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PALLADIUM(0)-PROMOTED SYNTHESIS OF FUNCTIONALLY SUBSTITUTED ALLENES BY MEANS OF ORGANOZINC COMPOUNDS

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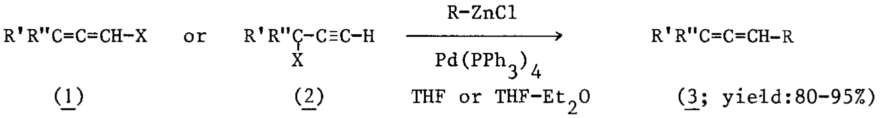
Summary: The paper describes new routes to aryl-, vinyl-, and 1-alkynylallenes and to diallenes *via* $Pd(PPh_3)_4$-promoted reaction of propargylic or allenic halides with appropriate organozinc halides. Propargylic acetates are also suited to prepare such allenes.

The ability of transition metals to promote many cross-coupling reactions has opened new perspectives in organic synthesis. In particular palladium(0) complexes have found nice applications, *e.g.* to natural product syntheses.[1]
A recent communication[2] on the $PdCl_2/Ph_3P/$*i*-Bu_2AlH-catalysed reaction of propargylic and allenic halides with Grignard reagents prompts us to report our preliminary results in this field. In the communication just mentioned it has been shown that in the presence of 10 mole% of the catalyst propargylic and allenic halides are converted into mixtures of allenes and 1-alkynes in a ratio $\geqslant$90:10 in fair to good yields (48-98%) when treated with excess of octyl- or *p*-tolylmagnesium halides.
We have observed, however, that the reaction of PhMgBr with *e.g.* PhCH=C=CH-X (X=Br or I) in the presence of a catalytic amount of $Pd(PPh_3)_4$ does not proceed cleanly because of substantial halogen-metal exchange in the allene by the Grignard compound with formation of Ph-X and PhCH=C=CH-MgX. We have now found (see eq.1) that the use of PhZnCl in the presence of 0.5-2.0 mole% of $Pd(PPh_3)_4$ gives the desired allene PhCH=C=CHPh in excellent yield (∼90%) and with high regioselectivity ($\geqslant$99%).[3] Vinylzinc chloride is likewise able of giving this reaction (regioselectivity $\geqslant$ 99%). The latter reaction seems to be an attractive new method to prepare vinylallenes. Allenes also arise in excellent yields by reaction of propargylic bromides or acetates with PhZnCl and H_2C=CH-ZnCl in the presence of 0.5-2.0 mole% of $Pd(PPh_3)_4$.
In the 1,3-substitution products thus formed acetylenic contaminants could not be detected.
A very useful extension is the excellent formation of allenynes by reaction of propargylic or allenic bromides with 1-alkynylzinc chlorides in the presence of the catalyst $Pd(PPh_3)_4$. Also propargylic acetates can be used for this reaction. The allenyne structure is found in a number of natural products.[4] In equation (1) several examples of this interesting approach to allenynes are given. As is shown in this equation, it is even possible to prepare allenediynes.



$$\underset{(1)}{R'R''C{=}C{=}CH\text{-}X} \quad \text{or} \quad \underset{(2)}{R'R''\underset{X}{C}\text{-}C{\equiv}C\text{-}H} \xrightarrow[\text{Pd(PPh}_3)_4 \;\; \text{THF or THF-Et}_2\text{O}]{\text{R-ZnCl}} \underset{(3;\ \text{yield:80-95\%})}{R'R''C{=}C{=}CH\text{-}R} \qquad (1)$$

$1 \longrightarrow 3$

X=Br: R',R"=H,H; H,Me or Me,Me; R= Ph, TMSC≡C, PhC≡C, $H_2C{=}C(Me)C{\equiv}C$, or H-C≡C-C≡C

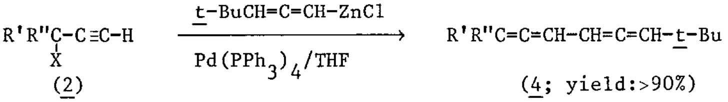
X=I : R',R"=H,Ph; R= Ph, $H_2C{=}CH$, or TMSC≡C

$2 \longrightarrow 3$

X=Br: R',R"=H,H; H,Me or Me,Me; R= Ph, $H_2C{=}CH$, TMSC≡C, PhC≡C, $H_2C{=}C(Me)C{\equiv}C$, or H-C≡C-C≡C

X=OC(O)Me: R',R"= Me,Me; R= Ph (TMS=Me_3Si)

Also a highly regioselective (≥99%) reaction is observed when propargylic bromides or acetates (2, see eq.2) are treated with *t*-BuCH=C=CH-ZnCl. Reaction of 2 with this reagent in the presence of 0.5-2.0 mole% of $Pd(PPh_3)_4$ gives conjugated diallenes 4 (eq.2) in high yields. In contrast with 2, allenic halides 1 (see eq.1) undergo substantial halogen-metal exchange by *t*-BuCH=C=CH-ZnCl. This causes the formation of three diallenes when 1 (R',R"=Me,Me; X=Br) is allowed to react with *t*-BuCH=C=CH-ZnCl (R-ZnCl) in the presence of $Pd(PPh_3)_4$ (2 mole%), viz. $(R'R''C{=}C{=}CH\text{-})_2$, R-R, and R'R"C=C=CH-R. The latter route seems therefore only suited to prepare symmetrically substituted allenes 4. For the synthesis of unsymmetrically substituted diallenes 4 the route depicted in eq.2 must be followed:



$$\underset{(2)}{R'R''\underset{X}{C}\text{-}C{\equiv}C\text{-}H} \xrightarrow[\text{Pd(PPh}_3)_4\text{/THF}]{t\text{-BuCH=C=CH-ZnCl}} \underset{(4;\ \text{yield:>90\%})}{R'R''C{=}C{=}CH\text{-}CH{=}C{=}CH\text{-}t\text{-}Bu} \qquad (2)$$

X=Br: R',R"=H,H; H,Me; or Me,Me

X=OC(O)Me: R',R"= Me,Me

The reactions described in the equations (1) and (2) most likely proceed *via* R'R"C=C=CH-Pd(II)-X, compounds which arise by oxidative addition of 1 or 2 to the catalyst. Substitution of X by R and subsequent reductive elimination then gives 3 or 4.

Currently, we actively pursue our study in this area.

References

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