The cocyclotrimerization of alkynes and acetonitrile with CpCoCOD as catalyst

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Abstract

Mixtures of the alkynes and acetonitrile were cyclotrimerized with CpCoCOD as catalyst to form pyridine derivatives. The system can be thermally or photochemically activated. The cocyclotrimerization reaction is a pseudo first order process and the photochemically activated reaction at 20°C has a rate constant of 3.66×10^{-3} s^{-1} while that of the thermally activated system at 140°C is 4.23×10^{-4} s^{-1}. The distribution of the products formed if a mixture of hex-1-yne, phenylacetylene and acetonitrile is used indicates an almost random coordination of the alkynes on the cobalt before the nitrile coordinates. The nitrile cocyclotrimerizes rather with a hex-1-yne containing intermediate than with the phenylacetylene containing intermediate to form pyridine derivatives.

Keywords: Alkyne; Acetonitrile; Cobalt; Cocyclotrimerization; Cyclopentadienyl complexes; CpCoCOD; Pyridine derivatives

1. Introduction

The first cobalt complex catalyzed cocyclotrimerization of alkynes and nitriles was reported by Yamazaki and Wakatsuki in 1973 [1] using a phosphine stabilized cyclopentadienylcobalt(III) complex. Bönnemann et al. [2] concentrated in their research on soluble organocobalt catalysts and developed this method into a well established process. The isolation of a number of phosphine stabilized CpCo complexes by Wakatsuki et al. [3] which may be regarded as intermediates in the catalytic cycle gave a big contribution to the understanding of the mechanism of the cocyclotrimerization reaction.

The mechanism [4] can be considered as a stepwise addition of two alkyne molecules to the central cobalt atom, a ring closure to give a cobalt cyclopentadiene intermediate, then an insertion of the nitrile followed by the reductive elimination of the pyridine product.

In a study of the reaction of propyne and propionitrile [4] in an autoclave at 87°C and 90°C with a CpCo containing catalyst the following results were obtained:

· The reaction order with respect to the propyne is 1.7 with an Arrhenius energy of activation of 96 kJ mol^{-1} of pyridine formed.

· The rate of pyridine formation depends upon the square of the concentration of the alkyne in solution and is independent of the concentration of the nitrile.

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In 1989 Schultz et al. [5] reported that substituted pyridines can be synthesized under mild conditions by the cocyclotrimerization of acetylene and nitriles in the presence of cobalt complexes while the mixture was irradiated with light between 360 and 500 nm.

If CpCoCOD was used as catalyst in the cocyclotrimerization of hex-1-yne with acetonitrile [6] pyridine derivatives formed with a yield of 95% at 140°C after 2 h. Under irradiation the yield was 95% at room temperature after 2 h.

Various alkynes can be cyclotrimerized and mixtures of alkynes can be cocyclotrimerized with $NbCl_5$ as catalyst and $C_2H_5AlCl_2$ as cocatalyst in CCl_4 at room temperature [7]. The amount of the different cyclotrimers formed with regard to the mole fraction of the starting materials tends to distribute itself according to a statistically random distribution. This indicates that there is a statistically random coordination of alkynes on the catalytic species after which ring closure occurs to form the cyclotrimeric products.

The reaction between hex-1-yne and acetonitrile with CpCoCOD as catalyst produces pyridine as well as benzene derivatives. The relative yield of the pyridine and the benzene compounds depends on whether heating or irradiation was used. In the thermic process the molar ratio of pyridine to benzene derivatives is in the order of 27:1 while in the photo-assisted process in the sun, the ratio is 93:1 [6]. If the alkynes (X and Y) cocyclotrimerize with a nitrile (Z) also on a random manner provided that the nitriles do not react with themselves, the cyclotrimer product spectrum can be represented by

$$X + Y + Z \rightarrow$$

$$X_3 + X_2Y + XY_2 + Y_3 + X_2Z + Y_2Z + XYZ$$
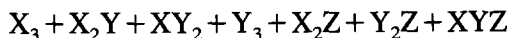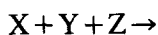
In this study the influence of the alkyne and alkyne mixtures, activation of the cocyclotrimerization of hex-1-yne, phenylacetylene and acetonitrile were investigated using CpCoCOD as catalyst.

2. Experimental

The CpCoCOD was prepared using procedures described in the literature [8,9]. A solution of 7.7×10^{-3} mol dm^{-3} CpCoCOD in dry CH_3CN and n-octane (as internal standard) was prepared and 1 cm^3 of this catalyst solution was placed by means of a syringe in a glass tube of 300 mm length and 3 mm i.d., sealed at one end. The hex-1-yne was then added so that the mole ratio hex-1-yne/Co = 236.8. The tube was sealed before heating for 5 h in a furnace or irradiating with a water-cooled Hg lamp (Quarzlampen Gesellschaft (Hanau) type Q700 (750 W)) at room temperature (20°C). If a mixture of alkynes was used the total amount of triple bonds was kept at a constant value of 1.84×10^{-3} mol in the reactor. The reactions were terminated by adding 5.5×10^{-4} mol H_2O to the system. The product mixture was analyzed with a Carlo Erba 4100 gas chromatograph with a capillary column (FS-SE-30, CB-0.25, 15 m$\times$0.32 mm). The products were identified by GC–MS measurements or by comparison with the authentic compounds.

An IR spectrophotometer cell with an adjustable path length and fitted with quarts windows was used to record the intensity of the C–H stretch vibration of the alkynes at 3295 cm^{-1}.

3. Results and discussion

To activate the cocyclotrimerization reaction of hex-1-yne and acetonitrile photochemical methods at room temperature or thermal methods can be used.

3.1. Photochemical activation

The decrease in the concentration of hex-1-yne as function of time during the cocyclotrimerization reaction with acetonitrile under irradiation with CpCoCOD as catalyst was determined by IR measurements. The results are presented in Fig. 1.

Three stages can be identify during the reaction course: A fast uptake of 2 mole hex-1-yne per
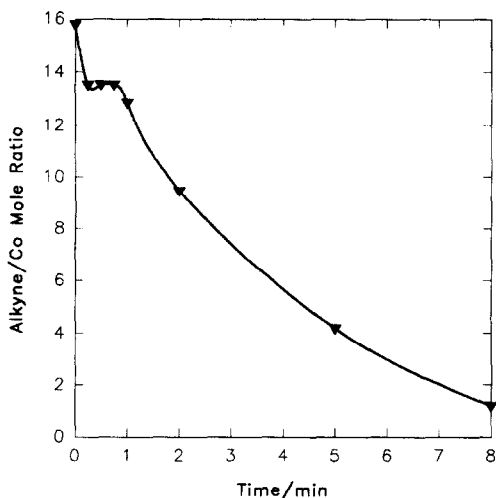
Fig. 1. The decrease in alkyne content with time of irradiation during the cocyclotrimerization of hex-1-yne and acetonitrile with CpCoCD as catalyst at 20°C.
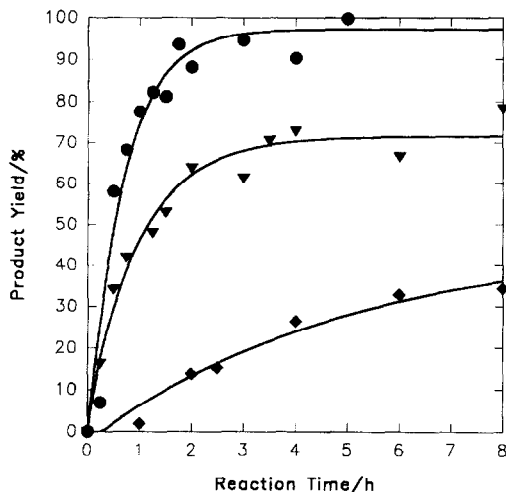

Fig. 2. The influence of the reaction time on the product yield during the cocyclotrimerization of hex-1-yne and acetonitrile at (◆ : 100°C, ▼ : 120°C, ● : 140°C).

mole cobalt (phase A), then a period with little or no consumption of the hex-1-yne (phase B) followed by a fast uptake of the alkyne during which the pyridine derivatives are formed (phase C).

The integral method together with the equation $kt_t = \ln(A_0/A_t)$ is applied to the data obtained during phase C to determine the rate constant, k, of the cocyclotrimerization reaction. A_0 is the concentration of the alkyne at the starting time, t_0, of phase C and after a time t the concentration of the alkyne is A_t. The mean value of the rate constant

determined this way is 3.66×10^{-3} s^{-1} with a correlation coefficient between 0.989 and 0.999. These results indicate that the cocyclotrimerization reaction (phase C) is a pseudo first order process with respect to the alkyne.

3.2. Thermal activation

If mixtures of hex-1-yne and acetonitrile with CpCoCOD are heated for different times and at different temperatures, it is found that the product yield increases with higher temperature and increased heating time (Fig. 2).

The reaction rate constant for the thermal activated cocyclotrimerization reaction can be obtained by using the data in Fig. 2. If it is assumed that the reaction is a first order process, the integral method can be applied by using the following equation:

$$\ln\{(P.O.)_\alpha - (P.O.)_t\} =$$
$$-kt + \ln\{(P.O.)_\alpha - (P.O.)_0\}$$

with $(P.O.)_t$ the product yield at time t and $(P.O.)_\alpha$ the final product yield. The rate constant can be obtained from the slope in Fig. 3 if $\ln\{(P.O.)_\alpha - (P.O.)_t\}$ is plotted against t.

The product formed via a first order process because a linear relationship exists between
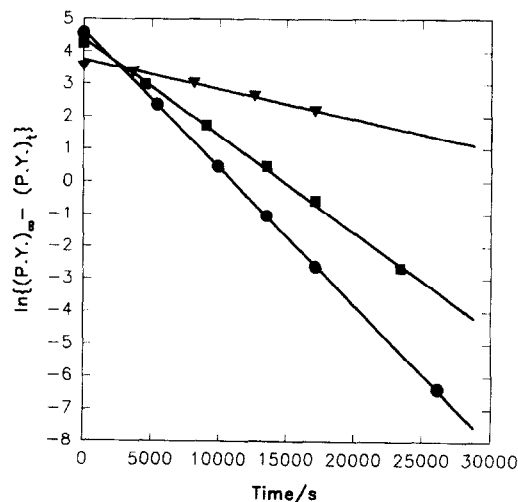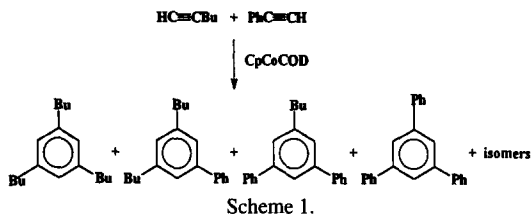

Fig. 3. The relationship between $\ln\{(P.O.)_\alpha - (P.O.)_t\}$ and the reaction time with $(P.O.)_\alpha$ the final product yield and $(P.O.)_t$ the product yield at time t for the cocyclotrimerization of hex-1-yne and acetonitrile (▼ : 100°C, ■ : 120°C, ● : 140°C).

Scheme 1.

$\ln\{(P.O.)_\alpha - (P.O.)_t\}$ and the reaction time. The rate constants obtained from the slopes are at $100°C, 0.87 \times 10^{-4} s^{-1}$, at $120°C\ 2.89 \times 10^{-4} s^{-1}$ and at $140°C\ 4.23 \times 10^{-4}\ s^{-1}$. The activation energy for the reaction is calculated as 49.6 kJ mol^{-1}.

3.3. Product distribution

Cocyclotrimerization of hex-1-yne and phenylacetylene

Hex-1-yne ($BuC\equiv CH$) and phenylacetylene cocyclotrimerize in the presence of $NbCl_5$ and $C_2H_5AlCl_2$ as catalyst. True distribution of the types of products formed is determined by the mole fraction of the alkynes initially present [7]. If CpCoCOD is used as catalyst these alkynes react in the same way to form different cocyclotrimers I, II, III and IV (Scheme 1).

The relationship between the product distribution and the phenylacetylene is indicated in Fig. 4 with Fig. 4(A) the photochemically and Fig. 4(B) the thermally activated system.

Fig. 4(A + B) shows a statistically random distribution of the cyclotrimers formed. A distortion occurs because the phenylacetylene associates

much easier with the catalyst to form the cyclotrimer that is richer in the phenyl groups than in the butyl groups.

Cocyclotrimerization of hex-1-yne and phenyl acetylene in the presence of acetonitrile

The types of products formed during the cocyclotrimerization of hex-1-yne, phenylacetylene and acetonitrile, can be divided into two series; the pyridine derivatives (V, VI and VII) (Scheme 2) and the benzene derivatives I, II, III and IV (Scheme 1).

To investigate the distribution of these products, the assumption is made that the nitrile has a constant influence on the cyclotrimerization reaction because it is used as the solvent and is always present in an excess and also that the distribution of the products is only determined by mole fraction of the alkynes present in the mixture under these conditions.

To simplify the presentation of the yield and product distribution the pyridine compounds and the benzene compounds are going to be presented separately.

The distribution of the pyridine compounds with regard to the mole fraction of the alkynes (initially) present is presented in Fig. 5(A) for the photochemically activated system and in Fig. 5(B) for the thermally activated system.

The benzene derivatives (I, II, III and IV) distribution with regard to the phenylacetylene mole fraction is given in Fig. 6(A) for the photochem-
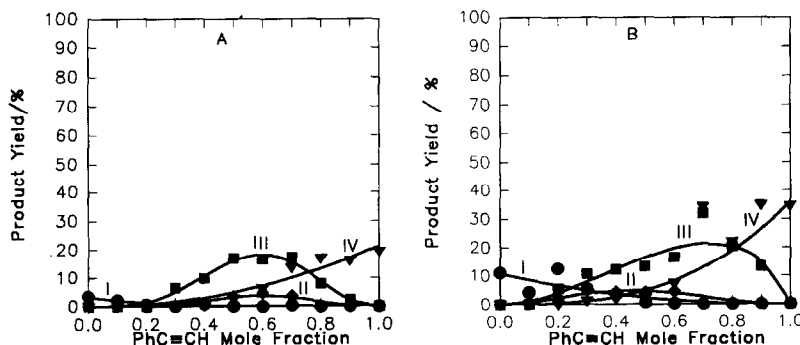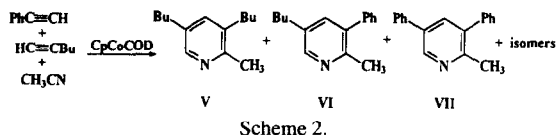

Fig. 4. The influence of the phenylacetylene mole fraction on the yield and distribution of the products during the cocyclotrimerization of phenylacetylene and hex-1-yne. (A) Photochemically activated at room temperature. (B) Thermally activated at 140°C. (I) $Bu_3C_6H_3$, (II) $Bu_2PhC_6H_3$, (III) $BuPh_2C_6H_3$, (IV) $Ph_3C_6H_3$.

Scheme 2.

ically and Fig. 6(B) for the thermally activated system.

In Fig. 7(A + B) the relationship between the mole pyridine and benzene derivatives formed during the reaction of hex-1-yne, phenylacetylene and acetonitrile is given for the photochemically and thermally processes.

At a low phenylacetylene mole fraction the main products formed are the pyridine derivatives, but as the phenylacetylene content increases, the yield of pyridine compounds declines and the yield of the benzene derivatives increases. The thermally activated systems produce at a high phenylacetylene mole fraction, almost the same amount of pyridine and benzene derivatives, but

the photochemically activated systems always produce more pyridine derivatives.

During the course of the cocyclotrimerization reaction a number of consecutive reactions must occur when CpCoCOD is used as catalyst.

The first reaction is a rapid uptake of 2 mole alkyne per mole cobalt catalyst. That implies that the COD ligand must be displaced. Bönnemann [9] indicated that this is the case while studying thermal activated systems.

During the induction period very little or no further consumption of the alkyne can be observed. A ring closure reaction to form a metallacyclopentadiene is possible at this stage but on hydrolysis the hydrolysis product $C_{12}H_{22}$ (if hex-1-yne was used as alkyne) could not be identified. The formation of the metallacyclopentadiene should then only occur at the end of the induction period (Scheme 3).
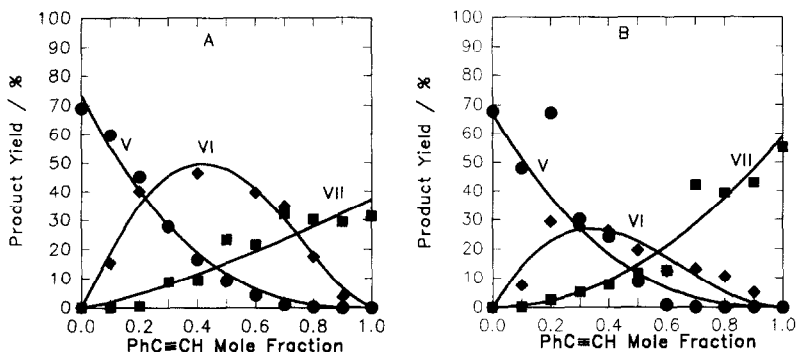

Fig. 5. The influence of phenylacetylene mole fraction on the yield and distribution of the pyridine compounds during the cocyclotrimerization of hex-1-yne and phenylacetylene in acetonitrile. (A) Photochemically activated system at room temperature. (B) Thermally activated system at 140°C. (V) $Bu_2MeC_5NH_2$, (VI) $BuPhMeC_5NH_2$, (VII) $Ph_2MeC_5NH_2$.
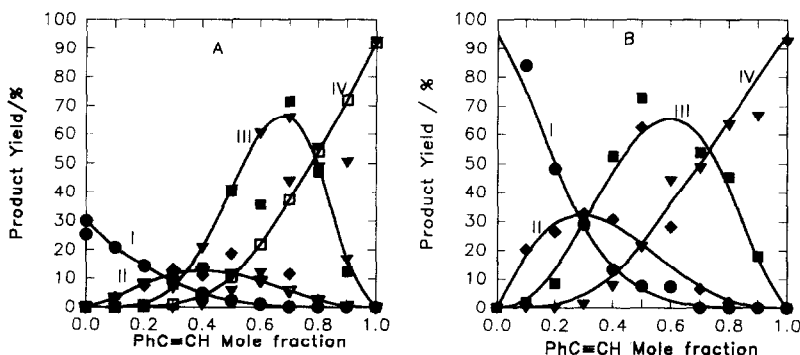

Fig. 6. The influence of the phenylacetylene mole fraction on the yield and distribution of the benzene derivatives formed during the cocyclotrimerization of hex-1-yne, phenylacetylene in acetonitrile. (A) Photochemically activated at room temperature. (B) Thermally activated system at 140°C. (I) $Bu_3C_6H_3$, (II) $Bu_2PhC_6H_3$, (III) $BuPh_2C_6H_3$, (IV) $Ph_3C_6H_3$.
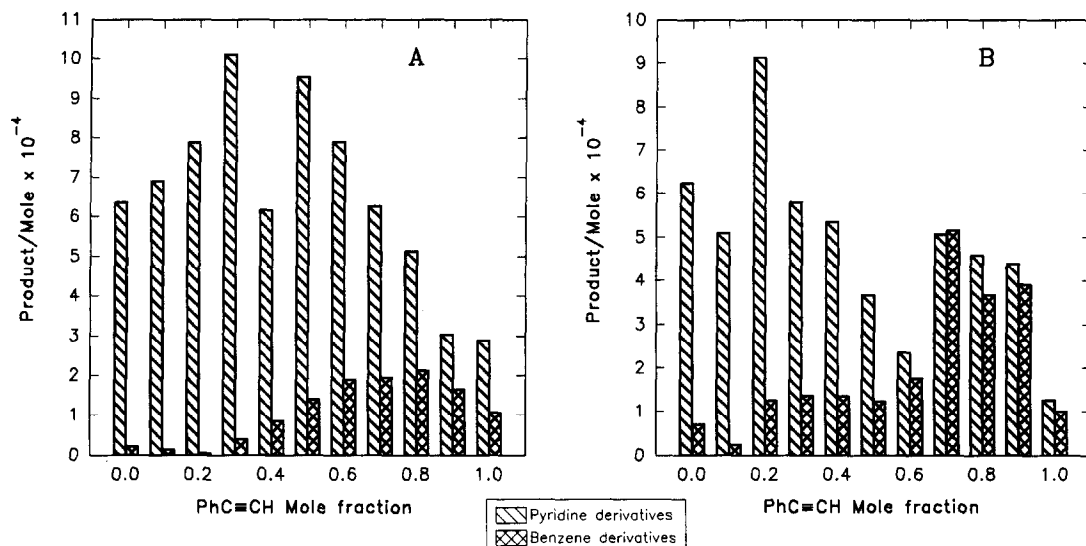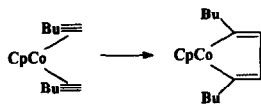
Fig. 7. The influence of the phenylacetylene mole fraction on the yield of pyridine and benzene derivatives during the cocyclotrimerization of hex-1-yne, phenylacetylene and acetonitrile. (A) Photochemically activated at room temperature. (B) Thermally activated systems at 140°C.

Scheme 3.

The existence of a metallacyclopentadiene was indicated by Wakatsuki [1] by performing the cyclotrimerization reaction in the presence of triphenylphosphine.

After the coordination of another alkyne to the metallacyclopentadiene intermediate in the absence of the nitrile, the benzene derivative is formed. The distribution of the products formed (Fig. 4) indicates that an almost statistically random coordination of the alkynes occurred at the metal centre. It is, however, clear that a preference is given to the formation of the benzene derivative that is richer in the phenyl substituent than in the butyl substituent.

If an acetonitrile molecule is added to the metallacyclopentadiene the pyridine derivative will be formed. The relationship between the pyridine and benzene derivative product distribution and the phenylacetylene mole fraction in Figs. 5, 6 and 7

indicated also a random distribution of products with some deviation from the ideal. The acetonitrile cocyclotrimerizes rather with an intermediate that is richer in the hex-1-yne component than in the phenylacetylene component to form the pyridine derivative.

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