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Polymerization of Phenylacetylene by Titanocene Dichloride

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Summary

The polymerization of phenylacetylene was investigated using $Cp_2TiCl_2/C_2H_5AlCl_2$ ($Cp = \pi$-cyclopentadienyl) as the homogeneous catalyst. The mechanism of addition of phenylacetylene is by successive 2+2 cycloadditions, as evidenced by the isolation of a ladder compound composed of fused cyclobutane rings. The ladder compound, which is an intermediate of the reaction, is converted catalytically to the final polyconjugated polymer.

Introduction

In previous studies on the mechanism of catalyzed addition reactions of alkynes, we found that group VIB transition metal complexes promoted 2+2 cycloadditions producing first cyclobutadienes, then Dewar benzenes, etc., finally leading to a ladder compound composed of fused cyclobutane rings. The ladder compound, an intermediate in the reactions, is converted catalytically to the final polyacetylene polymer. Catalysts that promote this type of mechanism are $ArM(CO)_3$ (Ar = arene; M = Cr, Mo, W) (WOON and FARONA 1974), WCl_6 (NAVARRO and FARONA 1976), and polystyrene-supported molybdenum (VATANATHAM and FARONA, 1980a and 1980b). It was speculated that the group VIB catalysts might be unique in promoting 2+2 cycloadditions, since catalysts based on the groups VIIB and VIB transition metals, where investigated, all promote successive insertion addition reactions.

It was, therefore, of interest to investigate the early transition metals to determine the type of reaction promoted among alkynes. This paper reports the results of the polymerization of phenylacetylene by the $Cp_2TiCl_2/C_2H_5AlCl_2$ catalyst system.

Experimental

Reactions were carried out under dry nitrogen in a flask equipped with a nitrogen inlet, a reflux condenser connected to an oil bubbler, and a rubber septum. Into the flask were placed 5 ml of dry benzene and 0.25 g (1.67 mmole) of titanocene dichloride; the

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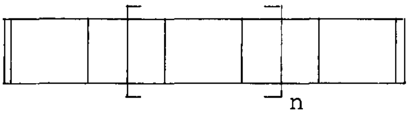
mixture was stirred until a homogeneous solution was obtained. At that point 1.6 ml (3.2 mmole) of 2M ethylaluminum dichloride in chlorobenzene was injected through the septum. The color changed immediately from red to dark green. Phenylacetylene (5 ml, 4.65 g, 0.0455 mole) was injected dropwise into the catalyst solution. (The reaction that ensues is highly exothermic; therefore, the rate of addition of phenylacetylene and the temperature must be controlled.) The reaction was terminated by adding the reaction mixture to ice water. The organic portion of the reaction was extracted with toluene, and the products were separated by column chromatography on neutral alumina.

Results and Discussion

The experimental approach given above is general; in fact, the reaction was carried out at various temperatures and reaction times. When the reaction was carried out at elevated temperatures (80°C) for two hours, the products isolated were polyphenylacetylene (90%) and 1,3,5-triphenylbenzene (10%) at 100% conversion of phenylacetylene. At ambient temperatures for two hours, the reaction yielded polyphenylacetylene (70%), 1,3,5-triphenylbenzene (24%), and 1,2,4-triphenylbenzene (6%). When the reaction was carried out at 12°C for 15 minutes, the products that were isolated were polyphenylacetylene (16%) and the ladder compound (10%). Unreacted phenylacetylene was also recovered.

The nmr and infrared spectra of the ladder compound are identical to those reported earlier (WOON and FARONA 1974), and a ^{13}C nmr spectrum showed the presence of both aromatic and aliphatic carbon atoms. The ladder compound converts quantitatively to polyphenylacetylene when treated in a separate reaction with the catalyst. The proposed structure of the ladder compound is shown below, without the phenyl substituents.



Clearly, the ladder compound is an intermediate in the polymerization reaction of phenylacetylene, and its structure indicates that the addition process is by way of successive 2+2 cycloadditions, similar to that proposed for the reaction catalyzed by $ArMo(CO)_3$ (WOON and FARONA 1974).

On occasion, small yields of triphenyl Dewarbenzenes were isolated in these reactions, and treatment with the catalyst converted the Dewarbenzenes to 1,2,4- and 1,3,5-triphenylbenzene. This appears to be the source of the triphenylbenzene molecules isolated in the reactions.

There is one clear method of differentiation of a cycloaddition mechanism from one of successive insertion. This lies primarily in the mode of initiation of the reaction, where in the latter mechanism, all group VIIB and VIII catalysts form a metal acetylide from insertion of the metal into an acetylenic C-H bond. Because of this requirement, catalysts of the groups VIIB and VIII metals are active only toward terminal acetylenes. All types of acetylenes are polymerized by group VIB catalysts, which promote 2+2 cycloadditions.

In order to test the contention that titanocene dichloride promotes successive cycloadditions, the internal acetylenes 2-butyne and diphenylacetylene were subjected to reaction conditions. In the case of 2-butyne, a mixture of hexamethylbenzene and hexamethyl Dewar benzene was obtained. The reaction of diphenylacetylene led to the isolation of two products: hexaphenylbenzene and hexaphenyl Dewar benzene. The latter showed properties identical with those reported elsewhere for hexaphenyl Dewar benzene (VATANATHAM and FARONA 1980). The isolation of the Dewar benzene molecules provides strong evidence that titanocene dichloride promotes 2+2 cycloadditions.

It appears at this time that catalysts based on the group IVB metals promote addition reactions of alkynes in a manner similar to those of the group VIB metals. Studies currently in progress using the analogous zirconocene dichloride as a catalyst in alkyne reactions indicate that 2+2 cycloaddition reactions also occur with this catalyst.

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