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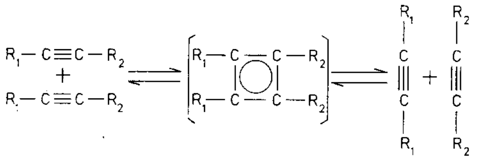
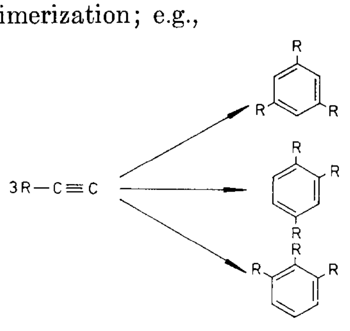
NOTES

Disproportionation and Cyclotrimerization of Alkynes Over Supported Tungsten Oxide

In 1964 Banks and Bailey (*1*) reported a new catalytic process, the disproportionation of alkenes in which linear alkenes are converted into homologues of both shorter and longer carbon chains. Supported oxides of tungsten, molybdenum, and rhenium are mentioned as the most active catalysts. Pennella *et al.* (*2*) showed that the disproportionation reaction is not limited to alkenes. They found that supported tungsten oxide also catalyzes the disproportionation of pentyne-2. They suggested a mechanism analogous to the mechanism proposed for disproportionation of alkenes:



We have found disproportionation not to be limited to β-alkynes; α-alkynes also yield disproportionation products when the proper reaction conditions are chosen. Besides disproportionation, a quantitatively more important reaction appeared to be cyclotrimerization; e.g.,



The literature on cyclotrimerization of alkynes has recently been reviewed (*3*).

EXPERIMENTAL

The catalyst was prepared by impregnating silica (Davison 111) with ammonium *para*tungstate. The catalyst was activated *in situ* with air at 580°C for one hour and for another hour in a stream of helium at the same temperature. This yielded a catalyst containing 5.5% tungsten oxide with a specific surface area of 310 m^2/g, a porosity of 0.8 ml/g and an average pore radius of 50 Å. The silica used in the blank experiments was treated in the same manner as the supported tungsten oxide catalyst. Ethyne, propyne, and butyne-1 were obtained from J. T. Baker, pentyne-1 and pentyne-2 from Th. Schuchard.

The investigations were carried out in a stainless–steel reactor mounted in an electric furnace and equipped with conventional devices for the control of pressure, temperature, and gas flow. A mixture of about 10% alkyne and 90% helium was passed continuously through the reactor. Helium was dried over molecular sieve 3A and purified from oxygen by a hydrogenated copper catalyst obtained from BASF (R3-11). The experiments were carried out at a total pressure of about 1 atm and temperatures between 100 and 550°C. The gaseous and liquid products were analyzed separately. The higher molecular weight products were condensed by passing the product stream through a cold trap at 0°C, and the noncondensable effluent was periodically sampled with a hypodermic syringe. Gas-chromatographic separation of the gaseous products was performed on a 5 m × ¼ in. column packed with 15%

diisodecylphthalate on Chromosorb. The liquid products were analyzed on a 2 m × ⅛ in. column packed with silicone rubber. The products were identified by measuring their retention times. The presence of a number of products was confirmed with the aid of refractive index measurements and by means of mass, NMR, and ir spectrometry.

RESULTS

Blank experiments with the catalyst support in which propyne and butyne-1 were passed over calcined silica at temperatures to 550°C showed no disproportionation or cyclotrimerization.

To obtain an impression of the stability of the aromatic compounds formed, a pulse of 1,2,4-trimethylbenzene was injected into the reactor filled with activated catalyst at 450–550°C. Neither in the liquid phase nor in the gas phase were products formed.

Table 1 shows that disproportionation can be realized with all alkynes investigated; of course a possible disproportionation of ethyne could not be observed because ethyne gives in case of disproportionation ethyne again.

The ratio of the weight of liquid product to weight of starting material was in all cases between 0.3 and 0.7. The results suggest that the disproportionation activity of supported tungsten oxide towards α-alkynes is lower than towards β-alkynes. However, the reason for the lower percentages of disproportionation products in the case of α-alkynes may be found in the simultaneously occurring cyclotrimerization, which at temperatures below 300°C is nearly quantitative for propyne, butyne-1, and pentyne-1. The fact that for these alkynes lower cyclotrimerization conversions cor-

TABLE 1
SURVEY OF EXPERIMENTAL RESULTS

Starting material[a]	Temperature (°C)	Products of disproportionation (wt% of starting material)	Trialkylbenzenes (wt% of liquid products)	Remarks
Ethyne	250–500	—	—	50% of the liquid reaction products consisted of benzene.
Propyne	90–145	Not detected	90	Presence of 1,3,5- and 1,2,4-trimethylbenzene confirmed by NMR and ir.
	465	1	50	
	495	7	50	
Butyne-1	110–260	Not detected	99	Presence of hexyne confirmed by mass spectrometry. Presence of triethylbenzene confirmed by NMR and ir. Liquid phase contains diethylbenzene (NMR, ir).
	460–500	3	50	
Pentyne-1	250–270	Not detected	84	Presence of tri-*n*-propylbenzene confirmed by NMR and ir. Presence of octyne confirmed by mass spectrometry.
	270–360	1.5	74	
	360–490	9	54	
Pentyne-2	294	1.5	Not measured	IR spectrometry shows the liquid phase is composed of aromatic compounds for more than 90% in all three cases. The gas phase in the experiment at 366°C is nearly quantitatively composed of butyne-2, pentyne-2, and hexyne.
	366	26	Not measured	
	446–450	11	Not measured	

[a] weight hourly space velocity (WHSV): 1–4 g alkyne/g catalyst/hour.

TABLE 2

Ratio of 1,2,4- to 1,3,5-Trialkylbenzenes Formed in the Cyclotrimerization of Propyne, Butyne-1, and Pentyne-1 at Different Temperatures

Starting alkyne	Ratio of 1,2,4 to 1,3,5 isomers formed	
	100–300°C	300–550°C
Propyne	3.7	1.6
Butyne-1	3.6	1.4
Pentyne-1	1.2	1.0

respond with higher disproportionation conversions supports this interpretation. Quantitatively the most important reaction is cyclotrimerization to benzene derivatives. At moderate temperatures the selectivity of this reaction for the α-alkynes investigated is very high. At high temperatures other reactions occur besides cyclotrimerization and disproportionation. Thus, in an experiment with propyne at 465°C, 20% of the liquid products were xylenes; this was confirmed by NMR-spectrometry.

Table 2 summarizes the ratio of the isomers formed by cyclotrimerization. The products of cyclotrimerization of the α-alkynes investigated were mainly 1,2,4- and 1,3,5-trialkylbenzenes; the formation of 1,2,3-isomers could be neglected. Only at temperatures above 300°C were small amounts of the 1,2,3-isomer formed; however, they never exceeded 2% by weight of the total amount of trimers.

According to Whitesides and Ehmann (*4*) mechanisms of cyclotrimerization can be divided into two groups:

(*a*) cyclotrimerization via a cyclobutadiene intermediate,

(*b*) cyclotrimerization via other mechanisms. The authors derived the conclusion that for α-alkynes the theoretical product distribution in *case* (*a*) amounts to (1,2,3):(1,2,4):(1,3,5) = 1:5:2 and in *case* (*b*) to 0:3:1. They infer that the cyclobutadiene mechanism can be rigorously excluded when 1,2,3-trialkylbenzene is not a reaction product. Following this reasoning it is clear from the results shown in Table 2 that mechanism (*a*) is excluded at temperatures below 300°C. At higher temperatures the cyclobutadiene mechanism is not rigorously excluded; in our opinion, however, it is more probable that the small amounts of the 1,2,3-isomer have been formed by side reactions and consecutive reactions, which evidently occur.

References

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A Test for the Development of Protonic Acidity in Alumina at Elevated Temperatures

Various acid catalyzed reactions such as alcohol dehydration, double bond and skeletal isomerizations, and hydrocarbon cracking are catalyzed by alumina. The acidic properties of aluminas have frequently been studied by ir-spectroscopic methods (*1–4*) using pyridine as a base ($pK_a = 5.25$ at 25°C in aqueous solution)