Pergamon

Tetrahedron Letters, Vol. 35, No. 24, pp. 4137-4140, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $7.00+0.00

0040-4039(94)E0729-H

Polymerization of Substituted Acetylenes Catalyzed by the Anionic Tungsten μ-Hydride Complexes

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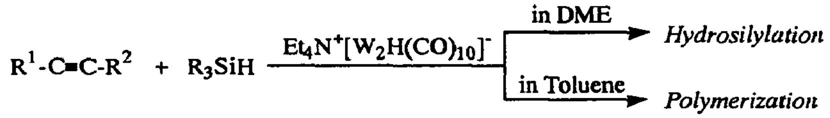
Abstracts: *Polymerization of substituted acetylenes in the presence of hydrosilanes was achieved catalyzed by μ-hydridedecacarbonyldiwolframate (0). This reaction is efficient not only for polymerization of monosubstituted acetylenes but also for that of relatively hindered disubstituted acetylenes to give polymer with high molecular weight.*

Polymerization of acetylenes has been the subject of extensive investigation, from a view point of importance of polyacetylenes as the functional materials for permeability of gases.[1] In recent years, several transition metals have been developed for the catalysts to polymerize acetylenes under mild conditions.[2] However, the effectiveness of those transition metal catalysts was strongly depended on the structure of acetylenes, namely the kind and number of substituent groups on carbon-carbon triple bond. So the research of effective catalyst for polymerization of a variety of acetylenes with high yields and molecular weights has been of interest for many chemists in this field. Independently, we have studied hydrosilylation reactions of dienes and alkynes using Group 6 μ-hydride complex catalysts[3]; $Et_4N[M_2H(CO)_{10}]$, M=Cr, Mo, W, where the hydrosilylation reactions were easily took place in DME, however, we have found the reactions in toluene were resulted in the production of polyacetylenes with trace amount of hydrosilylated products under the same reaction conditions. We now report on the reaction of substituted acetylenes catalyzed by μ-hydridedecacarbonyldiwolframate (0) in the presence of silanes to provide polyacetylenes with high degrees of polymerization from both mono- and di-substituted alkynes.



The tungsten μ-hydride catalysts used for the present reactions were prepared as follows: hexacarbonyltungsten was reduced with 2.3 equiv. of sodium borohydride in absolute tetrahydrofuran (reflux, 3-6 h) to the sodium μ-hydridedecacarbonyldiwolframate (**A**). This sodium salt was not so stable under ordinary conditions, so converted into the tetraethylammonium (**B**), tetrabutylphosphonium (**C**), tetraphenylphosphonium (**D**), and bis(triphenylphosphoranylidene)ammonium (**E**) salt by the treatment in ethanol at 0 °C overnight with Et_4NBr, *n*-Bu_4PBr, Ph_4PBr, and $(Ph_3P=)_2NCl$, respectively.

$$\mathrm{W(CO)_6} \xrightarrow[\text{reflux}]{\substack{\mathrm{NaBH_4} \\ \text{in THF}}} \underset{\mathbf{A}}{\mathrm{Na[W_2H(CO)_{10}]}} \xrightarrow{\mathrm{QX}} \mathrm{Q[W_2H(CO)_{10}]} \quad \begin{array}{l} \mathbf{B}\text{: } \mathrm{Q{=}Et_4N,\ X{=}Br} \\ \text{C: } \mathrm{Q{=}}n\mathrm{\text{-}Bu_4P,\ X{=}Br} \\ \text{D: } \mathrm{Q{=}Ph_4P,\ X{=}Br} \\ \text{E: } \mathrm{Q{=}(Ph_3P)_2N,\ X{=}Cl} \end{array}$$

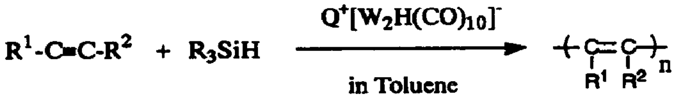
Typical procedure is as follows: 1-Phenyl-1-propyne (1.0 mmol) was heated at 100 °C for 20 h with triethylsilane (1.0 mmol) and tungsten catalyst **B** (0.01 mmol) in absolute toluene (1.0 ml) under Ar to be converted into a gelatinous material with trace amount of hydrosilylated products. To the aim for purification of the obtained polymer, the gel was dissolved in toluene (10 ml) and added dropwise to rapidly stirred methanol (100 ml) with removing of insoluble materials by filtration to give a poly(1-phenyl-1-propyne) (22.7 %) as a colorless substance. The obtained polymers were identified by IR and ^{1}H NMR spectra, and their molecular weights were determined by gel permeation chromatography (GPC).[4] The polymerization at lower temperature (80 °C) afforded the lower yield of products but their molecular weights were found to be rather high, and the reaction under high concentration conditions improved the yields as well as the molecular weight of obtained polymers at 80 °C. Although there is no silyl moiety in the obtained polymers, an equimolar amount of triethylsilane was required for the present polymerization in high yields. Thus, the reaction with 0.5 equiv. of triethylsilane resulted in a poor yield, and methanol-insoluble material was produced no longer with 0.1 equiv. of the silane. It is noteworthy that the selection of substituents on silicon atom of used silanes is very important factor in this polymerization. No polymer was obtained on using Et_4Si, $MeCl_2SiH$, Me_2ClSiH, and Ph_2SiH_2. Bulky trialkylsilanes are preferable for the production of polymers with high yields as well as with high molecular weight. Highest molecular weight ($MN = 1.58 \times 10^6$) of polymer was obtained in 69.6 % yield when tributylsilane was used under the same reaction conditions. Triphenylsilane was found to be also effective as an additive, giving the polymer in best yield (80.2 %). The other tungsten μ-hydride complexes bearing various counter cation are of effectiveness. All of sodium (**A**), tetrabutyl (**C**), tetraphenyl (**D**), and bis(triphenylphosphoranylidene)ammonium (**E**) complexes are more active than **B** to give polymers in better yields. It has been reported that "*classical*" W catalysts are ineffectual catalyst for the polymerization of disubstituted acetylene such as 1-phenyl-1-propyne.[5] In sharp contrast with the reports,[5b,d] the present tungsten μ-hydride complexes can polymerize 1-phenyl-1-propyne with high degrees of polymerization, which was comparable to that of poly(1-phenyl-1-propyne) catalyzed by Ta and Nb catalysts.[6]

New catalyst system, combination of tungsten μ-hydride complexes and silanes, is effective for the polymerization of not only disubstituted acetylenes but also terminal acetylenes. For example, poly(phenylacetylene)s were obtained as yellow to orange materials in good yields under the same conditions as above. Polymerization of more sterically hindered acetylene, 3,3-dimethyl-1-butyne[7] and trimethylsilylacetylene[8,9], furnished the polymers in moderate yields.

It's already known that "classical" W catalyzed reactions of acetylenes bearing normal alkyl group result in the formation of oligomers of acetylenes, sometimes together with cyclic trimers,[10] however, this catalyst system gave the polymer in moderate yields.

In conclusion, we have shown that the polymerization of substituted acetylenes by the reaction with hydrosilanes and tungsten μ-hydride catalysts to provide polyacetylenes with good yields and molecular weights. This reaction is efficient not only for polymerization of monosubstituted acetylenes but also for that of relatively hindered disubstituted acetylene. Application of this polymerization reaction and clarification of the role of hydrosilanes are now investigated.

Table Polymerization of Substituted Acetylenes Catalyzed by Tungsten μ-hydride Complexes



$$R^1\text{-}C{\equiv}C\text{-}R^2 + R_3SiH \xrightarrow[\text{in Toluene}]{Q^+[W_2H(CO)_{10}]^-} \left(\underset{R^1}{C}{=}\underset{R^2}{C}\right)_n$$

Tungsten catalyst;
A: Q=Na
B: Q=Et_4N
C: Q=n-Bu_4P;
D: Q=Ph_4P
E: Q=$(Ph_3P)_2N$

Entry	Acetylene[a]	Cat.	Silane equiv.	Toluene ml	Temp. °C	Yield[b] %	MN/10^5	MW/10^5	MW/MN
1	Ph-C≡C-Me	B	Et_3SiH (1.0)	1.0	80	4.3	6.92	12.7	1.84
2	Ph-C≡C-Me	B	Et_3SiH (1.0)	0.5	80	23.3	5.41	10.2	1.88
3	Ph-C≡C-Me	B	Et_3SiH (1.0)	0.2	80	39.9	9.10	16.0	1.76
4	Ph-C≡C-Me	B	Et_3SiH (1.0)	1.0	100	22.7	5.58	11.7	2.11
5	Ph-C≡C-Me	B	Et_3SiH (0.5)	1.0	100	8.9	4.01	9.49	2.37
6	Ph-C≡C-Me	B	Et_3SiH (0.1)	1.0	100	—	—	—	—
7	Ph-C≡C-Me	B	Et_3SiH (1.0)	1.0	120	21.0	2.14	4.70	2.19
8	Ph-C≡C-Me	B	Et_2SiH_2 (1.0)	1.0	100	7.7	2.39	5.78	3.17
9	Ph-C≡C-Me	B	t-$BuMe_2SiH$ (1.0)	1.0	100	50.3	13.1	20.1	1.60
10	Ph-C≡C-Me	B	n-Bu_3SiH (1.0)	1.0	100	69.6	15.8	23.6	1.50
11	Ph-C≡C-Me	B	Ph_3SiH (1.0)	1.0	100	80.2	5.32	9.80	1.84
12	Ph-C≡C-Me	A	Et_3SiH (1.0)	1.0	100	33.4	3.16	6.02	1.90
13	Ph-C≡C-Me	C	Et_3SiH (1.0)	1.0	100	45.6	2.82	6.18	2.19
14	Ph-C≡C-Me	D	Et_3SiH (1.0)	1.0	100	50.2	1.30	3.75	2.88
15	Ph-C≡C-Me	E	Et_3SiH (1.0)	1.0	100	46.1	2.50	7.08	2.83
16	Ph-C≡C-H	B	Et_3SiH (1.0)	1.0	100	66.1	0.168	0.301	1.80
17	t-Bu-C≡C-H	B	Et_3SiH (1.0)	1.0	100	30.7	1.15	1.49	1.29
18	1-Octyne	B	Et_3SiH (1.0)	1.0	80	31.4[c]	0.142	0.231	1.63
19	Me_3Si-C≡C-H	B	Et_3SiH (1.0)	1.0	100	54.6[d]	—	—	—

a) In all cases, 1.0 mmol of acetylenes and 0.01 mmol of catalysts were used. b) Yields of methanol-insoluble materials. c) Methanol-insoluble oily material was obtained. d) Toluene-insoluble polymer.

Acknowledgment

The authors would like to thank Dr. Yu Nagase (SCRC) for his useful advice and comments.

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(*Received in Japan* 19 *February* 1994)