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Reactions of Diphenylacetylene with Carbon Monoxide Catalyzed by Polystyrene-Supported Molybdenum

INTRODUCTION

In reactions of acetylenes, $ArMo(CO)_3$ (Ar = arene) promotes linear polymerization of both internal and terminal alkynes. Investigation of the mechanism of polymerization by group VIB transition metal catalysts revealed that acetylenes undergo a series of 2 + 2 cycloadditions to cyclobutadiene, Dewarbenzene, etc., leading to a ladder compound of fused cyclobutane rings. This ladder compound, which was isolated, then quantitatively converts to the final polyconjugated polymer (*1*).

An attempt to incorporate $Mo(CO)_3$ groups on polystyrene led instead to a polystyrene-supported molybdenum which was found to be active toward promoting reactions of phenylacetylene under carbon monoxide (*2*). The preparation and properties of the catalyst are given in another publication (*2*).

METHODS

A mixture of 10.0 g (0.056 mol) of diphenylacetylene and 5.0 g of the polystyrenemolybdenum catalyst in 50 ml of benzene was heated in an autoclave, fitted with a glass insert, at 250°C under 34.0 atm of carbon monoxide pressure for 15 hr. After the reaction mixture had cooled to room temperature, methylene chloride was used to take up the product from the insert. A white solid was observed on the beads, and this was extracted with toluene in a Soxhlet apparatus. The toluene solution was cooled in a refrigerator yielding a white precipitate which was filtered from the solvent and dried in a stream of nitrogen. The compound (1.0 g, 15.2%) showed a melting point (425°C), infrared spectrum and mass spectrum (parent *m/e* 534) consistent with that of hexaphenylbenzene.

The solvent was evaporated from the methylene chloride solution, yielding a dark-colored, gummy material. The crude product was subjected to sublimation (40°C, 1×20^{-2} Torr, 1 Torr = 133.3 N m^{-2}) and yielded 50 mg of a white material identified as biphenyl by melting point (70–72°C) and infrared spectrum.

The crude product was dissolved in toluene and subjected to tlc on silica sheets with several solvents. The separation was then carried out by column chromatography with solvents indicated by the tlc studies. The crude material was dissolved in carbon tetrachloride and added to an alumina column. The first band was eluted with a 10 : 1 (v/v) carbon tetrachloride–ether solution; the band was collected and dried, yielding 1.0 g (15.2%) of a yellow-green semisolid. This compound showed infrared absorptions consistent with those expected for a phenyl ring, and the NMR spectrum exhibited aromatic proton signals centered at δ 7.2 ppm. The mass spectrum showed a parent peak at *m/e* 534 and a major fragment at *m/e* 356. The ultraviolet absorptions occurred at λ max 208 (ϵ 25,600), 280 (23,000), and 297 (18,300) nm. The compound was dissolved in methylene chloride and treated with a catalytic amount of dichlorobis (benzonitrile) palladium(II) for 6 hr at 40°C. A quantitative isomerization to hexaphenylbenzene occurred, identified by melting point (425°C) and other spectroscopic evidence.

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This yellow-green semisolid is therefore characterized as hexaphenylDewarbenzene (*3*).

The second band was eluted with toluene, collected, and dried on a rotary evaporator. A yellow solid was recovered (4.2 g, 63.6%) which showed a melting point of 103–105°C. Infrared, NMR, and mass spectrometric evidence indicated that this compound was an oligomer of diphenylacetylene with a molecular weight (mass spectral) of 712.

A third band was eluted with chloroform, collected, and concentrated to about 2 ml. This was poured into 10 ml of methanol, resulting in a yellow-orange precipitate. The solid was collected and recrystallized from 95% ethanol from which a yellow solid was obtained with melting point 126–127°C. The infrared, mass, and NMR spectrometric evidence led to the characterization of this compound as 2,3,4,5-tetraphenylcyclopentenone.

The last band was eluted with a 3 : 1 (v/v) ether/methanol solution and yielded a yellow-brown solid, mp 93–95°C (0.3 g, 4.5%). The compound was characterized by infrared, mass, and NMR spectra, and elemental analysis, as octaphenyltricyclo[5.2.0.0.^{2,6}]nona-4,8-diene-3-one. Anal. Calcd for $C_{57}H_{40}O$: C, 92.40; H, 5.44; O, 2.16%. Found: C, 92.30; H, 5.60; O, 2.20%.

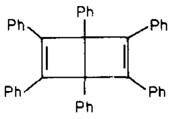
RESULTS AND DISCUSSION

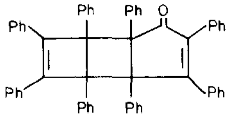
Noncatalytic Reactions

The polydiphenylacetylene produced in this work appears to be thermally induced. In a separate experiment, the reaction of diphenylacetylene was carried out over blank polystyrene beads. The polymer which was isolated showed molecular weight and spectrometric properties identical to those obtained in the catalyzed reactions.

Catalytic Reactions

Compounds containing fused four-membered rings are produced in this reaction, hexaphenylDewarbenzene and the tricyclic ketone octaphenyltricyclo[5.2.0.0^{2,6}]nona-4,8-diene-3-one:





The Dewarbenzene structure is supported by mass spectrometry (parent *m/e* is 534) and it is converted to hexaphenylbenzene catalytically by $(C_6H_5CN)_2PdCl_2$, which is known to effect this conversion (*4*).

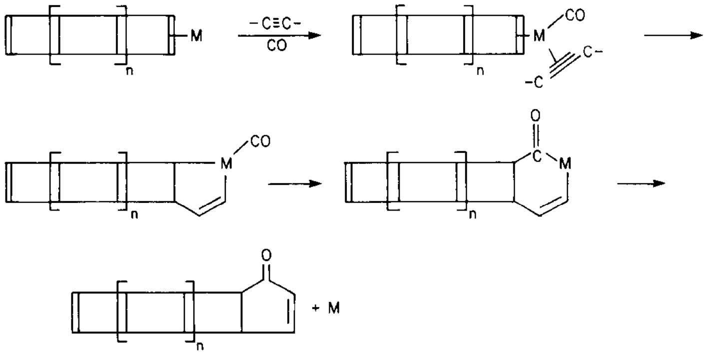
The tricyclic ketone shows a carbonyl band at 1700 cm^{-1} in the infrared spectrum, which is consistent with a cyclopentenone ring (*5*). Infrared bands at 1010 and 760 cm^{-1} are assigned to ν(C–C) and δ_β (ring) in a cyclobutane ring, respectively (*6*). Mass spectrometric fragments are *m/e* 651, 562, 473, 384, 356, 267, and 178, which correspond to $(C_6H_5C)_nCO$ with a range $n = 4$–8. The *m/e* 384 peak represents a cyclopentadienone ring.

The other carbonyl-containing compound is identified as 2,3,4,5-tetraphenylcyclopentenone by a comparison of melting point and other spectrometric data with the authentic compound reported by Rio and Sang (*7*). The two hydrogens on adjacent carbons of the cyclopentenone ring most likely arise from free-radical abstraction from benzene solvent. The fact that biphenyl was isolated from the rection mixture supports this view.

The reactions of methylphenylacetylene and cyclohexylacetylene with CO using the polystyrene-supported molybdenum catalyst also led to products containing fused cyclobutane rings. Tricyclic, tetracyclic, and pentacyclic ketones were isolated and characterized.

Mechanism

For the compounds in which carbon monoxide is inserted, a mechanism based on that proposed by McVey and Maitlis (*8*) can be invoked. Apparently, a series of 2 + 2 cycloadditions occurs and this is terminated by CO insertion. Thus



The formation of tetraphenylcyclopentenone apparently involves free radicals; a mechanism for its formation is proposed according to the studies of Best *et al.* (*9*).

It is clear that the polymer-bound catalyst promotes 2 + 2 cycloaddition reactions of acetylenes in much the same manner as that described for the arenemolybdenum tricarbonyl catalysts (*1*). This conclusion is based on the structures of the compounds obtained, and also the fact that both terminal and internal acetylenes undergo the same types of reactions.

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