

Polymer of Acetylenic Nitriles

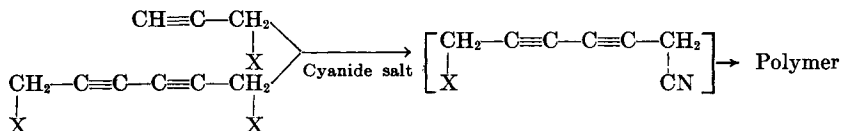
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Synopsis

Efforts to prepare 1,6-dicyano-2,4-hexadiyne resulted in the formation of insoluble, chemically inert, high-melting "brick dust" type polymeric materials. Similar appearing products arose from the dihalo-, ditosyl-, and dihydroxy- hexadiyne derivatives as well as propargyl halide starting materials. It appears that diacetylenic diols and their propargylic precursors undergo direct nitration.

INTRODUCTION

Some cyanoacetylenic compounds have been reportedly prepared by heating the corresponding iodide with an alkali cyanide in aqueous solution or with a xylene slurry of cuprous cyanide.¹ However, when an effort was made to extend this reaction to synthesize diacetylenic dinitriles from diacetylenic dihalides, finely divided "brick dust" type polymeric derivatives resulted. These cyanohexadiyne polymeric derivatives resulted from the reaction of a cyanide salt such as sodium or cuprous cyanide with a solution or slurry of a 1,6-disubstituted 2,4-hexadiyne derivative such as the 1,6-dichloro-, 1,6-dibromo-, 1,6-ditosyl-, and 1,6-dihydroxy hexadiyne derivatives or propargyl bromide.



The polymeric products apparently contain the nitrile or similar function as evidenced by unsaturation; infrared examination of the polymer has indicated that both the nitrile and imino ($-\text{C}=\text{N}-$) functions are present. The materials were found to be insoluble in organic solvents, and to be unaffected by hot concentrated H_2SO_4 at 100°C . A melting point determination of the polymer in a sealed capillary tube under nitrogen indicated the material to be visibly unchanged up to 600°C . Further heating was discontinued when the outside of the aluminum melting block began to melt (660°C).

DISCUSSION

The chemistry of the simpler acetylenic nitriles remains to be well defined. Moreover, even less is known about the diacetylenic dinitriles.

One of the few latter reported compounds is dicyano-acetylene or 1,4-dicyano-1,3-butadiyne, a completely conjugated nonhydrogen-containing organic synthesized by the oxidative dimerization of propiolonitrile.²⁻⁵ Dicyanoacetylene is reported to polymerize to a black powder in the presence of base.⁶ However, the diacetylenic nitriles and derivatives described herein are not completely conjugated and contain methylene buffer groups.

From the extremely high melting point and the initial structure of the hexadiyne molecule, it is reasonable to assume an aromaticlike structure of the product. Aromatic structures are more stable and more difficult to degrade thermally by pyrolytic treatment than the aliphatics, which generally begin to decompose in the range of 200–300°C. The physical properties of these materials are strikingly similar to those of products resulting from the high-pressure condensation of dinitriles which were also insoluble, brittle, and unsinterable solid black polymeric "brick dust" materials. The properties of these latter materials have been ascribed⁷ to the result of extreme "polybonding principle," i.e., skeletal atoms are joined in "chains" through several routes such as polycyclic or condensed ring systems. Here structures continue to exist even when a single carbon-carbon bond is broken because the natural bond angles maintains atom proximity, allowing for "bond healing" after dissipation of excess energy. Therefore, those structures containing the largest amount of polybonding tend towards a lack of flexibility, and exist as "brick dusts," resisting sintering even under extreme conditions.

A fused linear unsaturated polymer containing nitrogen is reported⁸⁻¹¹ to form by the thermal degradation of polyacrylonitrile having good thermal resistance, and which may at least in part be similar to the cyanohexadiyne polymers.

This cyanohexadiyne polymeric derivative may be aromatic and linear or alicyclic and graphitically fused. It is known that nitriles polymerize to give the triazine ring. This triazine nucleus has been incorporated in high temperature-resistance polymers.¹² Thus cyanohexadiyne intermediates containing a similar dual nitrilic function could conceivably react to form a triazine polymer; the hexadiyne portion of the molecule would act as the potential benzenoid rings, and would be expected to be thermally stable.

EXPERIMENTAL AND RESULTS

Preparation of Cyanoacetylenes and Derivatives by Direct Nitrilation

The difficulty of preparing acetylenic nitriles via direct nitrilation of the halide has been recognized by other workers: viz., Johnson¹³ who was unsuccessful in synthesizing 1,4-dicyano-2-butyne from the corresponding dihalide by the reaction with an alkali metal cyanide or cuprous cyanide in various solvents. Newman and Wotiz¹ were able to prepare 1-cyano-

2-heptyne only under more extreme conditions, i.e., by heating a xylene solution of the bromide with cuprous cyanide at 157°C. for 30 min. An effort to prepare butynonitrile by refluxing propargyl bromide with aqueous sodium cyanide gave a low yield of liquid which distilled at 55°C./1 mm. and failed to give an identifiable acid when subjected to caustic hydrolysis.

Nitrilation of 1,4-Disubstituted 2,4-Hexadiyne Derivatives

The hexadiyne derivatives employed in these nitrilation reactions included the dibromo, dichloro, and ditosyl compounds and were synthesized from hexadiynediol according to the procedure of Armitage and Whiting.¹⁴ The dibromo hexadiyne preparation was slightly modified, i.e., an isopropyl ether solution was treated with PBr_3 resulting in 84% yield of product, whereas when benzene (the recommended solvent) was employed, a 65% yield was reported.

In a typical nitrilation reaction, a mixture consisting of 1,6-dibromo-2,4-hexadiyne (or an isopropyl ether or isopropyl ether-ethanol solution of this starting material) and sodium cyanide in a stoichiometric molar ratio of 1: 2 slurried in 10 wt.-% excess of water was refluxed for 6 hr. to yield an almost quantitative yield (based on dibromohexadiyne) of brown polymeric product. The product was found to be insoluble in common organic solvents and unaffected by hot concentrated sulfuric acid at 100°C. In addition, the polymeric material was observed to be unsaturated and apparently to contain the cyano moiety as evidenced by the elimination of ammonia when treated with caustic. Infrared examination confirmed the presence of the cyano group, and also indicated imino linkages. The elemental analysis indicated that the material contained an average of one cyano group per monomer.

ANAL. Calcd. for $C_7H_4NBr \cdot \frac{3}{4} H_2O$; C, 43.00%; H, 2.83%; N, 7.17%; Br, 40.9%. Found: C, 42.97%; H, 2.63%; N, 7.41%; Br, 40.6%.

With this procedure similar dark, fine polymeric powders were obtained with hexadiynediol and with both the 1,6-dibromo- and 1,6-ditosyl-hexadiynes. It was observed that refluxing a dry benzene-cuprous cyanide slurry containing 1,6-dibromo-2,4-hexadiyne for 24 hr. yielded no product. However, when xylene was substituted for the benzene in the slurry, polymers similar to those obtained with the use of aqueous sodium cyanide resulted.

It was further observed that the degree of nitrilation of the product could be increased in the one instance tried. Subjecting the cyanobromohexadiyne polymer obtained from dibromohexadiyne and aqueous sodium cyanide containing 7% nitrogen (see above) to further and more drastic refluxing with a cuprous cyanide-xylene slurry increased the nitrogen content to 12%. The fully nitrilated material should contain almost twice that amount of nitrogen (21.88%).

Preparation of Cyanoacetylenes and Derivatives by Direct Nitrilation of the Alcohol

The direct replacement of a primary aliphatic hydroxyl with a cyano group under mild reaction conditions is unusual, except where a labile hydroxyl such as an allylic one is involved. The reaction of cuprous cyanide and concentrated hydrochloric acid upon allyl alcohol leads to allyl cyanide.¹⁵ Other allylic diols, such as the hexadiynediols, have been converted to the dinitrile by using copper ferrocyanide and concentrated hydrochloric acid at 90°C.,¹⁶ hydrogen cyanide and copper bromide,¹⁷ and copper chloride ammonium chloride and copper powder.¹⁸

To date, the direct conversion of acetylenic alcohols to nitriles has not been reported. The attempted reaction of propargyl alcohol, a mono-hydroxy acetylenic compound with sodium cyanide, was found to yield only starting material, while butynediol, a dihydroxy acetylenic derivative, resisted nitrilation with hydrogen cyanide in the presence of cuprous chloride and ammonium chloride and was effectively converted only under the more drastic conditions. Evidence of nitrilation of butynediol was obtained by maintaining a stoichiometric reaction mixture of butynediol, hydrogen cyanide, and Raney nickel in a stirring autoclave at a temperature of 160°C. and pressure of 125 psi for 4 hr. The black polymeric product, insoluble in all organic solvents, could not be further purified and when analyzed for nitrogen appeared to be made up of hydroxy-nitrobutyne monomeric units.

ANAL. Calcd. for C_6H_6NO : N, 14.73%. Found: N, 14.06%.

Nitrilation of Propargyl Derivatives

When it was established that a hydroxyl group of an α,β -diacetylenic diol could be effectively substituted, an effort was made to extend this study to an α,β -acetylenic alcohol, viz., propargyl alcohol. Refluxing of propargyl alcohol in both aqueous sodium cyanide and xylene slurries for extended periods of time under conditions previously described for the formation of polymeric materials did not yield any products. However, when propargyl bromide was refluxed with an xylene slurry of cuprous cyanide, a polymeric material was obtained not unlike the product from the reaction of cuprous cyanide and 1,6-dibromo-2,4-hexadiyne. If these polymers are similar, then the production of such a polymer from propargyl bromide would necessitate an intermediate air oxidative coupling reaction, which could be catalyzable by the cuprous cyanide in a manner similar to that employed with cuprous and ammonium chlorides in the presence of air. The product analyzed for a cyanobromohexadiyne polymer.

ANAL. Calcd. for C_7H_4NBr : N, 7.70%. Found: N, 7.67%.

The effect of air on this reaction was ascertained by repeating it under similar conditions except that a nitrogen atmosphere was employed. The

polymer yield in the absence of air was only 20% of that previously obtained, i.e., when air was permitted.

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Résumé

En essayant de préparer le 1,6-dicyano-2,4-hexadiyne, on a obtenu un polymère insoluble, chimiquement inerte et à point de fusion élevé. Des produits du même genre se forment à partir des dérivés dihalogénés, ditosylés et dihydroxylés de l'hexadiyne, aussi bien à partir des halogénures de propargyle. Il semble que les diols diacétyléniques et leurs précurseurs propargyliques subissent une nitrilation directe.

Zusammenfassung

Versuche zur Darstellung von 1,6-Dicyano-2,4-hexadiin führten zur Bildung eines unlöslichen, chemisch inerten hochschmelzenden ziegelstaubartigen Polymeren. Produkte von ähnlichem Aussehen entstanden aus Dihalo-, Ditosyl- und Dihydroxyhexadiinderivaten und auch aus Propargylhalogenid als Ausgangsmaterial. Es scheint, dass Diacetylendiole und ihre Propargylvorstufen direkt nitriliert werden.

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