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CODIMERIZATION OF ACETYLENES AND ALLYL HALIDES BY Pd-BENZONITRILE COMPLEXES

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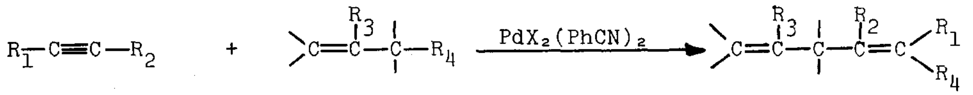
The oligomerization of olefins or acetylenes using transition metal compounds has been thoroughly examined. Little is known, however, concerning the cooligomerization of acetylenes and monoolefins.[1,2)] In the case of palladium catalysts, only one example of cooligomerization has been reported. Mushak and Battiste observed that diphenylacetylene reacted with terminal olefins such as ethylene, propylene, and butene to give the conjugated dienes of 2:1 adducts.[2)]

In this communication, we wish to report the catalytic codimerization of acetylenes and allyl halides in the presence of palladium-benzonitrile complexes to 1,4-pentadiene derivatives under mild conditions. This reaction seems to be useful in one-step procedure for the synthesis of variously substituted 1,4-pentadienes.[3)]



(1a) $R_1=Ph,R_2=H$
(1b) $R_1=Ph,R_2=Ph$
(1c) $R_1=H,R_2=H$

(2a) $R_3=H,R_4=Cl$
(2b) $R_3=Cl,R_4=Cl$
(2c) $R_3=H,R_4=Br$

(3a) $R_1=Ph,R_2=H,R_3=H,R_4=Cl$
(3b) $R_1=Ph,R_2=Ph,R_3=H,R_4=Cl$
(3c) $R_1=H,R_2=H,R_3=H,R_4=Cl$
(3d) $R_1=Ph,R_2=H,R_3=Cl,R_4=Cl$
(3e) $R_1=Ph,R_2=H,R_3=H,R_4=Br$

In general method of codimerization, acetylene was added to the stirred nitromethane solution of allyl halide and palladium-benzonitrile complex at room temperature. The reaction was exothermic and complete in ca. 2 hr. The products have been isolated by preparative gas chromatography and identified on the basis of spectroscopic and elemental analysis (Table 1).

In the reaction of phenylacetylene (1a) with allyl chloride (2a) in the presence of $PdCl_2(PhCN)_2$,[4)] the gas chromatogram of the reaction mixture showed only one major compound which was identified 1-phenyl-1-chloro-1,4-pentadiene (3a). The structure is the 1:1 1a/2a adduct. The reaction is catalytic in palladium and 1:1 addition reaction would probably be first example in the co-oligomerization of acetylenes and monoolefins using transition metal catalysts so far as we know.

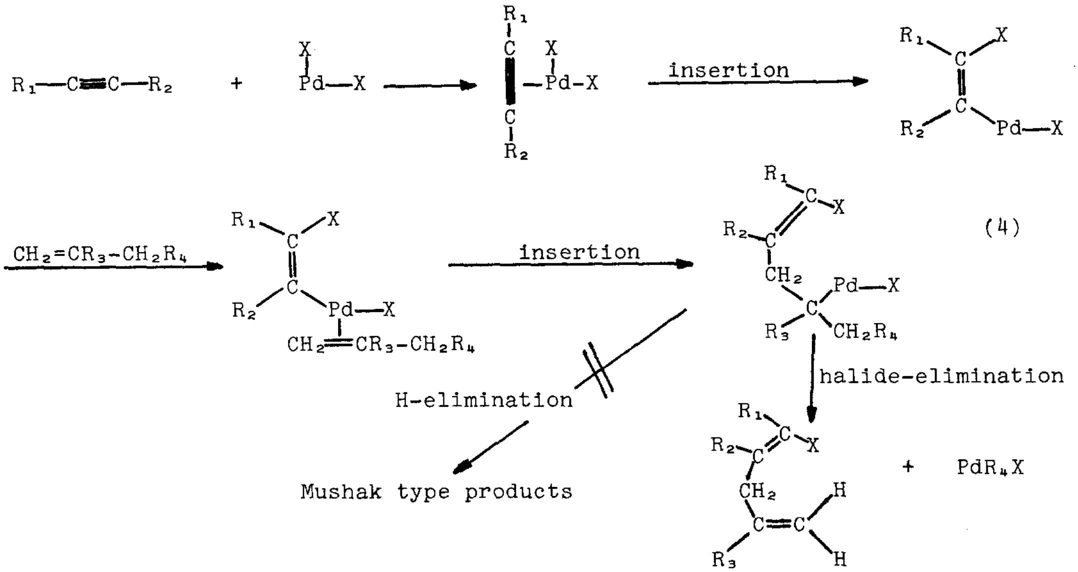
The scope of this codimerization with other acetylenes has been investigated. Diphenylacetylene (1b) and acetylene (1c) reacted with 2a in the presence of $PdCl_2(PhCN)_2$ to give good yields of codimer, 3b[5)] and 3c (a mixture of 3c-1 and 3c-2) respectively which were structually analogous to 3a. In the case of acetylene, two isomers of 3c-1 and 3c-2 corresponding to cis-trans isomerism about the chloride substituted double bond could be isolated. Ratios of 3c-2 (trans)/3c-1 (cis) increased with an increase of palladium content.[6)] 2,3-Dichloropropylene also reacted with 1a to give 3d as a main product.

In order to study the halide effects, the reaction of allyl bromide (2c) with 1a using $PdBr_2(PhCN)_2$ was carried out, producing a codimer containing bromide (3e) and in the presence of $PdCl_2(PhCN)_2$, the reaction of 1a and 2c gave a mixture of 3a (86 %) and 3e (400 %).[8)]

A possible mechanism for this codimerization has been given in Scheme 1 and involves the insertion of an acetylene into a Pd-halogen bond as the first step, followed by the insertion of a coordinated olefin into a Pd-vinyl bond and a halide elimination. The mechanism via an intermediate 4 is analogous to that of Mushak reaction[9)] but in this reaction, palladium in 4 must abstract not hydrogen but halogen atom at β-position because palladium is more reactive for the halide elimination than for the hydride.[10)] A similar complex as an intermediate 4 has been isolated in the reaction of t-buthyl phenyl acetylene with $[(C_2H_4)PdCl_2]_2$ by Hosokawa et al.[11)]

Detailed study of mechanism and synthetic utilities of this reaction are now under investigation.

Scheme 1



Reference

1-a) T.L.Cairns, V.A.Engelhardt, H.L.Jackson, G.H.Kolb, and J.C.Sauer, J. Amer. Chem. Soc., 74, 5636 (1952).

b) A.J.Chalk, J. Amer. Chem. Soc., 94, 5928 (1972).

c) D.M.Singleton, Tetrahedron Letters, 1245 (1973).

d) C.W.Bird, "Transition Metal Intermediates in Organic Synthesis", Logos, London, England (1967), p 30.

2) P.Mushak and M.A.Battiste, Chem. Commun., 1146 (1969).

3) See, for example, C.A.Buehler and D.E.Peason, Ed., "Survey of Organic Syntheses", Wiley-Interscience, New York•London•Sydney•Toronto (1970), p 84-87.

4) A crystalline complex was obtained, the structure of which was not yet investigated.

5) 1:2 adduct of 1b and 2a could not be isolated.

6) In the stoichiometric codimerization of 1c and styrene to trans, cis-1-phenyl-4-chloro-1,3-butadiene and trans,trans-1-phenyl-4-chloro-1,3-butadiene, the similar phenomena could also be observed.[7]

7) Unpublished data, K.Kaneda. The results will be published elsewhere.

8) Based on palladium used.

9) P.M.Maitlis, "The Organic Chemistry of Palladium", Academic Press, New York and London (1971), vol 2, p 38.

10) R.F.Heck, J. Organometal Chem., 33, 399 (1971).

11) T.Hosokawa, I.Moritani, and S.Nishioka, Tetrahedron Letters, 3833 (1969).

Table 1. Yields and identification of the Products.
Reaction Time ; 2 hr
Temperature ; Room Temperature

Product		3a	3b	3c-1	3c-2	3d	3e
Yields$^{a)}$		950(95)$^{b)}$ 600(60)$^{d)}$	950(95)$^{b)}$	1670$^{c)}$	660$^{c)}$	240$^{d,e)}$ (48)	870$^{d,e)}$ (87)
NMR$^{f)}$ (ppm, CCl_4)	Ha,Hb	4.83-5.16 (m)	4.92-5.20 (m)	4.80-5.24 (m)	4.78-5.22 (m)	5.21 (s)	4.96-5.25 (m)
	Hc	5.54-6.00 (m)	5.60-6.02 (m)	5.40-6.13 (m)	5.40-6.14 (m)	—	5.64-6.03 (m)
	Hd	3.06 (t)	3.48 (d)	2.78-3.13 (m)	2.62-3.00 (m)	3.43 (d)	3.10(t)
	He	5.94 (t)	—	5.40-6.13 (m)	5.40-6.14 (m)	6.16 (t)	6.15 (t)
	Hf	—	—			—	—
	Ph.	7.02-7.44 (m)	6.85-7.19 (m)	—	—	7.20-7.26 (m)	7.17-7.55 (m)
IR (cm^{-1}, Neat)	$\delta Ch_2{=}Ch-$	918 (s) 995 (s)	918 (s) 997 (s)	913 (s) 985 (s)	915 (s) 985 (s)	—	915 (s) 995 (s)
	other	—	—	690 (s) $\delta(\overset{H}{>}C{=}C\overset{H}{<})$	938 (s) $\delta(\overset{H}{>}C{=}C\underset{H}{<})$	885 (s) $\delta(CH_2{=}C<)$	—

a) Measured by glpc using internal standard.

%, Based on palladium catalysts used (%, based on acetylenes used).

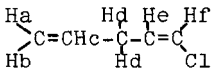
b) $PdCl_2(PhCN)_2$ 1 mmole, allyl halides 30 ml and acetylenes 10 mmole.

c) $PdCl_2(PhCN)_2$ 0.5 mmole and allyl halide 30 ml in acetylene atmosphere.

d) $PdCl_2(PhCN)_2$ 1 mmole, allyl halides 50 mmole and phenylacetylene 10 mmole (or 5 mmole for 3d) in nitromethane 30 ml solution.

e) Contained small isomers. (Not less than 10 % of main products. We could not determine their structures. But probably they have trans structures analogous to 3c-2.)

f) Ha-Hf are referred to the following nomenclature.



$$\begin{matrix} Ha \\ Hb \end{matrix}\!>C{=}CHc-\overset{Hd}{\underset{Hd}{C}}-\overset{He}{C}{=}C\begin{matrix} Hf \\ Cl \end{matrix}$$

Satisfactory mass spectra and elemental analysis data were obtained for 3a-3e.