mercurial were used.

References

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5. Occassionally, hexadiene yields exceed 100% based on the palladium(II) complex if the reactions are allowed to proceed long enough. The catalytic effect may be related to the formation of zerovalent palladium species during the reaction.
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