# SELECTIVE OLIGOMERIZATION OF PHENYLACETYLENE TO 1,2,4-TRIPHENYLBENZENE CATALYZED BY Ni(CO)<sub>3</sub>(P(O-i-C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>

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#### Summary

The Ni(0) monophosphite complex, Ni(CO)<sub>3</sub>L, where  $L = P(O \cdot \cdot C_3 H_7)_3$ , oligomerizes phenylacetylene to 1,2,4-triphenylbenzene with a selectivity greater than 95%. The reaction when carried out in boiling benzene shows a high activity for the catalyst, typically 200 mol alkyne per 1 mol Ni h<sup>-1</sup>. Below 70 °C the reaction does not proceed at all for substrate/catalyst molar ratios of the order of 300. Increasing the temperature increases the conversion of the substrate and decreases the induction period. Experiments carried out in the presence of CO and free L show a decreased reaction rate, indicating a possible competition of these ligands with the alkyne for the catalyst.

#### Introduction

Several papers have appeared concerning the oligomerization of alkyl and aryl monosubstituted alkynes by Ni(0) carbonyl compounds of the type Ni(CO)<sub>4-n</sub>L<sub>n</sub>, where n = 1,2 and  $L = PR_3$  with R being alkyl and/or aryl groups [1]. The nature of the reaction products, for the same substrate, has been found to depend on the catalyst, *i.e.* with linear (mainly dimers and trimers) and cyclic (benzene derivatives) oligomers being obtained. Usually, however, only mixtures of oligomers are produced. In the case of phenylacetylene, the nature of the main product of oligomerization with Ni(CO)<sub>2</sub>-(PPh<sub>3</sub>)<sub>2</sub> is controversial. According to some reports the reaction leads to 1,2,4-triphenylbenzene [2], whereas others state that this product is obtained only to a small extent [3]. A subsequent systematic study considered the oligomerization reaction of 1-heptyne and phenylacetylene in the presence of Ni(0) carbonyl complexes variously substituted with tertiary phosphines or phosphites with the object of clarifying the influence of the substituents

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on the activity and selectivity [4]. The final conclusions pointed out the difficulties of rationalizing the results. In this work we report on the oligomerization of phenylacetylene by Ni(CO)<sub>3</sub>P(O-i-C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>.

### Experimental

### Materials

Benzene was freed from water by storage over Na metal and then distilled under nitrogen. Other chemicals were commercial products and were used without further purification.

#### Instrumental methods

Infrared spectra were recorded on a Perkin–Elmer 597 spectrophotometer as Nujol mulls or as neat liquids between caesium iodide discs. NMR spectra were recorded on Varian FT-80A and XL-100 instruments. UV and visible spectra were obtained by means of a 210 Shimadzu spectrophotometer. GLC measurements were undertaken on a Hewlett Packard 5730 gas chromatograph (column, 10% UCC W982 Chromosorb W AW DMCS, 6 ft, flow rate 10 ml min<sup>-1</sup>, carrier gas He). HPLC measurements were made on a Perkin–Elmer Series 2 liquid chromatograph (column, Perkin–Elmer Lichrosorb RP-8, 10 m, 25 cm × 4.5 mm, mobile phase 25% H<sub>2</sub>O/75% CH<sub>3</sub>CN, room temp., flow rate 2 ml min<sup>-1</sup>, pressure 15 MPa, UV detector at 250 and 350 nm; retention times:phenylacetylene, 2.3 min; 1,2,4-triphenylbenzene, 6.5 min).

## Preparation of $Ni(CO)_3P(O-i-C_3H_7)_3$

The pure complex was obtained by means of a modification of that reported in the literature [5] since no solvent was used. A two-necked graded Schlenk tube was carefully evacuated, dipped into liquid nitrogen and connected with a cylinder containing Ni(CO)<sub>4</sub>. The white solid which condensed was gently warmed to its melting point and the volume of the resulting liquid measured (ca. 2 ml). Tri-isopropyl phosphite (3.5 ml; Ni(CO)<sub>4</sub>/  $P(O-i-C_3H_7)_3 \simeq 1.2)$  was then added to the re-solidified nickel tetracarbonyl under a nitrogen atmosphere. The resulting mixture was stirred magnetically, and slowly warmed up to 0  $^{\circ}$ C over ca. 2 - 3 h, during which time the Schlenk apparatus was connected with a bubbler to observe the evolution of carbon monoxide. A gentle stream of nitrogen was then passed through the mixture at room temperature to remove excess  $Ni(CO)_4$ , as checked by the resulting IR spectrum  $[\nu(C=0)$  at 2060 cm<sup>-1</sup>]. The colourless liquid obtained was identified as pure  $Ni(CO)_3P(O-i-C_3H_7)_3$  on the basis of its IR spectrum  $[\nu(C=O) \text{ at } 2070(s) \text{ and } 1995(vs) \text{ cm}^{-1}, \text{ neat liquid}], \text{ its } {}^{31}P-\{{}^{1}H\} \text{ NMR}$ spectrum in  $C_6D_6$  showing only one peak at 154.07 ppm downfield with respect to external 85% H<sub>3</sub>PO<sub>4</sub>.

#### Oligomerization reactions

Typical reactions were carried out as follows: Ni(CO)<sub>3</sub>P(O-i-C<sub>3</sub>H<sub>7</sub>)<sub>3</sub> (50.5 mg,  $1.44 \times 10^{-3}$  M) was added to 100 ml of a carefully deaerated benzene solution of phenylacetylene (0.183 M) at the reaction temperature. The solution was stirred magnetically and thermostatted in an oil bath (±1 °C). A slow stream of nitrogen was maintained to sweep away the carbon monoxide liberated from the catalyst. The course of the reaction was generally followed by means of GLC analysis of a series of aliquots drawn out at regular intervals. Only the disappearance of phenylacetylene was observed. Occasionally, the withdrawn samples were also analysed via HPLC and IR methods in order to investigate in detail the catalytic system, and in particular to detect possible labile intermediates. No such intermediates were observed, however.

To establish the selectivity of the catalyst, the reaction was carried out under the above conditions at 85 °C. On completion of the reaction (ca. 2 h), the volume of the solution was reduced *in vacuo* to ca. 5 ml and n-hexane (20 ml) was added. A pale yellow solid separated out from the solution when the latter was kept in a refrigerator at -20 °C overnight; this was filtered off and washed with cold n-hexane (yield 1.7 g; 90%). HPLC analysis of this compound indicated the presence of only one peak, which was demonstrated to be the pure compound. Spectroscopic data (IR, UV and <sup>1</sup>H NMR) for this solid (vide infra) indicate that it is 1,2,4-triphenylbenzene.

Concentration of the mother liquor gave a yellow oil (0.16 g), HPLC analysis of which at 250 and 350 nm yielded a main peak which was attributed to 1,2,4-triphenylbenzene and a very minor peak due to an unidentified compound. The IR spectrum of the oil confirmed the presence of 1,2,4-triphenylbenzene, but also exhibited two additional peaks at 868 and 965 cm<sup>-1</sup>, probably due to the minor component observed by HPLC analysis.

### Characterization of 1,2,4-triphenylbenzene

Successive recrystallization of the pale yellow solid from a benzene/ nhexane mixture gave an off-white crystalline solid melting at 120 °C. The UV spectrum of a solution of this material in CH<sub>3</sub>CN exhibited a minimum at 229 nm ( $\epsilon = 20200$ ), a maximum at 248 nm ( $\epsilon = 36700$ ), an inflection at 270 nm and no absorption above *ca.* 320 nm (Fig. 1).

The main infrared absorption peaks of the material dissolved in Nujol/ HCDB are: 3060(m), 3020(m), 1600(s), 1575(m), 1550(m), 1473(s), 1440(m), 1385(w), 1075(s), 1031(m), 1009(m), 917(m), 896(m), 843(vs), 780(s), 765(vs), 741(s), 714(s), 704(vs), 696(vs), 636(m), 629(m), 580(s), 540(s), 522(m) and 508(m) (cm<sup>-1</sup>) The solid had a molecular weight in 1,2dichloroethane at 43 °C of 304 (calcd. 306.4), while its <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub> was identical to that reported in the literature (Sadtler Catalog 5082 M) for 1,2,4-triphenylbenzene.





### **Results and discussion**

Under the reaction conditions employed, phenylacetylene is converted almost quantitatively into 1,2,4-triphenylbenzene with a selectivity of the order of 96 - 97%. Appreciable variations of selectivity have not been observed under the different experimental conditions (see below).

The influence of temperature and of the concentration of the substrate, catalyst and ligands (CO and tri-isopropylphosphite) on the course of the reaction are discussed briefly below.

#### Influence of temperature

A plot of the percentage conversion *versus* time for a substrate/catalyst molar ratio of 127 is shown in Fig. 2.

The most significant features of this plot are (a) at temperatures below 70 °C the reaction proceeds very slowly; (b) on increasing the temperature, the length of the induction period decreases; (c) at lower temperatures the reaction attains equilibrium at correspondingly smaller conversions (for example, at 70 °C the conversion is less than 30%); and (d) the course of the reaction is typical of an autocatalytic process, indicating that the active species are formed through interaction of the catalyst with the substrate. That equilibrium is achieved is demonstrated by the fact that at lower temperatures (where such equilibrium is more evident) the formation of catalytically inactive species, since the former are more stable thermally.

### Influence of free ligand concentration

## Free carbon monoxide

When carried out in solution saturated with CO the catalytic process is completely inhibited, demonstrating that the reaction path leading to the



Fig. 2. Temperature dependence of the rate of conversion of PhC=CH. Data correspond to 71 °C ( $^{\triangle}$ ), 75 °C (\*), 78 °C ( $^{\bigcirc}$ ) and 82 °C ( $^{\Box}$ ), respectively. [PhC=CH] = 0.183 M; [Ni(CO)L<sub>3</sub>] = 0.0144 M.

catalytically active species involves the substitution of the CO ligand by the added alkyne at the nickel centres. The possibility of dissociation of the phosphite ligand cannot, however, be ruled out but if that were to occur the excess CO would then probably react with the coordinatively unsaturated species to form  $Ni(CO)_4$ ; excess CO would prevent dissociation of the latter compound to afford the catalytically active species.

#### Free phosphite

Addition of tri-isopropylphosphite (molar ratio free phosphite/catalyst = 1 - 10) slows down the rate of conversion of the alkyne and also drastically reduces the yield of oligomers (Fig. 3). This suggests that free phosphite inhibits the oligomerization process through substitution of CO at the nickel centre and/or through a decrease in the dissociation of the initial complex, thus generating a low concentration of the coordinatively unsaturated species in the reacting system. In other words, free phosphite competes efficiently with the alkyne for the Ni complex.

### Influence of catalyst and substrate concentration

When the reaction is carried out at 80 °C at a constant concentration of catalyst  $(1.44 \times 10^{-3} \text{ M})$ , a change in the substrate concentration from 0.091 M to 0.70 M reduces the percentage conversion. Figure 4 enables the best conditions for the complete conversion of phenylacetylene to be chosen; for concentrations of alkyne higher than about 0.4 M the reaction is incomplete.



Fig. 3. Influence of free phosphite concentration on the conversion rate of PhC=CH. [L] = 0 ( $\bullet$ ); 0.0015 M ( $^{\circ}$ ); 0.03 M ( $^{\triangle}$ ); and 0.15 M (\*), respectively. [PhC=CH] = 0.183 M; [Ni(CO)L<sub>3</sub>] = 0.0144 M.



Fig. 4. Influence of phenylacetylene concentration on the conversion rate of PhC=CH. [PhC=CH] = 0.7 M ( $^{\circ}$ ); 0.36 M ( $^{\triangle}$ ); 0.183 M ( $^{\Box}$ ); and 0.09 M (\*), respectively. [Ni-(CO)L<sub>3</sub>] = 0.0144 M.

Under the same conditions, but with the substrate concentration maintained at 0.183 M, an increase in the catalyst concentration from  $1.44 \times 10^{-3}$  M to  $1.44 \times 10^{-2}$  M completely removes the induction period and shortens the time required for complete oligomerization (Fig. 5). This suggests that the steps leading to the generation of the catalytically active species are largely dependent on the concentration of the catalyst and, to a lesser extent, on the concentration of the substrate. The latter, on the other hand, plays a crucial role in determining the lifetime of the catalyst, suggest-ing the presence of non-catalytic, competitive and associative processes which depend on the substrate concentration.



Fig. 5. Influence of catalyst concentration on the conversion rate of PhC=CH. [Ni-(CO)L<sub>3</sub>] =  $1.44 \times 10^{-3}$  M ( $^{\circ}$ ); and  $1.44 \times 10^{-2}$  M ( $^{\circ}$ ), respectively. [PhC=CH] = 0.183 M.

## Conclusion

Although the composition of the product of the oligomerization of monosubstituted alkynes is to some extent dependent upon the nature of the catalyst, no clear trends may be discussed in the literature. The much higher selectivity of Ni(CO)<sub>3</sub>P(O-i-C<sub>3</sub>H<sub>7</sub>)<sub>3</sub> in contrast to Ni(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> in the oligomerization of phenylacetylene is not completely understood at this stage, and the existence of different pathways (*i.e.* involving either nickel hydride or nickelacyclopentadiene intermediates [1, 4]) complicates the situation even further. Although no intermediates have been isolated in the present study, the nature of the product (*i.e.* 1,2,4-triphenylbenzene) suggests that with Ni(CO)<sub>3</sub>P(O-i-C<sub>3</sub>H<sub>7</sub>)<sub>3</sub> the catalytic reaction proceeds through the intermediacy of nickelacyclopentadiene derivatives of the type



A catalytic cycle for the cyclotrimerization of monosubstituted alkynes to 1,2,4-substituted benzenes involving the above intermediate has been proposed recently [1]. A systematic investigation is in progress in our laboratory to assess the role of ancillary ligands in the catalyst and the nature of the alkyne in the oligomerization process.

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