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Preliminary communication

THE STEREOCHEMISTRY OF THE ADDITION OF HYDROSILANES TO ALKYL ACETYLENES CATALYZED BY TRIS(TRIPHENYLPHOSPHINE)-CHLORORHODIUM

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Summary

Tris(triphenylphosphine)chlororhodium was found to be an effective catalyst for the hydrosilylation of acetylenes. An unusual stereochemistry of addition was observed in the reaction of alkylacetylenes with hydrosilanes; the rhodium-catalyzed reaction involves a stereoselective *trans* addition.

The hydrosilylation of olefins and acetylenes has been studied extensively over a period of years [1], and many effective catalytic systems were found, e.g., UV light, benzoyl peroxide, Pt—C, H_2PtCl_6, $(Ph_3P)_3RhCl$. The stereochemistry of the addition of trichlorosilane to acetylenes has been thoroughly investigated by Benkeser and co-workers [2,3] and was shown to proceed through *cis* addition to give *trans* products in the presence of platinized charcoal and chloroplatinic acid [3], while *trans* addition was the predominant process in the case of free radical catalysts [3]. Although the hydrosilylation of olefins catalyzed by tris(triphenylphosphine)chlororhodium has been studied recently by several workers [4], very little attention has been given to similar reactions of acetylenes*. We describe in this communication our findings concerning the rhodium(I) complex-catalyzed hydrosilylation of acetylenes, with particular emphasis on the stereochemical course of the reaction.

The rhodium(I) complex readily catalyzed the addition of organohydrosilanes to terminal acetylenes to give the corresponding 1-organosilylalkenes under mild conditions in high yields. Results are summarized in Table 1.

In a typical procedure, tris(triphenylphosphine)chlororhodium (0.05 mol%

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* A patent claims the hydrosilylation of acetylenes in the presence of the rhodium(I) complex, but no examples were described. See U.S. Pat., 3,546,266 (1970).

relative to the hydrosilane used) was added to a 1/1 mixture of dimethylethylsilane and 1-hexyne and the reaction mixture was kept at 40° for 2 h. Distillation under reduced pressure gave a colorless liquid, dimethylethyl-1-hexenylsilane, boiling at 80°/23 mmHg, in 95 % yield.

TABLE 1

REACTION OF HYDROSILANES WITH 1-ALKYNES CATALYZED BY TRIS(TRIPHENYLPHOSPHINE)CHLORORHODIUM [a]

Alkyne	Hydrosilane	Yield [b] (%)	Product ratio [c] *cis*/*trans*
1-Pentyne	$EtMe_2SiH$	96	81/19
	$PhMe_2SiH$	94	69/31
	Et_3SiH	92	69/31
1-Hexyne	$EtMe_2SiH$	95	81/19
	$PhMe_2SiH$	98	72/28
	Et_3SiH	95	65/35
1-Heptyne	$EtMe_2SiH$	96	80/20
1-Octyne	$EtMe_2SiH$	97	80/20

[a] The NMR, IR and mass spectra, and elemental analyses of all vinyl silanes were consistent with the assigned structures.

[b] Yields were determinedby GLPC analyses.

[c] Product ratios were determined on the basis of NMR spectra.

As is seen from Table 1, the hydrosilylation of terminal acetylenes tends to proceed through *trans* addition, resulting in *cis* adducts. This trend is surprising since it is generally accepted that a transition metal or metal complex catalyzed hydrosilylation proceeds through stereospecific *cis* addition [1—3]. Further, a control experiment was performed in order to test the stability of the *cis* isomers, in which a mixture of 81 % *cis*- and 19 % *trans*-1-pentenylethyldimethylsilane was heated at 50° for 24 h in the presence of the rhodium(I) complex. Some *cis*—*trans* isomerization was indeed observed and a mixture of 75 % *cis* and 25 % *trans* isomer resulted. Thus, the isomerization of the *cis* isomer to the *trans* isomer may proceed to some extent during the hydrosilylation that had been performed at 40—50° for 1—2 h. However, another control experiment showed that isomerization of the *trans*-silyl olefins to the respective *cis* isomers does not occur under the conditions employed.

We have carried out the reaction of triethylsilane with these acetylenes in the presence of chloroplatinic acid for comparison purposes, and have found that the reaction involves a stereoselective (100 %) *cis* addition, in sharp contrast to the results obtained in hydrosilylations using the rhodium(I) complex.

As suggested by Benkeser and co-workers [3], the *cis* additions in the case of platinum—charcoal of chloroplatinic acid catalyst could be explained in a manner similar to the *cis* addition of hydrogen during catalytic hydrogenations. The stereoselectivities realized in this work resemble those obtained in the case of the peroxide-catalyzed reaction of trichlorosilane with acetylenes [3]. Thus, a possible mechanism which serves to explain the selectivities in our system might involve intervention of radical-like species (or transition state) during the reactions.

References

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