Tetrahedron Letters No. 23, pp 2005 - 2008, 1977. Pergamon Press. Printed in Great Britain.

CATALYTIC CODIMERIZATION OF STYRENE AND VARIOUS ACETYLENIC COMPOUNDS TO 1,3-DIENES USING PALLADIUM HALIDE-LITHIUM HALIDE SYSTEM

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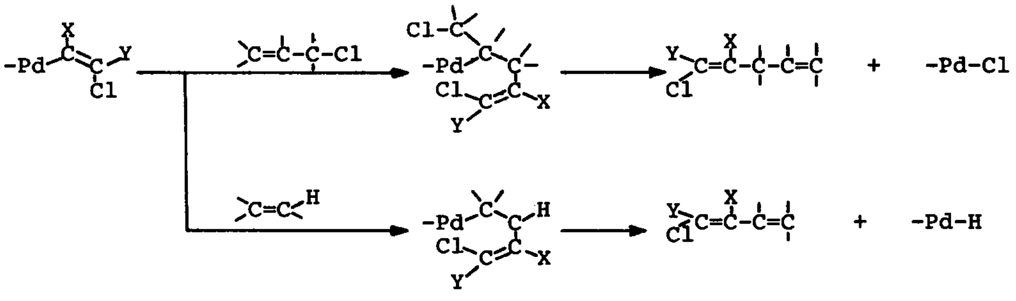
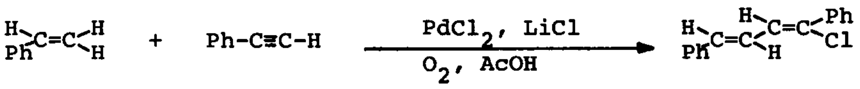
(Received in Japan 4 April 1977; received in UK for publication 28 April 1977)

Recently we reported catalytic cooligomerization of acetylenes and allyl halides with palladium complexes under mild conditions.[1] We have proposed a "Pd-halogen bond recycle mechanism" which contains the addition of Pd-halogen bond to acetylene, followed by the insertion of allyl halide and β-halogen elimination by Pd to regenerate Pd-halogen bond. It was expected that 1,3-diene could be formed if the olefin free from halogen in the place of allyl halide was used in this reaction system.



We have found expectedly that the reaction of styrene and phenylacetylene does proceed catalytically under an oxygen atmosphere.



$$\mathrm{PhCH{=}CH_2} + \mathrm{Ph{-}C{\equiv}C{-}H} \xrightarrow[\mathrm{O_2,\ AcOH}]{\mathrm{PdCl_2,\ LiCl}} \mathrm{PhCH{=}CH{-}CH{=}C(Ph)Cl}$$

To AcOH (60 ml) solution of $PdCl_2$ (103 mg, 0.6 mmol) and LiCl (1.02 g, 24 mmol) was added a mixture of styrene (25 g, 0.24 mol) and phenylacetylene (2.00 g, 20 mmol). The solution was stirred at room temperature for 24 hr under an oxygen atmosphere. Glpc analysis of the resulting solution showed that (Z,E)-1-chloro-1,4-diphenylbutadiene (1470 %, based on Pd) was formed.[2] After usual treatment, column chromatograph (alumina) gave the pure codimer (1.80 g). mp 113.5-114.5 °C.

IR(Nujol): 965 ($_{H}{>}C{=}C{<}^{H}$), 752, 690 cm^{-1} (mono sub. phenyl).

PMR(CCl_4): δ 6.70 (d, 1H, J=15 Hz, $^{Ph}_{\underline{H}}{>}C{=}C{<}^{H}$), 6.58 (d, 1H, J=10 Hz, $^{=C}_{\underline{H}}{>}C{=}C{<}^{Cl}_{Ph}$), 7.1-7.7 (m, 11H, $^{Ph}_{H}{>}C{=}C{<}^{\underline{H}}$, phenyls).

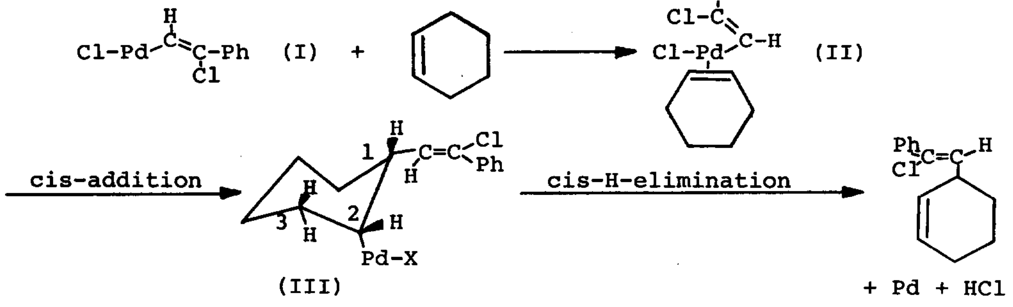
Similarly bromide homolog could be obtained by the use of $PdBr_2$ catalyst. The Z-configuration around the halogen substituted double bond was determined by the treatment of the bromide codimer with n-BuLi[3] to derive (E,E)-1,4-diphenylbutadiene. The yield of the codimer was stoichiometric to Pd under an argon atmosphere (51 %) and an additive HCl increased the yield (2220 %). The facts suggest that the function of O_2 is to regenerate Pd(II) from Pd(0).

$$Pd(0) \quad + \quad HCl \quad + \quad \frac{1}{2}O_2 \longrightarrow PdCl_2 \quad + \quad H_2O$$

$PdCl_2(PhCN)_2$-LiCl and $Pd(OAc)_2$-LiCl are not so active for the codimerization as the present catalyst.

This reaction can be applied to other acetylenic compounds (Table). In the reaction of monosubstituted acetylenic compounds, all substituents derived from the acetylenic reactant in 1,3-diene codimers are situated at the carbon bonding to halogen. The regioselectivities are higher than 95 % respectively. The reaction of styrene and diphenylacetylene using $PdCl_2(PhCN)_2$ has been reported by Mushak and Battiste.[4] However, in sharp contrast, our catalyst system gives only the codimer and not cotrimers. Further, in the reaction of other acetylenic compounds, cotrimers were not observed. Probably the difference between the formation of the codimer and cotrimer may depend on whether the Pd assists H-β-elimination or H-1,2-shift in the butenyl-palladium intermediate.[5]

On the other hand, the reaction of cyclohexene and phenylacetylene gave 1,4-diene product. The formation of the 1,4-diene can be consistently explained as follows.

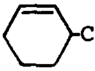


Pd-vinyl bond (I) adds to olefinic double bond in a cis manner to form intermediate (III) and then Pd must abstruct not the hydrogen at carbon (1) but the hydrogen at carbon (3) to give only the 1,4-diene product because the β-hydrogen elimination by Pd is cis-manner.[6]

The present procedure may provide a facile, useful method for the synthesis of various halogeno dienes. Recently vinyl halides are being paid attention as valuable intermediate compounds for the route to substituted olefins because the halogen can be replaced stereoselectively by alkyl and phenyl groups.[7]

Application of this codimerization to other olefins is in progress.

Table Codimerization of Styrene and Acetylenes[a]

Acetylene	Codimer product[b]	Yield %[c]
Ph-C≡CH	Ph-CH=CH-CH=CCl-Ph	1430 (43)
Ph-C≡CH	Ph-CH=CH-CH=CCl-Ph	51 (2)[d]
Ph-C≡CH	Ph-CH=CH-CH=CCl-Ph	2220 (67)[e]
Ph-C≡CH	Ph-CH=CH-CH=CBr-Ph	2440 (73)[f]
Pr^{n}-C≡CH	Ph-CH=CH-CH=CCl-Pr^{n}	2000 (60)
Bu^{n}-C≡CH	Ph-CH=CH-CH=CCl-Bu^{n}	1610 (48)
Am^{n}-C≡CH	Ph-CH=CH-CH=CCl-Am^{n}	1000 (30)
Et-C≡C-Et	Ph-CH=CH-CEt=CCl-Et	2190 (66)
Ph-C≡C-Ph	Ph-CH=CH-CPh=CCl-Ph	874 (26)[g]
Ph-C≡CH	CH=CCl-Ph	280 (8)[h]

a) Reaction conditions; $PdCl_2$ 0.6 mmol, LiCl 24 mmol, AcOH 60 ml, olefin 240 mmol, acetylene 20 mmol, O_2 bubbling, room temperature, 24 hr.

b) These new compounds give satisfactory elemental analysis and spectroscopic data.

c) Yields were determined by glpc analysis and based on Pd used (based on acetylene used).

d) Under an argon atmosphere. e) Additive HCl. f) $PdBr_2$ and LiBr used.

g) Reaction time; 48 hr. h) Cyclohexene used.

References and Notes

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2. Small amounts of 1,4-diphenylbutadiene and 1,4-diphenyl-1-butene (>100 %, based on Pd) were also formed.
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