

## COOLIGOMERIZATION OF PROPADIENE WITH PROPYNE CATALYSED BY NICKEL(0) COMPLEXES

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Cooligomerization of propadiene with propyne catalysed by bis(1,5-cyclooctadiene)nickel and tetrakis(triphenylphosphine)nickel gives a variety of products, including besides the cooligomers also the homooligomers of both monomers. The type of catalyst affects partially the product distribution due to changes in the degree of oligomerization. Cooligomerization of propadiene with 3-deuteriopropyne provided information about relative proportion of propadiene and propyne units in the oligomers.

At present, homogeneously catalysed oligomerizations of all the basic types of unsaturated hydrocarbons (alkenes, 1,3- and 1,2-alkadienes and alkynes) are well known<sup>1</sup>. Therefore, attention has been paid to the study of cooligomerization of hydrocarbons<sup>2</sup> and also to the cooligomerization with their hetero analogues<sup>3</sup>.

Oligomerizations of propadiene<sup>4,5</sup> and propyne<sup>6</sup> catalysed by nickel(0) complexes are well studied reactions. On the other hand, cooligomerizations of these mutually isomeric hydrocarbons have only scarcely been investigated<sup>7</sup>. For that reason, in the present work we report on the spectrum of products of this reaction.

*Catalysts.* Cooligomerization of propadiene with propyne was effected by Benson and Lindsey<sup>7</sup> with nickel(II) 2,4-pentanedionate as the catalyst. The catalytically active complex proper is believed<sup>8</sup> to contain zerovalent nickel that is formed from the nickel pentanedionate during induction period of the reaction. To suppress this period we have chosen directly nickel(0) complexes of two types. The first one was the so-called „naked” nickel, i.e. the nickel atom surrounded by weakly coordinating ligands which can be easily displaced during catalytic process. The second type was represented by a zerovalent nickel complex containing only phosphine ligands. We have used tetrakis(triphenylphosphine)nickel for this purpose.

*Identification of products.* Initial exploratory experiments showed that the cooligomerization of propadiene with propyne catalysed by zerovalent nickel complexes yields a variety of products. These are hydrocarbons of the formula  $(C_3H_4)_n$  (where  $n$  is the degree of oligomerization) which at the given degree of oligomerization are

constitutional or configurational isomers. Therefore, we have used gas chromatography/mass spectrometry as the suitable method for their unambiguous identification. Although retention times of the oligomers were not uniformly distributed on the time scale and were grouped into several sets according to the degree of oligomerization, with one exception (see later) all the oligomers were well separated from each other.

Another information concerning the identification of formed oligomers provided their mass spectrum which always showed sufficiently intense molecular ion. Although the spectra of some oligomers were essentially identical, the sufficiently reliable characteristics of a given individual compound was found to be the mass spectrum vs retention time couple under identical chromatographic conditions.

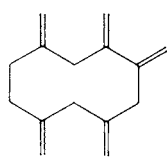
### *Homooligomerization*

In order to detect the possible presence of propadiene and propyne homooligomers in the mixture of oligomerization products, we examined first the homooligomerization of both monomers. The oligomerization of propadiene catalysed by bis(1,5-cyclooctadiene)nickel yields in accordance with reported data<sup>4,5</sup> 1,2,4,6,9-pentamethylenecyclodecane (*I*) and higher oligomers, while with tetrakis(triphenylphosphine)nickel, the reaction gives besides pentamer *I* also the tetramer 1,2,4,7-tetramethylenecyclooctane (*II*) and isomeric trimers, 1,2,4-trimethylenecyclohexane (*III*) and 1,3,5-trimethylenecyclohexane (*IV*). The structure of the products isolated by distillation with the use of analytical microcolumn was deduced from mass, <sup>1</sup>H and <sup>13</sup>C NMR and IR spectra which agreed with reported data<sup>4,5</sup>.

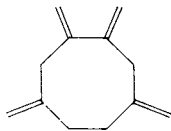
The oligomerization of propyne catalysed by bis(1,5-cyclooctadiene)nickel afforded the same products as were those reported by Simons and Lagowski<sup>6</sup>, i.e. a linear trimer, 2,4-dimethyl-1,3-heptadien-5-yne (*V*), cyclic trimers, 1,2,4-trimethylbenzene (*VI*) and 1,3,5-trimethylbenzene (*VII*), and cyclic tetramers, 1,3,5,7-tetramethylcyclooctatetraene (*VIII*), 1,2,4,6-tetramethylcyclooctatetraene (*IX*), and 1,2,4,7-tetramethylcyclooctatetraene (*X*).

The tetramers could not be individually isolated and thus the structure was assigned unambiguously only to the product *VIII* which was prepared by an independent synthesis<sup>9</sup>. However, the <sup>13</sup>C NMR spectrum of a mixture of tetramers which gave three different chromatographic peaks in GC/MS analysis with the essentially identical mass spectra indicates the presence of one minor and three main isomers. Carbon chemical shifts of the main products agree well with reported shifts<sup>6</sup> for substances *VIII*–*X*.

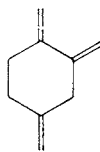
The structure of linear trimer *V* was derived from the structure of its Diels–Alder adduct<sup>6</sup> with tetracyanoethylene (*Va*) which in turn was determined from its mass and NMR spectra.



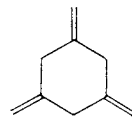
I



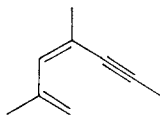
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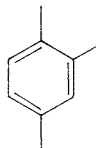
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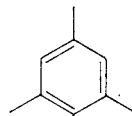
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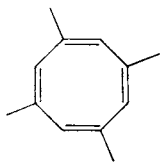
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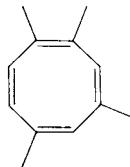
VI



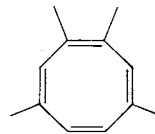
VII



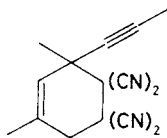
VIII



IX



X



Va

### Cooligomerization

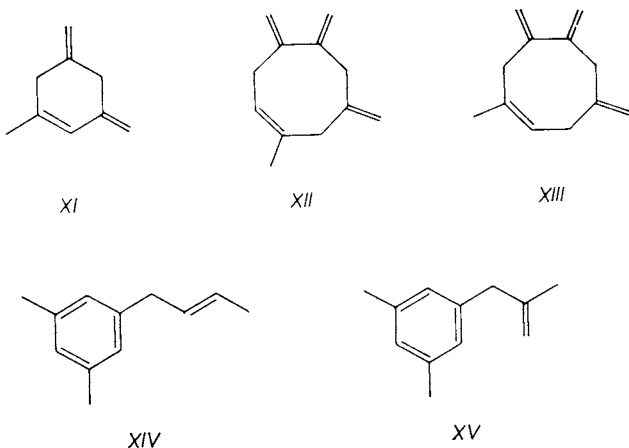
The cooligomerization of propadiene with propyne catalysed by bis(1,5-cyclooctadiene)nickel gives homooligomers of both monomers *I* and *V–X* and the following cooligomers: 1-methyl-3,5-dimethylenecyclohexene (*XI*), 1-methyl-4,5,7-trimethylenecyclooctene (*XII*), 2-methyl-4,5,7-trimethylenecyclooctene (*XIII*), (*E*)-1-(2-butenyl)-3,5-dimethylbenzene (*XIV*), and 3,5-dimethyl-1-(2-methyl-2-propenyl)benzene (*XV*).

Except products *XII* and *XIII*, the above cooligomers were isolated as individual substances by distillation on analytical microcolumn and their structure was assigned on the basis of  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, IR and mass spectra. Products *XII* and *XIII*

were not separated from each other, not even on using GC/MS method. The presence of two isomers in c. 2 : 1 ratio in the isolated mixture was detected by  $^{13}\text{C}$  NMR of the mixture.

The cooligomerization catalysed by tetrakis(triphenylphosphine)nickel leads to somewhat different results. Propyne cyclotetramers VIII–X are not formed. On the other hand, the reaction affords all the propadiene oligomers I–IV. As far as cooligomers are concerned, products XII and XIII are not produced but the cotrimer XI formed is accompanied by three other cotrimers designated as A, B, and C.

In addition to the above substances, further 28 minor products were detected in the reaction mixtures, the amount of which did not exceed 1 per cent.



### Deuterium Trace Experiments

As mentioned above, cooligomers are not formed in homooligomerizations. This indicates that in the oligomerizations, the mutual isomerization of propadiene and propyne does not proceed. However, double bond isomerization in intermediate nickel complex containing coordinated oligomeric ligand or isomerization of the already during cooligomerization formed oligomer producing its isomer cannot be excluded.

To determine relative proportion of the units of given monomers in individual oligomers, we performed cooligomerization of propadiene with 3-deuteriopropyne and analysed the product mixture so formed by GC/MS. The same conditions were used in the cooligomerization of propadiene with undeuteriated propyne. Chromatograms of both reaction mixtures were practically identical.

The number of  $m/z$  units by which the  $m/z$  value of molecular ion of the given oligomer is shifted toward higher values, gives the number of propyne units from

TABLE I  
Relative intensities of ions in the vicinity of molecular ions of oligomers in the oligomerizations with traced and untraced propyne

Compound	Reaction <sup>a</sup>	propyne					traced propyne				
		$M^{++} - 1$	$M^{++}$	$M^{++} + 1$	$M^{++} - 1$	$M^{++}$	$M^{++} + 1$	$M^{++} + 2$	$M^{++} + 3$	$M^{++} + 4$	$M^{++} + 5$
<i>I</i> <sup>b</sup>	CP	0	100	32	0	100	66	41			
<i>II</i>	CP	36	100	15	54	100	14				
<i>III</i>	CP	11	100	10	12	100	10				
<i>V</i>	CP	38	100	10				47	100	10	
	CH						15	42	100	12	
	HP	45	100	10				47	100	10	
<i>VI</i>	CP	24	100	10			21	80	100	10	
	CH	32	100	12		7	16	40	100	12	
	HP	28	100	11				32	100	11	
	HH	24	100	10				31	100	10	
<i>VII</i>	CP	12	100	11			24	100	42		
	CH	26	100	11		15	65	93	100	12	
	HP	26	100	11				31	100	10	
	HH	23	100	10				31	100	10	
<i>VIII</i>	CH	11	100	13					21	100	18
	HH	8	100	14					18	100	14



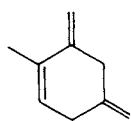
which the given oligomer was formed. If all oligomer molecules are formed at the same ratio of monomer units,  $(M^{+} + 1)$  and  $(M^{+} - 1)$  ions are formed in approximately the same relative proportion to molecular ion both for the traced and untraced oligomer.

The fact that 1,5-cyclooctadiene (from the catalyst) in the reaction mixtures with traced propyne does not contain deuterium documents the absence of intermolecular deuterium exchange during the reaction and subsequent chromatographic separation.

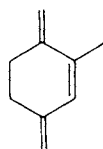
From Table I it is seen that products of the oligomerization can be divided into two groups. The first group includes the oligomers which are always formed from the same ratio of monomer units. Here are propadiene homooligomers, propyne homooligomers *V* and *VIII*–*X*, and cooligomers *XI*–*XIV*, *A*, *B*, and *C*. The high isotopic purity of these products speaks again for the absence of intermolecular deuterium exchange.

The second group of oligomers includes the products with noninteger number of deuterium atoms. Somewhat surprising is the fact that besides cooligomer *XV*, also propyne cyclotrimers *VI* and *VII* belong to this group. Although in homooligomerization the above compounds can be formed only from propyne, it seems likely that in the cooligomerization also propadiene molecule could be built in into the skeleton. Thus, the part of cyclotrimers *VI* and *VII* is formed from other cyclic cotrimers.

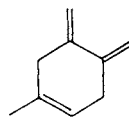
It is of interest that alkenyldimethylbenzenes *XIV* and *XV* are not formed from the same ratio of propadiene to propyne molecules (Table I), although at first sight both compounds are alike. While oligomer *XIV* contains only one propadiene molecule, the mass spectrum of traced product *XV* documents that approximately one half of the total amount of compound *XV* is formed during cooligomerization from two molecules of propadiene.



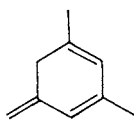
XVI



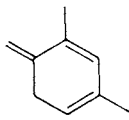
XVII



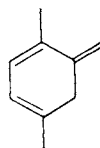
XVIII



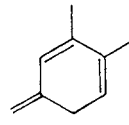
XIX



XX



XXI



XXII

From this finding one can deduce for compound *XIV* that the hydrogen transfer required for formation of this compound has to be an intramolecular process. Compound *XV* can be either a mixture of oligomers having the propadiene to propyne ratio 1 : 3 and 2 : 2, both being formed with intramolecular hydrogen transfer or such an intermolecular process should be admitted for this compound. The first alternative is more likely in view of the absence of deuterium in cyclooctadiene.

Another reason for performing trace experiments was our intention to determine the structure of cotrimers *A*, *B* and *C*. As follows from Table I, all the products are cooligomers of propadiene with propyne in the 2 : 1 ratio. If we deal with cyclic cotrimers, of eight possible structures *XI*, *XVI*–*XXII*, the structures *XIX* to *XXII* can be excluded because of their reverse propadiene to propyne ratio, along with the product *XI*.

#### Isomerization of Mixtures of Cotrimers

With the aim to prove the proposed structures *XVI*–*XVIII* for the cyclic cotrimers formed in the cooligomerization catalysed by tetrakis(triphenylphosphine)nickel, we have performed isomerizations (aromatizations) of mixtures of these three products together with oligomers *VI*, *VII*, and *XI* (altogether six compounds in the mixture), using rhodium trichloride hydrate in ethanol. Distillation of the reaction mixture from the cooligomerization yielded four fractions – the mixtures differently enriched by individual oligomers – the composition of which before isomerization was determined by gas chromatography. The same procedure was used to determine the composition after isomerization, where the mixtures contained only 1,2,4- and 1,3,5-trimethylbenzene. This confirms the cyclic structure of cooligomers *A*, *B*, and *C*.

TABLE II

Composition (in %) of a mixture of oligomers prior to and after their aromatization with rhodium trichloride in ethanol

Before isomerization							After isomerization	
<i>A</i>	<i>XI</i>	<i>B</i>	<i>C</i>	<i>VI</i>	<i>VII</i>	1,2,4- <sup>a</sup>	<i>VI</i>	<i>VII</i>
7	84	0	0	0	9	7	8	92
1	58	25	6	0	9	31	28	72
0	26	22	6	7	38	35	37	63
0	27	22	13	8	29	43	40	60

<sup>a</sup> Calculated under assumption that oligomers *A*, *B*, and *C* have the 1,2,4-arrangement of substituents.



These compounds should have the 1,2,4-arrangement of substituents (methyl or exomethylene) at the six-membered ring, since they contain one propyne unit and are not identical with cooligomer *XI*. Aromatization of these products would lead to formation of 1,2,4-trimethylbenzene, while the oligomer *XI* is converted into 1,3,5-trimethylbenzene by isomerization. The percentual amount of the oligomers with 1,2,4- and 1,3,5-arrangement in all the mixtures should be the same within experimental error as that before isomerization, which is really the case (see Table II).

Therefore, cyclic cotrimers of propadiene and propyne designated as *A*, *B*, and *C* were assigned the structures *XVI*, *XVII*, and *XVIII*.

### Conclusions

The cooligomerization of propadiene with propyne catalysed by nickel(0) complexes affords 15 main products in yields exceeding 1 per cent and 28 other minor products. On using nickel(0) complex containing phosphine ligands, the cooligomerization degree decreases by one compared to "naked nickel" (i.e. cyclic cotetramers *XII* and *XIII* are not formed) in accordance with the same decrease of the degree of oligomerization in the homooligomerization of propyne (cyclotetramers *VIII*–*X* are not formed) as well as in the homooligomerization of propadiene (also lower oligomers *II*–*IV* are formed).

Except the linear propyne trimer *V* and alkenylbenzenes *XIV* and *XV*, all the oligomers can be formed by subsequent combination of monomer units (the so-called zipper-type process), analogously to the cyclotetramerization of acetylene, in which case such a process was proved by Colborn and Vollhardt<sup>10</sup>.

It is worth mentioning that the oligomerization catalysed by nickel(0) produces the oligomers traced in the methyl group with high isotopic purity.

### EXPERIMENTAL

Bis(1,5-cyclooctadiene)nickel<sup>11</sup> and tetrakis(triphenylphosphine)nickel<sup>12</sup> were obtained by reported procedures, as indicated. Toluene (Lachema, Brno), propadiene and propyne (both Matheson, U.S.A.) were dried with toluene solution of sodium bis(2-methoxyethoxy)aluminium dihydride (Synhydrid produced by Lachema, Kolín). 3-Deuteriopropyne was prepared<sup>13</sup> and purified<sup>14</sup> by usual procedures and dried by passing over solid phosphorus pentoxide. Gas chromatography on the alumina wetted by 2% silicone oil showed that the compound is of 99.5% purity; the isotopic purity 98% was determined by mass spectrometry using Shimadzu QP-1 000 at ionization energy of 70 eV.

All manipulations with solid Ni(0) complexes were made in argon atmosphere using Schlenk vessel technique. The preparation and handling of Ni(0) complex solutions was made in vacuo of c.  $10^{-2}$  Pa. Similarly, also monomers were fed via distillation in vacuo.

*Spectral measurements.* Mass spectra of oligomer mixtures were measured on Jeol JMS DX-303 by GC/MS technique within  $m/z$  35–250 with the resolution  $R_{10\%} = 1\,500$ , accelerating voltage 3 kV, ionization energy 70 eV and ionization current 300  $\mu$ A. Chromatographic analysis

was made on 60 m-long quartz capillary column wetted by OV-101 silicone elastomer at the programmed temperature 100–235°C, 4°C min<sup>-1</sup> rate. IR spectra of isolated oligomers were recorded with Specord 75 IR spectrophotometer, using undiluted films of compounds between KBr windows. <sup>1</sup>H and <sup>13</sup>C NMR spectra of isolated oligomers were measured with Varian XL 200 spectrometer at 200 and 50.3 MHz, respectively. The reference compound for <sup>1</sup>H NMR spectra was hexamethyldisilane ( $\delta(\text{HMDSS}) = 0.04$ ) and that for <sup>13</sup>C NMR spectra was deuteriochloroform ( $\delta(\text{C}^2\text{HCl}_3) = 76.99$ ). Chemical shifts are given in  $\delta$  scale.

#### Oligomerization — General Procedure

The known amount of nickel catalyst was weighed and transferred into a vacuum flask. Then, 180–200 ml of toluene and the monomers were distilled into the flask which was sealed and placed into a temperature-controlled bath where it was maintained with magnetic stirring for a required reaction time. After cooling and flask opening, 5 g of diacetyldioxime were added and after at least one day-standing with intermittent shaking, the reaction mixture was filtered off. The solution of oligomers so obtained was freed off toluene in vacuo, using a semimicro-distillation column MS 500 (Fischer Labor-und Verfahrenstechnik, Bonn, F.R.G.). The condensed reaction mixture was then fractionated on the same column.

#### Homooligomerization of Propadiene

A total of 17.1 g of propadiene was allowed to react in the presence of 2.24 g of [Ni(PPh<sub>3</sub>)<sub>4</sub>] at 100°C for 20 h, giving a mixture of products which was divided into the following fractions by distillation: fraction 1, b.p. 47°C/2.7 kPa, 1.8 g, 75% *III* and 25% *IV*; fraction 2, b.p. 75°C/1.2 kPa, 3.5 g, *II*; fraction 3, b.p. 117°C/1.2 kPa, 1.5 g, *I*.

To obtain the pure trimer *III*, 18 g of propadiene were oligomerized in the presence of 3.8 g of [Ni(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>] as the catalyst at 100°C for 27 h. The reaction afforded the trimer fraction 4, b.p. 47°C/2.7 kPa, 2.0 g, *III*.

1,2,4-*Trimethylenecyclohexane* (*III*) — mass spectrum gives the formula C<sub>9</sub>H<sub>12</sub>; IR spectrum (cm<sup>-1</sup>): 3 069 s, 2 974 s, 2 935 s, 2 894 s, 2 836 m, 2 802 m, 1 781 w, 1 648 vs, 1 631 m, 1 434 s, 1 417 s, 1 287 w, 885 vs; <sup>1</sup>H NMR spectrum (C<sup>2</sup>HCl<sub>3</sub>): 2.31 s, 4 H (—CH<sub>2</sub>—); 2.97 m, 2 H (—CH<sub>2</sub>—); 4.67–4.74 bm, 4 H (=CH<sub>2</sub>); 4.97 m, 1 H (=CH<sub>2</sub>); 5.04 m, 1 H (=CH<sub>2</sub>).

A mixture of 1,2,4-*trimethylenecyclohexane* (*III*, 75%) and 1,3,5-*trimethylenecyclohexane* (*IV*, 25%) — mass spectra for both compounds give the formula C<sub>9</sub>H<sub>12</sub>; <sup>1</sup>H NMR spectrum of the mixture (C<sup>2</sup>HCl<sub>3</sub>): 2.31 s, 4 H (—CH<sub>2</sub>—); 2.93 m, 6 H' (—CH<sub>2</sub>—); 2.97 m, 2 H (—CH<sub>2</sub>—); 4.65–4.74 bm, 4 H 6 H' (=CH<sub>2</sub>); 4.97 m, 1 H (=CH<sub>2</sub>); 5.04 m, 1 H (=CH<sub>2</sub>); <sup>13</sup>C NMR spectrum of the mixture (C<sup>2</sup>HCl<sub>3</sub>): 34.44 t, 35.10 t, 42.23 t (2 C), 107.76 t, 108.12 t (2 C), 108.89 t, 145.84 s, 146.51 s, 147.67 s, 147.84 s.

1,2,4,7-*Tetramethylenecyclooctane* (*II*) — mass spectrum gives the formula C<sub>12</sub>H<sub>16</sub>; IR spectrum (cm<sup>-1</sup>): 3 066 s, 2 972 s, 2 922 vs, 2 851 m, 1 788 w, 1 637 vs, 1 622 s, 1 433 s, 1 279 w, 1 150 w, 889 vs; <sup>1</sup>H NMR spectrum (C<sup>2</sup>HCl<sub>3</sub>): 2.22 s, 4 H (—CH<sub>2</sub>—); 2.97 s, 4 H (—CH<sub>2</sub>—); 4.69–4.73 m, 6 H (=CH<sub>2</sub>); 4.87 m, 2 H (=CH<sub>2</sub>); <sup>13</sup>C NMR spectrum (C<sup>2</sup>HCl<sub>3</sub>): 36.68 t (2 C), 43.63 t (2 C), 112.46 t (2 C), 112.96 t (2 C), 149.01 s (2 C), 150.02 s (2 C).

1,2,4,6,9-*Pentamethylenecyclodecane* (*I*) — mass spectrum gives the formula C<sub>15</sub>H<sub>20</sub>; IR spectrum (cm<sup>-1</sup>): 3 067 s, 2 973 s, 2 918 s, 2 897 s, 2 846 m, 1 793 w, 1 731 vw, 1 636 vs, 1 592 m, 1 440 s, 1 276 w, 1 149 vw, 888 vs; <sup>1</sup>H NMR spectrum (C<sup>2</sup>HCl<sub>3</sub>): 2.26 s, 4 H (—CH<sub>2</sub>—); 2.80 s, 2 H (—CH<sub>2</sub>—); 3.00 s, 2 H (—CH<sub>2</sub>—); 3.02 s, 2 H (—CH<sub>2</sub>—); 4.80–4.94 bm, 8 H (=CH<sub>2</sub>); 5.14 d, 1 H (=CH<sub>2</sub>); 5.18 d, 1 H (=CH<sub>2</sub>); <sup>13</sup>C NMR spectrum (C<sup>2</sup>HCl<sub>3</sub>): 33.66 t, 34.88 t, 41.70 t, 42.15 t, 42.81 t, 113.32 t, 113.37 t, 114.01 t, 115.02 t, 115.30 t, 145.66 s, 146.70 s, 146.82 s, 147.12 s, 147.28 s.

## Homooligomerization of Propyne

A total of 18 g of propyne was oligomerized in the presence of 2 g of  $[\text{Ni}(\text{COD})_2]$  (COD = 1,5-cyclooctadiene) at 90°C for 20 h. The mixture so obtained was divided by distillation into three fractions: fraction 5, b.p. 162°C, 1.1 g *VII*; fraction 6, b.p. 63°C/2.4 kPa, 2.01 g *VI*; fraction 7, b.p. 98°C/3.3 kPa, 4.3 g, mixture of *VII*, *IX*, and *X*.

According to the GC/MS analysis, besides the above compounds, the reaction mixture contains also another substance. For identification purposes, the oligomerization of propyne was carried out again under the same conditions. Distillation afforded fraction 8 boiling at 27 to 41°C/0.67 kPa, 4.2 g, mixture of *V*, *VI*, and *VII* and fraction 9, b.p. 66°C/0.67 kPa, 4.5 g, practically identical with fraction 7.

Fraction 8 (1 g) was diluted with 1 ml of benzene and then 250 mg of solid tetracyanoethylene were added. After the cyanoethylene dissolution, 4 ml of pentane were added and the white crystalline precipitate was isolated by filtration with suction, washed with 4 ml of pentane and dried at 20 Pa for 0.5 h, giving 460 mg of the adduct (*Va*) of compound *V* with tetracyanoethylene.

1,3,5-*Trimethylbenzene* (*VII*) and 1,2,4-*trimethylbenzene* (*VI*) were identified by mass spectrum,  $^1\text{H}$  and  $^{13}\text{C}$  NMR and IR spectra; all the data agreed with reported values.

A mixture of 1,3,5,7-*tetramethylcyclooctatetraene* (*VIII*), 1,2,4,6-*tetramethylcyclooctatetraene* (*IX*) and 1,2,4,7-*tetramethylcyclooctatetraene* (*X*) — mass spectra for all three compounds gave the formula  $\text{C}_{12}\text{H}_{16}$ ;  $^1\text{H}$  NMR spectrum of the mixture ( $\text{C}^2\text{HCl}_3$ ): 1.63–1.80 m, 3 H ( $-\text{CH}_3$ ), 5.44–5.48 bm, 1 H ( $-\text{CH}=\text{}$ );  $^{13}\text{C}$  NMR spectrum of the mixture ( $\text{C}^2\text{HCl}_3$ ): 21.36 q, 21.58 q, 21.64 q, 21.75 q, 23.17 q, 23.37 q, 23.59 q, 23.65 q, 125.39 d, 125.54 d, 125.77 d, 125.81 d, 127.96 d; 128.05 d, 128.36 d, 137.93 s, 137.97 s, 138.27 s, 140.14 s, 140.30 s, 140.71 s, 140.75 s.

*Diels-Alder adduct Va* of 2,4-*dimethyl-1,3-heptadien-5-yne* with *tetracyanoethylene* — mass spectrum gives the formula  $\text{C}_{15}\text{H}_{12}\text{N}_4$ ;  $^1\text{H}$  NMR spectrum ( $\text{C}^2\text{HCl}_3$ ): 1.78 s, 3 H ( $-\text{CH}_3$ ); 1.87 s, 6 H ( $-\text{CH}_3$ ); 3.05 s, 2 H ( $-\text{CH}_2-$ ); 5.50 s, 1 H ( $-\text{CH}=\text{}$ );  $^{13}\text{C}$  NMR spectrum ( $\text{C}^2\text{HCl}_3$ ): 3.52 q, 22.38 q, 27.99 q, 36.38 t, 37.26 s, 39.43 s, 47.55 s, 74.87 s, 88.03 s, 109.43 s, 110.16 s, 110.27 s, 111.82 s, 124.21 d, 126.73 s.

## Cooligomerization of Propadiene with Propyne

A mixture of 12.6 g of propadiene and 6.3 g of propyne reacted in the presence of 1.5 g of  $[\text{Ni}(\text{COD})_2]$  at 40°C for 4 h to give a mixture of products which was cut by distillation into fraction 10, b.p. 52°C/2 kPa, 0.8 g, *XI*; fraction 11, b.p. 85°C/1.1 kPa, 0.6 g, mixture of *XII* and *XIII*.

A mixture of 14.4 g of propadiene and 7.2 g of propyne gave in the presence of  $[\text{Ni}(\text{PPh}_3)_4]$  (70°C, 22 h) a mixture of products which was cut by distillation into fraction 12, b.p. 64°C/3.3 kPa, 0.35 g, 7% *A*, 84% *XI*, 9% *VII*; fraction 13, b.p. 64°C/3.3 kPa, 0.43 g, 58% *XI*, 25% *B*, 6% *C*, 9% *VII*; fraction 14, b.p. 55°C/1.3 kPa, 0.60 g, 26% *XI*, 22% *B*, 6% *C*, 7% *VI*, 38% *VII*; fraction 15 boiling at 55 to 62°C/1.3 kPa, 0.34 g, 27% *XI*, 22% *B*, 13% *C*, 8% *VI*, 29% *VII*; fraction 16, b.p. 75°C/1.1 kPa, 2.21 g, *II*; fraction 17, b.p. 93°C/1.5 kPa, 0.15 g, *XV* and fraction 18, b.p. 103°C/1.5 kPa, 0.13 g, *XIV*.

1-*Methyl-3,5-dimethylenecyclohexene* (*XI*) — mass spectrum gives the formula  $\text{C}_9\text{H}_{12}$ ; IR spectrum ( $\text{cm}^{-1}$ ): 3 069 s, 3 001 s, 2 896 vs, 2 797 s, 1 762 vw, 1 735 vw, 1 647 vs, 1 607 s, 1 483 w, 1 435 s, 1 412 s, 1 374 m, 1 343 m, 1 276 w, 1 028 w, 879 vs, 726 w, 705 w, 647 w, 599 w, 534 m, 521 w;  $^1\text{H}$  NMR spectrum ( $\text{C}^2\text{HCl}_3$ ): 1.79 s, 3 H ( $-\text{CH}_3$ ); 2.78 s, 2 H ( $-\text{CH}_2-$ ); 2.99 s, 2 H ( $-\text{CH}_2-$ ); 4.68–4.80 m, 4 H ( $=\text{CH}_2$ ); 5.99 b, 1 H ( $-\text{CH}=\text{}$ );  $^{13}\text{C}$  NMR spectrum ( $\text{C}^2\text{HCl}_3$ ): 23.10 q, 38.75 t, 108.13 t, 108.34 t, 124.98 d, 137.60 s, 143.36 s, 143.58 s.

A mixture of 1-*methyl-4,5,7-trimethylenecyclooctene* (*XII*) and 2-*methyl-4,5,7-trimethylenecyclooctene* (*XIII*) — mass spectrum gives the formula  $\text{C}_{12}\text{H}_{16}$ ; IR spectrum ( $\text{cm}^{-1}$ ): 3 067 s,

2 961 s, 2 911 vs, 1 787 w, 1 632 s, 1 433 s, 1 371 m, 1 279 w, 1 062 m, 888 vs, 725 w, 593 w;  $^1\text{H}$  NMR spectrum of the mixture ( $\text{C}^2\text{HCl}_3$ ): 1.66 m, 3 H ( $-\text{CH}_3$ ); 1.70 m, 3 H' ( $-\text{CH}_3$ ); 2.86–3.05 m, 3 H 3 H'; 4.66–5.07, 3 H 3 H' ( $=\text{CH}_2$ ); 5.29 t, 1 H ( $=\text{CH}-$ ); 5.32 t, 1 H' ( $=\text{CH}-$ );  $^{13}\text{C}$  NMR spectrum of the mixture ( $\text{C}^2\text{HCl}_3$ ): 23.42 q, 24.45 q, 35.69 t, 36.25 t, 39.84 t, 40.76 t, 43.55 t, 43.61 t, 110.79 t, 110.00 t, 111.30 t, 111.52 t, 113.31 t, 113.69 t, 122.24 d, 122.46 d, 135.45 s, 135.94 s, 147.85 s, 149.85 s, 150.05 s, 150.15 s, 151.09 s.

3,5-Dimethyl-1-(2-methyl-2-propenyl)benzene (XV) — mass spectrum gives the formula  $\text{C}_{12}\text{H}_{16}$ ; IR spectrum ( $\text{cm}^{-1}$ ): 3 066 m, 3 006 s, 2 961 vs, 2 908 vs, 1 644 m, 1 600 vs, 1 435 s, 1 370 m, 883 vs, 843 m, 807 m, 689 m;  $^1\text{H}$  NMR spectrum ( $\text{C}^2\text{HCl}_3$ ): 1.63 s, 3 H ( $-\text{CH}_3$ ); 2.24 s, 6 H ( $-\text{CH}_3$ ); 3.20 s, 2 H ( $-\text{CH}_2-$ ); 4.69 s, 1 H ( $=\text{CH}_2$ ); 4.75 s 1 H ( $=\text{CH}_2$ ); 6.76 s, 2 H (arom.); 6.79 s, 1 H (arom.);  $^{13}\text{C}$  NMR spectrum ( $\text{C}^2\text{HCl}_3$ ): 21.19 q, 22.00 q, 44.52 t, 111.70 t, 126.68 d, 127.65 d, 137.60 s, 139.56 s, 145.18 s.

(E)-1-(2-Butenyl)-3,5-dimethylbenzene (XIV) — mass spectrum gives the formula  $\text{C}_{12}\text{H}_{16}$ ; IR spectrum ( $\text{cm}^{-1}$ ): 3 008 vs, 2 906 vs, 2 719 w, 1 755 vw, 1 715 vw, 1 602 vs, 1 446 s, 1 371 m, 1 053 m, 963 vs, 837 s, 690 s;  $^1\text{H}$  NMR spectrum ( $\text{C}^2\text{HCl}_3$ ): 1.64 d, 3 H ( $-\text{CH}_3$ ); 2.23 s, 6 H ( $-\text{CH}_3$ ); 3.19 d, 2 H ( $-\text{CH}_2-$ ); 5.46–5.50 m, 2 H ( $-\text{CH}=\text{CH}-$ ); 6.75 s, 2 H (arom.); 6.77 s, 1 H (arom.);  $^{13}\text{C}$  NMR spectrum ( $\text{C}^2\text{HCl}_3$ ): 17.83 q, 21.19 q, 38.94 t, 125.94 d, 126.24 d, 127.48 d, 130.29 d, 137.73 s, 140.90 s.

#### Deuterium Trace Study of Oligomerization

Two trace experiments were made with  $[\text{Ni}(\text{COD})_2]$  and another two with  $[\text{Ni}(\text{PPh}_3)_4]$  as catalysts, both at equimolar propadiene to 3-deuteriopropyne ratio. Behaviour of 3-deuteriopropyne itself was tested under similar conditions. Parallel to each of these four experiments, also the experiment with untraced propyne was carried out.

A glass ampoule was charged in vacuo with 4 ml of  $[\text{Ni}(\text{COD})_2]$  solution (concn.  $5.5 \cdot 10^{-3}$  mol  $\cdot \text{l}^{-1}$ ) or 4 ml of  $[\text{Ni}(\text{PPh}_3)_4]$  solution (concn.  $31.0 \cdot 10^{-3}$  mol  $\cdot \text{l}^{-1}$ ). Then, the required amount of monomers was added by condensation such that the total amount was 0.40 g. The ampoule was placed into a temperature-controlled bath and was vibrationally stirred at  $70^\circ\text{C}$  for 20 h ( $[\text{Ni}(\text{COD})_2]$ ) or 16 h ( $[\text{Ni}(\text{PPh}_3)_4]$ ). After opening the ampoule, its contents were filtered off over granulated active carbon and then analysed by GC/MS.

#### Isomerization of Cotrimers

A total of 100  $\mu\text{l}$  of the trimers was transferred into a glass ampoule and then 200  $\mu\text{l}$  of ethanol solution of  $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$  were added. Then the ampoule was cooled by liquid nitrogen, evacuated and sealed. The content was allowed to react with vibrational mixing at  $70^\circ\text{C}$  for 3.5 h. After cooling and opening, the mixture was analysed by gas chromatography, using 50 m-long capillary column wetted with OV-17 silicone at  $100^\circ\text{C}$ .

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#### REFERENCES

1. Jolly P. W. in the book: *Comprehensive Organometallic Chemistry* (G. Wilkinson, F. G. A. Stone and E. W. Abel, Eds), Vol. 8, p. 613. Pergamon Press, Oxford 1982.
2. Akhmedov V. M., Khanmetov A. A., Azizov A. G.: *Zh. Org. Khim.* 17, 1661 (1981).

3. Brun P., Tenaglia A., Waegel B.: *J. Mol. Catal.* **17**, 105 (1982).
4. Otsuka S., Tani K., Yamagata T.: *J. Chem. Soc., Dalton. Trans.* **1973**, 2421.
5. De Pasquale R. J.: *J. Organometal. Chem.* **32**, 381 (1971).
6. Simons L. H., Lagowski J. J.: *J. Org. Chem.* **43**, 3247 (1978).
7. Benson R. E., Lindsey R. V. jr: *J. Am. Chem. Soc.* **81**, 4250 (1959).
8. Reppe W., Schlichting O., Klager K., Toepel T.: *Justus Liebigs Ann. Chem.* **560**, 1 (1948).
9. De Mayo P., Yip R. W.: *Proc. Chem. Soc., London* **1964**, 84.
10. Colborn R. E., Vollhardt K. P. C.: *J. Am. Chem. Soc.* **108**, 5470 (1986).
11. Yamazaki N., Ohta T.: *Polym. J.* **4**, 616 (1973).
12. Ittel S. D.: *Inorg. Synth.* **17**, 117 (1977).
13. Priebe H., Nielsen C. J., Klæboe P.: *Spectrochimica Acta*, **A 36**, 1076 (1980).
14. Leicht L. C., Renaud R.: *Can. J. Chem.* **30**, 79 (1952).

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