Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Jones, G. D. and Doorenbos, H. E.(1985) 'The Codimerization and Cotrimerization of Vinylacetylene, Propargyl Alcohol, and Acetylene', Journal of Macromolecular Science, Part A, 22: 2, 161 — 166

To link to this Article: DOI: 10.1080/00222338508063303

URL: http://dx.doi.org/10.1080/00222338508063303

J. MACROMOL. SCI. CHEM., A22(2), pp. 161-166 (1985)

The Codimerization and Cotrimerization of Vinylacetylene, Propargyl Alcohol, and Acetylene

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ABSTRACT

Propargyl alcohol was codimerized with acetylene, and 4-penten-2-yn-1-ol was obtained. Propargyl alcohol was cotrimerized, but the main product was the homotrimer whether the comonomer was vinylacetylene or 2-methylbutenyne. The cotrimerization of 1,1-dimethylpropargyl alcohol was more easily regulated. With acetylene it gave the m- and p-di-α-hydroxypropylbenzenes.

TEXT

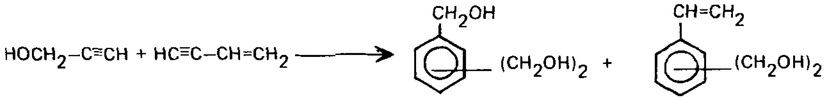
Propargyl alcohol has been homodimerized [1] and trimerized [2]. 1-Hexyne has been codimerized with phenylacetylene [1]. Divinylacetylene has been cotrimerized with acetylene [3, 4].

We codimerized propargyl alcohol with acetylene over cuprous chloride and obtained, apparently as the sole isomer, 4-penten-2-yn-1-ol, a known compound:

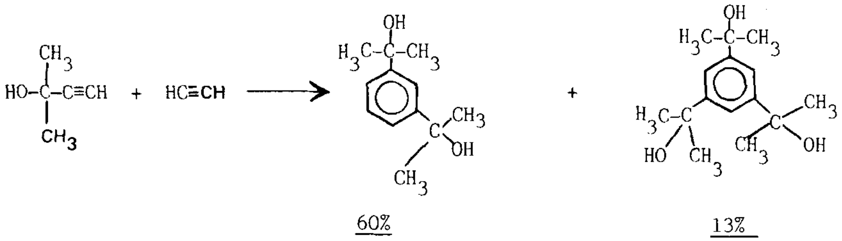
$$HOCH_2{-}C{\equiv}CH \xrightarrow{CuCl} [HOCH_2{-}C{\equiv}C{-}Cu] \xrightarrow{C_2H_2} HOCH_2{-}C{\equiv}C{-}CH{=}CH_2$$

0022-233X/85/2202-0161$3.50/0

We cotrimerized propargyl alcohol with excess vinylacetylene using bis(triphenylphosphine) nickel dicarbonyl catalyst and obtained mainly the homotrimer of propargyl alcohol plus some vinylxylenediol:



We found 1,1-dimethylpropargyl alcohol more easily regulated and cotrimerized it with acetylene to obtain the m-di- and 1,3,5-tri-α-hydroxypropylbenzenes as the major products:



We cotrimerized 2-methylbutenyne and propargyl alcohol (in 1.5 weight ratio) using nickel tris-(triphenyl phosphite) as the catalyst. The conversion at room temperature was 6.6% in 1 day and 9.3% after 4 days. By reverse phase liquid chromatography we obtained six products having the estimated weight ratio 647, 814, 22, 24, 1, 1. We had available as standards: m- and p-divinylbenzenes, vinylbenzyl alcohol, and 1,4-xylylenediol. We concluded that the two large early peaks were the 1,2,4- and 1,3,5-isomers of the homotrimer of propargyl alcohol, that the next two peaks were isomers of isopropenylxylylenediol, and the two small peaks were of diisopropenylbenzyl alcohol.

Using a Ziegler catalyst $[4(C_2H_5)_2AlCl + TiCl_3]$, we cotrimerized vinylacetylene (VA) with acetylene and obtained benzene, styrene, divinylbenzene (DVB), and trivinylbenzene (TVB) (Table 1). The reaction at 10°C was rapid, as shown by the drop in acetylene pressure from 200 to 100 psig in 2 min. The conversion was 100 mol of alkyne per mole of $TiCl_3$. The yield was 77%. A feed mixture containing 31 mol% vinylacetylene gave a product mixture containing 36 mol% combined vinylacetylene. The ratio of isomers of divinylbenzene was m:o:p = 3:1:1. There are six sequences of reaction which would give divinylbenzene; four would give the meta-isomer, one the ortho-isomer, and one the para-isomer.

These data show that the vinylacetylene reacts slightly faster than

TABLE 1. Cotrimerization of Acetylene and Vinylacetylene

Grams C_2H_2 added	Grams VA added	% Trimer products			
		Benzene	Styrene	DVB	TVB
2.0	1.0	52.2	33.1	12.6	2.02
2.0	1.8	25.2	46.1	24.1	4.6

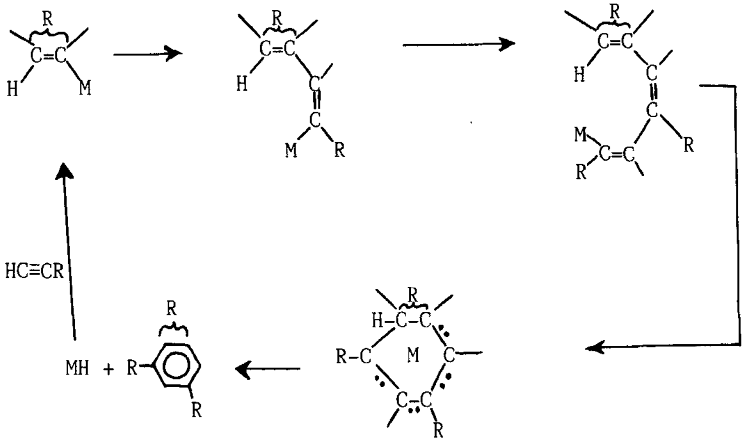
the acetylene since the amount of trivinylbenzene formed is more than doubled when the feed ratio of vinylacetylene to acetylene is less than 2.

We found no styrene in the homotrimerization of vinylacetylene.

DISCUSSION

Homodimerization of acetylenes over cuprous catalysts is known to give 1,4-disubstituted butenynes [5]. The mechanism, even if it occurs within a coordination shell containing both monomers, must involve one acting as the nucleophile and the other as the electrophile. Apparently, these roles are played by propargyl alcohol and acetylene, respectively.

Likewise in trimerization, whether a metallocene intermediate is assumed or not, there must be steps like those in a Ziegler polymerization of an olefin. We prefer a hydride transfer mechanism and ascribe most of the isomer determination to the nonselectivity of the hydride initiation. The propagation must be one of cis addition. The cyclization involves addition to the triene tail:



Only in trans addition would one expect to make styrene from vinylacetylene by a hydride mechanism. The cis addition dimer is not suitably oriented.

The report [8] that a deuterated catalyst ($TiAlD_4 + CoX_2$) gave only a 20% deuterated trimer is consistent (if the trimer was cyclic) with a hydride transfer mechanism. In the case in which initiation was terminal, trimerization would be accompanied by loss of deuteride approximately half the time; when initiation was nonterminal, every time.

EXPERIMENTAL

Preparation of 4-Penten-2-yn-1-ol

The catalyst was prepared by heating overnight at 65°C in a closed vessel the following mixture: cuprous chloride (3.3 g), ammonium chloride (2.4 g), copper dust (0.15 g), water (4.17 g), and concentrated hydrochloric acid (0.075 g).

Propargyl alcohol (3 g) was added to the catalyst, the vessel was pressurized to 200 psig with acetylene, and the mixture was placed on a shaker at 80-85°C for 10 h. The product was filtered, and the filtrate was extracted with methylene chloride. The methylene chloride was distilled, and the residue was analyzed by mass spectroscopy. It was found to have the same pattern as pentenynol made by the reaction of formaldehyde with Grignard reagent made from vinylacetylene, a known reaction [6]. The boiling point of the product has been reported [7].

Ziegler-Catalyzed Trimerizations

The $TiCl_3$ was added to the glass reactor in a dry box under N_2. Then the solvent, toluene, was added. To this mixture we added the Et_2AlCl (25% in toluene), and the reactor was closed and removed from the dry box. Vinylacetylene was added either from an S. S. addition funnel or by sweeping the vinylacetylene into the reactor with a stream of acetylene gas. (The vinylacetylene was purchased as a 50% solution in xylene. The vinylacetylene was removed from the solvent by distillation into a S. S. Hoke cylinder where it was stored neat.) The reactor was maintained at ~0°C during the addition, and the reactor contents were stirred magnetically. At the end of the addition, the catalyst activity was quenched by the addition of a small amount of methanol (exothermic). (Addition of water to quench the reaction caused polymerization of the active vinyl groups.) The contents of the reactor were filtered with the aid of vacuum (aspirator), and the recovered filtrate was analyzed by gas chromatography on a 21' × 1/8" S. S. column packed with 6% Bentone-34 and 3% DC-550

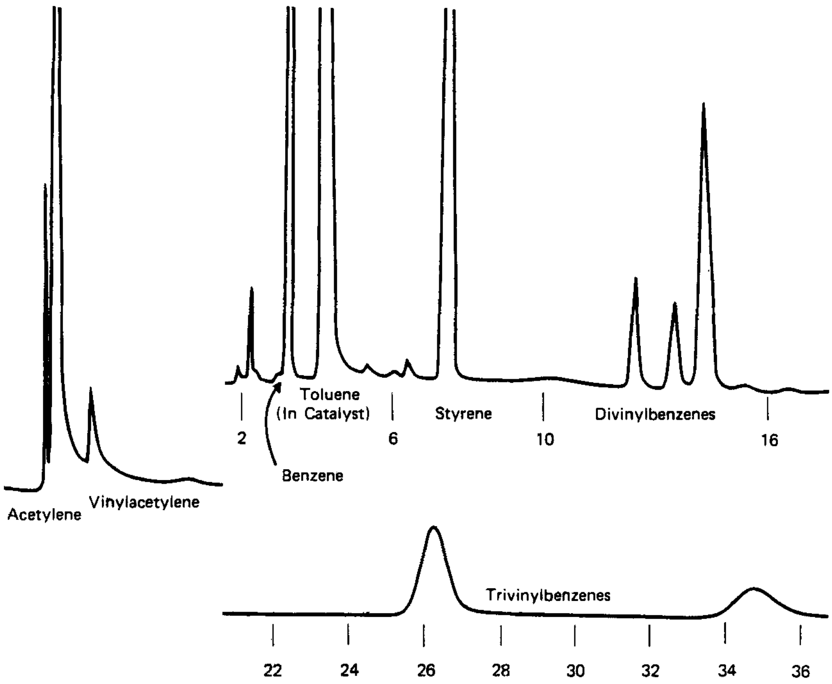


FIG. 1. Gas chromatograph of cotrimer of acetylene and vinylacetylene; minutes.

using a TC detector. The temperature program was as follows: 100°C for 2 min followed by a temperature rise of 8°/min up to 170°C for 32 min. A typical chromatogram is shown in Fig. 1, and an example of a typical cotrimerization run is detailed below.

Into a Fischer-Porter high-pressure glass reactor equipped with stirring bar, we placed 0.153 g (0.001 mol) of $TiCl_3$, 1.9 mL of 25% solution of diethyl aluminum chloride in toluene (0.004 mol), and ~10 mL of toluene. The reactor was closed and placed in a beaker of water kept at ~0°C. With stirring, a total of 0.52 g (0.01 mol) of vinylacetylene and 2.6 g (0.1 mol) of acetylene were added to the reactor over a period of 3 h. At the end of this time, the reaction was stopped by the addition of 0.5 mL of methanol. The mixture was filtered to remove the catalyst. The filtrate (10.13 g) showed the presence of 16.48% (1.67 g) of benzene, 4.05% (0.41 g) styrene, and 0.49% (0.05 g) of divinylbenzenes by gas chromatography (area percent). The catalyst was slurried in a small amount of toluene and the mixture filtered. From the washings (4.63 g) we obtained 4.10% (0.19 g) benzene, 1.29% (0.06 g) styrene, and 0.21% (0.01 g) of divinylbenzenes. The sum of the weight of these products is 2.39 g, which represents a 77% recovery. This also represents 110 mol of alkyne per mole of titanium.

Under the same conditions as above, from vinylacetylene only two compounds were produced–the two isomers of trivinylbenzene. These were 1,2,4- and 1,3,5-trivinylbenzene, formed in a ratio of ~2:1.

Acetylene, Vinylacetylene, and 1-Butyne

The above three materials were cotrimerized under the same conditions as given above. Again, a variety of products was obtained. These consisted of benzene, styrene, divinylbenzenes, and trivinylbenzenes along with at least seven other major products–presumably the isomers of ethyldivinylbenzenes (3), ethylvinylbenzene (2), diethylbenzene, and ethylbenzene. These were not identified but are assumed based on the retention times relative to the known times for the known products.

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Accepted by editor March 26, 1984
Received for publication April 27, 1984