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Polymerization of Acetylenes by Zirconocene Dichloride/Ethylaluminum Dichloride

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Summary

The $Cp_2ZrCl_2/C_2H_5AlCl_2$ system (Cp = π-cyclopentadienyl) was found to be an active catalyst for polymerization of alkynes. Both internal and terminal alkynes were polymerized by this homogeneous catalytic system. Spectroscopic observation of a zirconacyclopentadiene compound in the above reaction led to the investigation of zirconacyclopentadienes as possible reaction intermediates. The zirconacyclopentadiene on reaction with phenylacetylene produced larger zirconacycles and poly(phenylacetylene). Apparently, the mechanism of polymerization of alkynes is by successive insertion of the alkyne into the zirconium-carbon bond, producing expanded zirconacycles, elimination of which results in the formation of a polyalkyne.

Introduction

Although a considerable number of papers in journals and patents have appeared on the polymerization of olefins by Ziegler-Natta catalysts, relatively little research has been reported on the polymerization of alkynes, particularly in the elucidation of the catalytic role of the transition metal. In our laboratory, we have found that group VIB transition metal complexes promote polymerization of acetylenes by a 2+2 cycloaddition mechanism (WOON and FARONA 1974; NAVARRO and FARONA 1976, VATANATHAM and FARONA 1980) and that $Re(CO)_5Cl$, a group VIIB catalyst, promotes polymerization by successive insertion reactions (TSONIS and FARONA 1979).

It was of interest to investigate the role of early transition metal compounds in promoting addition reactions of acetylenes. A previous paper reported some studies on $Cp_2TiCl_2/C_2H_5AlCl_2$ as a catalyst system for these reactions (FAMILI and FARONA 1980). This work is concerned with alkyne polymerizations catalyzed by $Cp_2ZrCl_2/C_2H_5AlCl_2$.

Experimental

Materials. Methylphenylacetylene, 1-hexyne and

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2-butyne were purchased from Farchan and were deoxygenated by purging with nitrogen. Zirconocene dichloride, ethylaluminum dichloride and diphenylacetylene were obtained from Aldrich Chemical Co. and used as received. Phenylacetylene was purchased from Aldrich Chemical Co. and distilled at 20°C under vacuum (10^{-1} torr).

Physical methods. Infrared (ir) spectra were measured on a Perkin-Elmer 597 grating infrared spectrometer. Nuclear magnetic resonance (nmr) spectra were determined on a Varian EM 360 spectrometer using CCl_4 or $CDCl_3$ as solvents. Tetramethylsilane was used as an internal standard in all analyses. Elemental analyses and molecular weights (vapor pressure osmometry) were determined by Galbraith Laboratories. Melting points were taken on a Thomas Hoover Capillary melting point apparatus and are uncorrected.

Polymerization of phenylacetylene. The polymerization was carried out under nitrogen in a 100-ml, three-necked flask equipped with a rubber septum, a gas adapter which served as a nitrogen inlet, and a reflux condenser connected to an oil bubbler (nitrogen outlet). Into the flask was placed 0.584 g (2.0 mmol) of zirconocene dichloride. The reaction flask was flushed with nitrogen for 15 min. Dry benzene (20 ml) was then injected into the reaction flask and the suspension was stirred magnetically. Then 2 ml (4.0 mmol) of 2M ethylaluminum dichloride in chlorobenzene was injected into the flask. The solution became homogeneous instantly and acquired a light yellow color. After 30 min 5 ml (4.65 g, 45.5 mmol) of phenylacetylene was injected dropwise into the reaction flask over a period of 15 min. The reaction mixture was then heated at 80°C for 8 hr. The reaction mixture turned dark red and gradually became viscous. It was then poured into ice water followed by extraction with benzene. The benzene layer, upon vacuum distillation, yielded a red-brown solid. The distillate showed about 2% of the original amount of phenylacetylene remained unreacted, when tested by gas chromatography. The red-brown residue was then dissolved in a minimum amount of CCl_4 and subjected to column chromatography on neutral alumina. Elution with 1:2 (v/v) CCl_4/ether brought down a reddish-yellow band. This fraction on evaporation of the solvent yielded 3.8 g of a yellow-red solid, which was characterized as poly(phenylacetylene) on the basis of its spectral properties, elemental analyses and molecular weight.

Polymerization of other acetylenes. The monomers 1-hexyne, methylphenylacetylene, and diphenylacetylene were also induced to polymerize by methods analogous to that described above for phenylacetylene. In the case of diphenylacetylene, a solution of the monomer in chlorobenzene was injected into the reaction flask. Elemental analyses for all polymers were acceptable.

Details are presented in Table I.

Reaction of 2-butyne with $Cp_2ZrCl_2/C_2H_5AlCl_2$. Into a flask containing 15 ml of dry benzene and 0.584 g (2 mmol) of zirconocene dichloride was added 2.6 ml (4 mmol) of a 25% solution of ethylaluminum dichloride in heptane. The reaction flask was equipped with a dry ice/acetone-cooled condenser. The condenser temperature was maintained between -10°C and -30°C. After 30 min, 10 ml of 2-butyne was injected into the reaction flask. The reaction was magnetically stirred at 20°C for 6 hr. The reaction flask was then transferred into a nitrogen-filled glove box. The solvent was removed by means of a vacuum pump at 30°C. The black-red residue was then dissolved in a small amount of benzene and filtered to remove solid impurities. Cold pentane (5 ml) was added to the filtrate to precipitate a small amount of brown-black solid, which was filtered from the solution. The filtrate was evaporated to dryness yielding a reddish-purple solid. The nmr spectrum of this crude product showed several peaks, three of which (δ 6.05, δ 1.93, δ 1.80 ppm) were identical with the peaks obtained in the nmr spectrum of bis (h^5-cyclopentadienyl)1,2,3,4-tetramethylzirconacyclopentadiene (THANEDAR and FARONA 1982). Attempted further purification of the reddish-purple solid by column chromatography resulted in decomposition to yield a black, insoluble material.

TABLE I

Alkyne Polymerization Catalyzed by Zirconocene Dichloride/Ethylaluminum Dichloride

Alkyne	Reaction Conditions	Yield (%)	M.P.	$\overline{Mn}$
$C_6H_5C{\equiv}CH$	neat, 25°C, 1 hr, or benzene, 80°C, 8 hr	81.72	224-27°C	800, 1,500
$C_4H_9C{\equiv}C\text{-}H$	benzene, reflux, 6 hr	50.6	viscous oil	900
$C_6H_5C{\equiv}CCH_3$	benzene, 75°C, 6 hr	37.71	152-54°C	1,200
$C_6H_5C{\equiv}CC_6H_5$	chlorobenzene, reflux, 6 hr	71.0	180°C	2,000

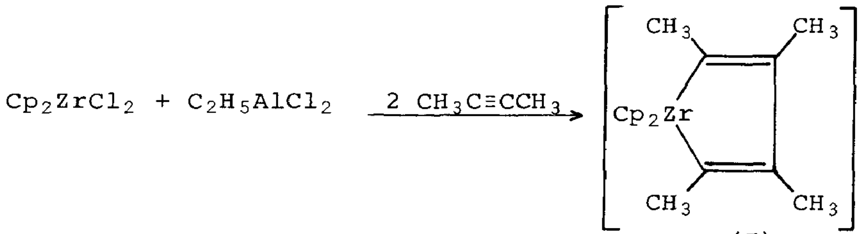
Results and Discussion

The catalytic system we have studied is of interest for three reasons. First, catalysts for the polymerization of internal acetylenes are uncommon (KATZ and LEE 1980). Secondly, zirconium complexes have not, in general, found much employment as homogeneous catalysts, and thirdly, reactions of transition metal compounds with acetylenes often yield mixtures of cyclotrimers and linear polymers. The catalytic system reported in this work produces linear, polyconjugated polymers exclusively.

The *cis* and *trans* nature of the polymers synthesized in this work as well as their linear conjugated properties were deduced and characterized by ir and nmr spectroscopy. The spectral properties of the polymers synthesized in this work also compare well with those reported in the literature: poly(phenylacetylene) and poly(1-hexyne) (WOON 1974); poly(methylphenylacetylene) (SASAKI et al. 1976); and poly(diphenylacetylene) (CHERKASHIN et al. 1976).

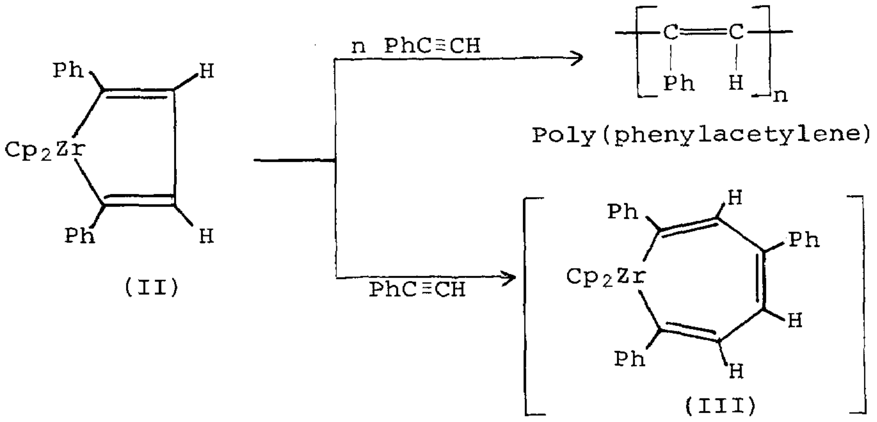
The infrared spectrum of poly(phenylacetylene) showed bands in the 910-870 cm^{-1} (*cis* unsaturation), 1625-1600 cm^{-1} (conjugated C=C stretching vibration). The formation of linear polyconjugation is supported by nmr spectroscopic analysis. In the proton nmr spectrum of poly(phenylacetylene) a broad olefinic proton absorption peak appears to overlap the aromatic proton absorption. The deshielding of the olefinic proton in poly(phenylacetylene) is attributed to the conjugation of the ethylenic bond with an unsaturated group, the general result of which is a shift of the olefinic proton signals to lower fields. Comparison of the spectral properties of poly(phenylacetylene) with those reported previously (MASUDA 1976, SIMIONESCU and PERCEC 1980) indicates a *cis*-transoidal structure for the polymer prepared in this work.

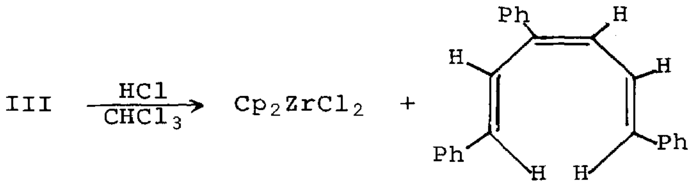
From the reaction of 2-butyne with Cp_2ZrCl_2/$C_2H_5AlCl_2$ a reddish-purple solid was isolated. The nmr spectrum of this compound showed several peaks. Among these, three singlets at δ 6.05, δ 1.93 and δ 1.80 were identical to those exhibited in the nmr spectrum of authentic bis(h^5-cyclopentadienyl)1,2,3,4-tetramethylzirconacyclopentadiene (I) (THANEDAR and FARONA 1982).



(I)

Metallocyclopentadienes have often been proposed as intermediates in catalytic reactions of alkynes promoted by transition metal complexes. Spectroscopic detection of zirconacyclopentadiene in the above reaction raised the possibility that this compound may be an intermediate in the polymerization process. In order to test this contention, in a separate reaction a catalytic amount of bis(h^5-cyclopentadienyl)diphenylzirconacyclopentadiene (II) (prepared by a method analogous to that reported by THANEDAR and FARONA 1982) was allowed to react with phenylacetylene at 60°C for 6 hr. A yellow solid was isolated from this reaction, which was identified as poly(phenylacetylene) as its spectral properties were identical to those of the polymer synthesized using the $Cp_2ZrCl_2/C_2H_5AlCl_2$ system.

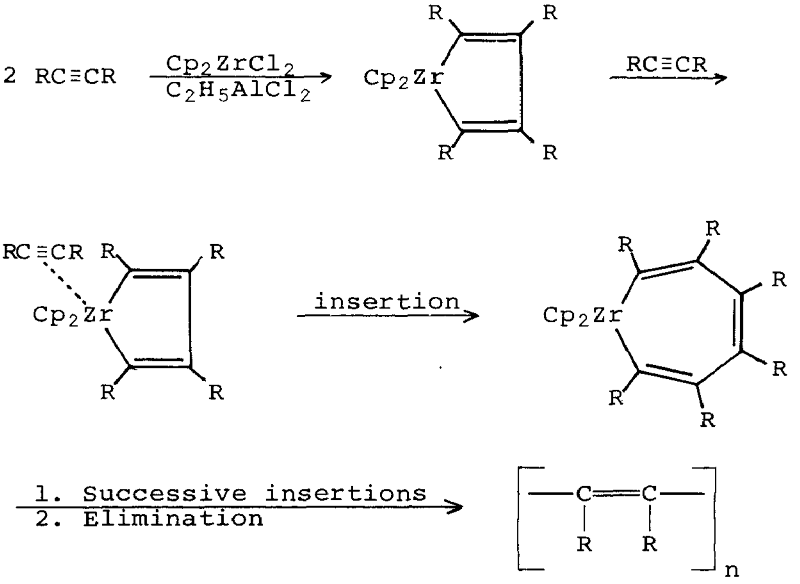




Furthermore, when complex II was allowed to react with a stoichiometric amount of phenylacetylene, isolated from the reaction was a highly air sensitive red solid. The proton nmr spectrum of this product showed a broad multiplet at δ 7.0 (18 H, aromatic and vinylic protons) and a singlet at δ 6.1 (10 H, Cp protons). The red compound on reaction with HCl yielded zirconocene dichloride and a yellowish-white solid. The nmr spectrum of the latter solid showed the presence of both vinylic protons (multiplet, δ 6.2) and aromatic protons (multiplet, δ 7.1). The mass spectrum showed a parent peak at m/e 308. The yellowish-white compound was identified as 1,3,6-triphenylhexatriene on the basis of its spectral properties and by comparing its m.p. (133-134°C) to that of the authentic compound (m.p. 134°C) (BESTMANN and KRATZER 1962). The red compound appears to be bis(h^5-cyclopentadienyl)2,4,7-triphenylzirconacycloheptatriene (III).

Mechanism

From the results discussed above several facts are noteworthy. It appears that zirconacyclopentadienes are produced in the polymerization reactions of acetylenes. The zirconacyclopentadienes, on subsequent reactions with alkynes, produce expanded zirconacycles and polyacetylenes. Based on this information the following scheme is proposed for the polymerization of acetylenes by the $Cp_2ZrCl_2/C_2H_5AlCl_2$ system.



At present, the termination step is not clear, but could come about by reductive elimination to form a polyconjugated ring and regenerate the active catalyst, or could react with some proton source to yield the linear polymer and the catalyst precursor.

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