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# SELECTIVE LINEAR COTRIMERIZATION OF ACETYLENE AND ALLYL HALIDES CATALYZED BY PALLADIUM ACETATE AND LITHIUM HALIDES

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Recently we reported the codimerization of acetylene and allyl halides with palladium benzonitrile complex to give 1,4-pentadiene derivatives.1) In the relation to this reaction, we have found that the palladium acetate - lithium halides system catalyzes the cotrimerization of acetylene and allyl halides to give the 2:1 linear cotrimers of acetylene and allyl halides selectively. On the 2:1 cotrimerization of acetylene and monoolefin, little is known concerning the selective linear cotrimerization by transition metals although cyclotrimerizations catalyzed by Ni and Rh complexes have been already reported.2) Now we wished to communicate the selective cotrimerization of acetylene and allyl halides using palladium acetate - lithium halides catalysts under mild conditions.

$$HC{\equiv}CH \;+\; CH_2{=}CHCH_2X \;\xrightarrow[AcOH]{Pd(OAc)_2\ -\ LiX}\; CH_2{=}CH{-}CH_2{-}CH{=}CH{-}CH{=}CHX$$

( X = halogen ) (A)

A typical reaction procedure is given below. To a solution of 2.25 g (10 mmol) of $Pd(OAc)_2$ and 2.12 g(50 mmol) of LiCl in 90 ml of AcOH was added 23.0 g(300 mmol) of allyl chloride. The reaction mixture was stirred under a constant bubbling of acetylene at room temperature for 2 hr. Gas chromatogram of the resulting mixture showed 1-chloro-1,3,6-heptatriene (A)(500% based on Pd) and 1-chloro-1,4-pentadiene(19%).[1] After usual treatment, distillation gave pure cotrimer[3] (A, 3.51 g); bp. 34 -35°C/ 7 mmHg; UV (MeOH): $\lambda_{max}$ 237 nm ($\varepsilon_{max}$ 26,700); IR (neat): 1640, 1585 (-C=C-C=C-), 990, 913 ($CH_2$=CH-), 973 (trans -CH=CH-), and 713 $cm^{-1}$ (cis -CH=CH-); PMR ($CCl_4$): 2.88 (t, 2H, $-C\underline{H}_2-$), 4.8 -5.2 (m, 2H, $\underline{H}_2C=$), 5.5 -6.1 (m, 3H, $H_2C=C\underline{H}-$, $-C\underline{H}=C\underline{H}Cl$), and 6.1 -6.6 ppm (m, 2H, $-C\underline{H}=C\underline{H}-CH=CHCl$).

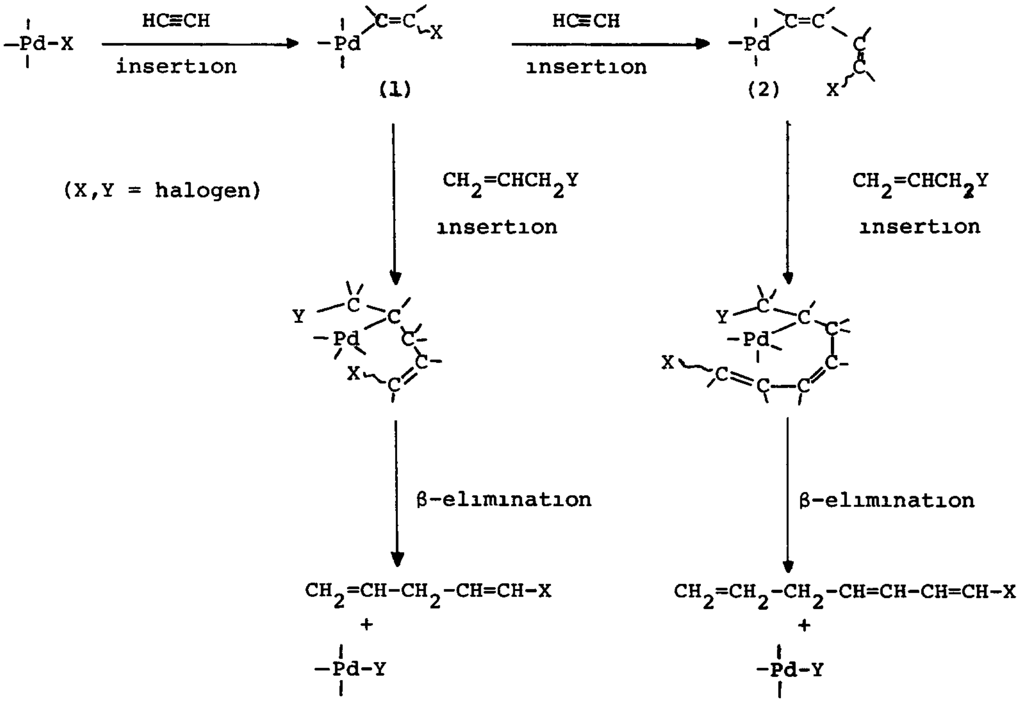
The structure assignment for A was based on the spectral properties cited and on the following chemical behaviors. Catalytic hydrogenations of A over the polymer-rhodium complex[4] or $Ni_2B$ afforded 1-chloroheptane and 1-chloro-1,3-heptadiene respectively. UV of the latter (MeOH): $\lambda_{max}$ 237 nm; IR (neat): 970 (trans -CH=CH-) and 712 $cm^{-1}$ (cis -CH=CH-); PMR ($CCl_4$): 0.94 (t, 3H, $-C\underline{H}_3$), 1.2 -1.7 (m, 2H, $-C\underline{H}_2-CH_3$), 2.0 -2.3 (m, 2H, $-CH=CH-C\underline{H}_2-$), 5.3 -6.0 (m, 2H, $-C\underline{H}=C\underline{H}Cl$), and 6.0 -6.8 ppm (m, 2H, $-C\underline{H}=C\underline{H}-CH_2-$). Treatment of A with $NaNH_2$ gave 1,3-heptadien-5-yne as main product.[5] IR ($CCl_4$): 2220 (-C≡C-), 995, 905 ($CH_2$=CH-), and 940 $cm^{-1}$ (trans -CH=CH-);[6] PMR ($CCl_4$): 1.94 (d, 3H, $-C\equiv C-C\underline{H}_3$), 5.0 -5.3 (m, 2H, $\underline{H}_2C=$), 5.52 (d, 1H, $-CH=C\underline{H}-C\equiv C-$), and 6,1 -6.6 ppm (m, 2H, $H_2C=C\underline{H}-C\underline{H}=CH-$),

Similarly bromo and iodo analogues could be obtained in 490% and 260%[7] yields respectively using the corresponding allyl halide and lithium halide. Palladium catalysts such as $(Ph_4As)_2[Pd_2Cl_6]$, $(Et_4N)_2[Pd_2Cl_6]$, $PdX_2$-LiX and $PdX_2(PhCN)_2$-LiX (X-halogen) were found to be active for this cotrimerization, but had low cotrimer selectivities to codimer. Ni, Co, Fe and Rh transition metal halides had no catalytic function.

In order to investigate the product path of this cotrimer, the reaction of dideuterated acetylene with allyl chloride was carried out under same conditions. The PMR spectrum of the obtained triene [ PMR ($CCl_4$): 2.89 (d, 2H, $-C\underline{H}_2-$), 4.8 -5.2 (m, 2H, $\underline{H}_2C=$), and 5.5 -6.1 ppm (m, 1H, $H_2C=C\underline{H}-$) ] showed only the characteristic pattern of allyl group ($H_2C=CH-CH_2-$), and no butadienyl protons. This result shows that the cotrimer is composed of two acetylene and one allyl chloride molecules. Furthermore we confirmed that the cotrimer did not result from the codimer product reacting with allyl halide.

The reaction would be elucidated by the following scheme. Two molecules of acetylene stepwise insert into a Pd-halogen bond to form σ-butadienyl-Pd-complex (2), followed by insertion of allyl halide into a Pd-butadienyl σ-bond to give the cotrimer product with an accompanying β-halogen elimination. The similar σ-butadienyl complex as an intermediate (2) recently was isolated by P. M. Maitlis et el.[8] The codimer product would be formed by the reaction of the intermediate species (1) and allyl halide.[1] The above scheme is compatible with the result of dideuterated acetylene.

Scheme



The catalytic cotrimerization reaction reported here is very useful for the preparation of 1-halogenoheptatriene derivatives and the details will be reported in full.

## References and Notes

1) K. Kaneda, F. Kawamoto, Y. Fujuwara, T. Imanaka, and S. Teranishi, Tetrahedro Letters, 1067 (1974).

2) (a) V.W. Reppe and W. J. Scweckendiek, Annalen., 560, 104 (1948).
   (b) A. J. Chalk, J. Amer. Chem. Soc., 94, 5928 (1972).
   (c) D. M. Singleton, Tetrahedron Letters, 1245 (1973).

3) Elemental analysis and molecular weight (mass spectrum) were consistent with the structure shown.

4) The polymer-rhodium complex was newly prepared by the reaction of polymeric diphenyl benzil phosphine in ethanol with rhodium trichloride: M. Terasawa, K. Kaneda, T. Imanaka, S. Teranisni, The 30th Spring Annual Meeting of the Chemical Society of Japan at Osaka, April (1974)/ Entry No. 1C26.

5) Besides this product, a small amount of 1,2,4,6-heptatetraene was detected.

6) D. A. Ben-Efraim and F. Sondheimer, Tetrahedron, 25, 2842 (1969).

7) Reaction time: 24 hr. Iodide reacted more slowly.

8) B. E. Mann, P. M. Bailey, and P. M. Maitlis, J. Amer. Chem. Soc., 97, 1275 (1975).