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NICKEL-CATALYZED OLIGOMERIZATION OF FUNCTIONALIZED CONJUGATED DIENES

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Summary

The cyclodimerization of several functionalized dienes with nickel(0) catalysts has been studied. When a functional group, such as a methoxycarbonyl or a trimethylsiloxy group, is bonded directly to the terminal carbon of the diene grouping, a completely regio- and stereo-selective dimerization is observed and *trans*-1,2-disubstituted cycloocta-3,7-dienes are formed in good yields (80–90%). When one carbon atom separates the functional group from the diene group, the yield drops significantly (to 30%), and the stereoselectivity and the clean nature of the reaction are completely lost. The effect of the nature of the nickel catalyst and the influence of the reductive organoaluminum species are discussed. The particular structure and the stereochemical features of the cyclooctadiene derivatives allow a better understanding of the various steps involved in the catalytic process. A reaction mechanism is proposed.

Introduction

Telomerization of conjugated dienes has been extensively studied [1] as an approach to functionalized polyenes which might be used for the synthesis of natural products [2]. In the present paper we report our results on the synthetic potential of the oligomerization of functionalized conjugated dienes having the general formula: $H_2C{=}CH{-}CH{=}CH{-}(CH_2)_n{-}\Sigma$. The functional group Σ can behave as an internal ligand [3] and control the outcome of the oligomerization or co-oligomerization (with butadiene) reaction. We have previously shown (Fig. 1.) [4] that the co-oligomerization of butadiene with a hindered Schiff base involves one molecule of each species, instead of two molecules of butadiene, as usually observed [5]. The Schiff base probably isomerizes to a dienamine, which reacts as such. The secondary nitrogen atom blocks a coordination site on the metal, thus preventing the insertion of another butadiene unit [3,4].

It was therefore of interest to study the coordinating properties of the functional group in functionalized conjugated dienes. Such properties would be expected to depend on (i) the nature of the heteroatom, (ii) the steric factors (resulting from diene substitution and from Σ itself), and (iii) the length of the chain carrying the ligand (the *n* value).

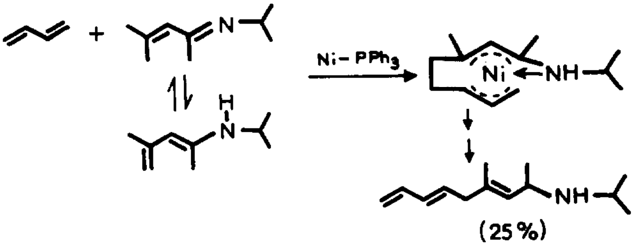


Fig. 1. The polar group acting as the internal ligand during the co-oligomerisation of a functionalized diene with butadiene.

Results and discussion

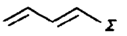
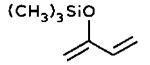
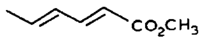
Preparation of the functionalized conjugated dienes

Known procedures have been used to synthesize the dienes reported in Table 1.

We selected terminal functional groups containing an heteroatom such as oxygen or nitrogen; we did not consider phosphorus, which would stabilize the metal strongly and so block the catalytic reaction.

TABLE 1

FUNCTIONALIZED DIENES WHICH HAVE BEEN USED IN THE CYCLOOLIGOMERIZATION REACTION WITH NICKEL CATALYSTS

Functionalized diene		Σ	Ref.
	**1**	$OSi(CH_3)_3$	6
	3	$OCOCH_3$	7
	4	$N(C_2H_5)_2$	8
	5	$N(i\text{-}C_3H_7)COCH_3$	9
	6	CO_2CH_3	10
	7	$CONH(i\text{-}C_3H_7)$	This work
	**2**		6
	**8**		Commercial (Prolabo)

Oligomerization of conjugated functionalised dienes catalysed by zerovalent nickel

The method of catalyst preparation can have an influence on the results (see below). We used two types of catalysts:

(a) Zerovalent nickel generated "in situ" by the reduction of nickel acetylacetonate with ethoxydiethylaluminum or triethylaluminum:

$$3\,Ni(acac)_2 + 3\,Et_2AlOEt \rightarrow$$
$$3\,Ni^0 + 2\,Al(acac)_3 + Al(OEt)_3 + 3\,C_2H_4 + 3\,C_2H_6 \qquad (1)$$

(b) Bis(cycloocta-1,5 diene)nickel, obtained according to the Shunn technique [11]:

$$3\ \mathrm{Ni(acac)_2} + 6\ \mathrm{COD} + 2\ \mathrm{Et_3Al} \rightarrow$$

$$3\ \mathrm{Ni(COD)_2} + 2\ \mathrm{Al(acac)_3} + 3\ \mathrm{C_2H_4} + 3\ \mathrm{C_2H_6} \qquad (2)$$

A nickel(0) catalyst is obtained with both methods, but in the first case it can be considered as "naked" nickel, whereas in the second it is coordinated with COD. Furthermore, in the first procedure the organoaluminum derivatives remain in the reaction medium after the reduction, whereas in the second the nickel catalyst does not contain any aluminum (see experimental section).

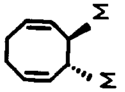
It should be emphasized that the presence of triphenylphosphine as an ancillary ligand is absolutely necessary for an efficient catalyst. When it is absent, the reduction seems to occur when the reducing agent is added to the reaction mixture (with a characteristic change of colour from green to orange), but metallic nickel precipitates as soon as the heating is started (entry 2). This is also the case with some dienes, even in presence of triphenylphosphine (entry 11). The catalytic system is therefore most likely to be a "nickel-ligand" system where one of the coordination site is blocked, thus making trimerization reactions difficult.

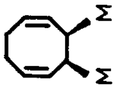
When the terminal Σ substituent is a trimethylsiloxy group (entries 3 and 6) or a carbomethoxy group (entries 15, 16), a stereo- and regio-selective cyclodimerization is indeed observed. Zerovalent nickel is the real catalyst (compare entries 1, 5 and 6 or 13, 14 and 16). The essential factor controlling this process seems to be the electronic nature of the Σ group (entry 10, 11, 12 and 17). But, as already observed for non-functionalized dienes [1], substitution plays a decisive role: 2-trimethylsiloxybuta-1,3-diene **2** and methyl sorbate **8** do not exhibit any reactivity (entries 7 and 8 and 18 to 20).

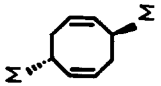
Structure determination

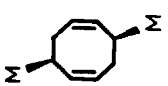
The structure and the stereochemistry of the products have been determined using essentially ^{13}C NMR spectroscopy and chemical correlations.

Spectroscopic data (see below) showed that the dimers obtained were cycloocta-1,5-dienes with the functions 3,4-*trans*, 3,4-*cis*, 3,7-*trans* or 3,7-*cis*:









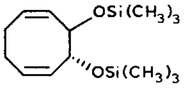
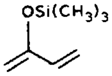
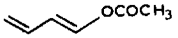
	I	II	III	IV
Group symmetry	C_2	C_s	D_2	C_2

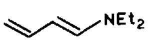
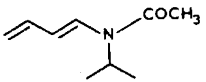
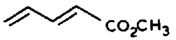
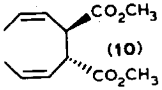
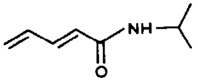
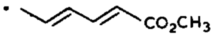
Depending on the symmetry group to which each of these isomers belongs it would exhibit either chemically equivalent groups (isomers I, III and IV) or enantiotopic groups (isomer II). In ^{1}H or ^{13}C NMR the equivalent and enantiotopic groups have identical chemical shifts [12]. As a consequence, only half of the signals should be observed (i.e. in the ^{13}C NMR spectra there should be four distinct signals for the eight ring carbon atoms). A similar analysis can be made for the saturated derivatives, V to VIII, corresponding to I to IV.

(*Continued on p. 348*)

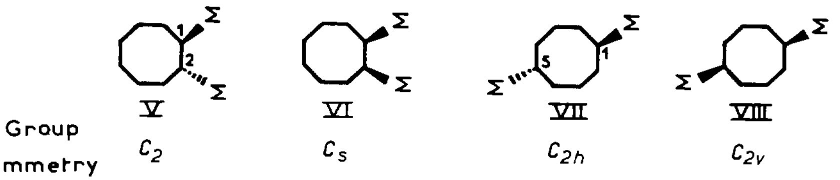
TABLE 2

NICKEL-CATALYSED OLIGOMERIZATION OF FUNCTIONALIZED CONJUGATED DIENES

Entry	Diene [a]	Catalyst [a]			Experimental conditions	Results
		Ni(acac)$_2$	PPh$_3$	Et$_2$AlOEt		
	 (1)					
1	10	1	1	–	Benzene, 3 d, 60°C	Unchanged diene
2	10	1	–	2.25	Benzene, 3 d, 60°C	Ni precipitation
3	10	1	1	2.25	Benzene, 3 d, 60°C	26%  (9)
4	10	1	1	2.25	Benzene, 9 d, 60°C	47%
5	10	1	1	2.25	Benzene, 18 d, 60°C	90%
6	10	1 [b]	1	–	Benzene, 2 d, 60°C	20%
	 (2)					
7	11	1	1	2.25	Benzene, 24 h, 70°C	Conversion 1%
8	10	1	1	2.25	Benzene, 8 d, 80°C	2 Products
9	14	1	1	2	Toluene, 7 h, 100°C	Ni precipitation
	 (3)					
10	10	1	1	2.25	Benzene, 16 h, 60°C	–

	 (4)						
11	10	1	1	2.25	Benzene, 2 d, 70°C	Ni precipitation	
	 (5)						
12	10	1	1	3	Benzene, 24 h, 60°C	–	
	 (6)						
13	10	–	–	–	Benzene, 23 h, 60°C	Unchanged diene	
14	20	1	1	–	Benzene, 23 h, 60°C	Unchanged diene	
15	20	1	1	2	Benzene, 9 h, 60°C	 (10)	11%
16		1	1	2	Benzene, 23 h, 60°C		83%
	 (7)						
17	10	1	1	2.25	Benzene, 24 h, 60°C	–	
	 (8)						
18	16	1	1	1	Benzene, 23 h, 60°C	Unchanged diene	
19	20	1	1	2	Benzene, 18 h, 100°C	Unchanged diene	
20	10	1	1	2.25	Benzene, 7 d, 60°C	Unchanged diene	

[a] Numbers show mol ratio of components. [b] $Ni(COD)_2$.



Only isomers III and IV change symmetry when reduced to VII and VIII. In VIII there are three sets of equivalent nuclei which give three distinct signals in the ^{13}C NMR spectrum. These signals can be assigned to carbons 1 and 5; 2, 4, 6 and 8; and 3 and 7. *

A comparison between the ^{13}C NMR spectra of the cyclodimers and the corresponding reduced compounds (Table 3) provides a ready assignment of the Σ substituent at the 3 and 4 ring positions.

At first sight the presence of single signals for the carbon atoms of the trimethylsiloxy group in **9**, for the ester carbonyl carbons and for the methyl ester carbons in **10** suggests a *cis*-related configuration for the two Σ groups. However, a *trans* stereochemistry was assigned as a result of the chemical transformations shown in Fig. 2 (for the trimethylsilylated derivative **9**) and in Fig. 3 (for the dicarbomethoxy derivative **10**).

Derivative **9** is hydrolyzed under mildly basic conditions to the diol **14**, which is hydrogenated to the *trans*-cyclooctane-1,2-diol, **11**, which is identical (in its spectral features) with an authentic sample prepared by the solvolysis of epoxycyclooctane, **15**, in a buffered medium (formic acid, sodium formate), followed by hydrolysis according to the Cope procedure [13].

Catalytic reduction of the diester **10** (Fig. 3) yields the dimethyl cyclooctane-1,2-dicarboxylate **12** of unknown stereochemistry. The saponification of the latter gives the 1,2-cyclooctane dicarboxylic acid **16**, which is known to be *trans* whatever the stereochemistry of the initial ester might be [14]. The esterification of the diacid **16** with diazomethane yields the *trans* diester **12**, the spectral data of which are identical with those of the derivative obtained by reduction of **10**. The catalytic hydrogenation of the diester **10** proceeds directly without any isomerization. Consequently this

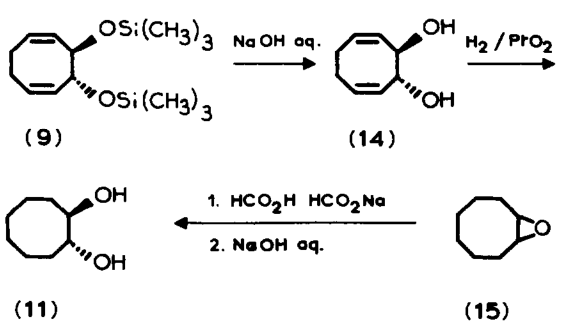


Fig. 2. Conversion of the trimethylsilylated derivative **9** into cyclooctane-1,2-diol (**11**).

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* For sake of homogeneity we kept the same carbon numbering throughout the present paper.

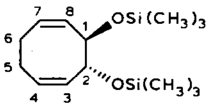
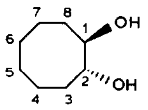
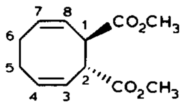
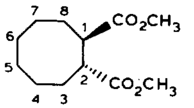
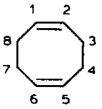
sequence allows the assignment of a *trans* stereochemistry to **10**.

It can be seen from Fig. 4 that if the Σ groups are *trans*, the usual tub or chair conformation of cyclooctadiene [15] is not consistent with the equivalence of the carbon NMR signals observed for the trimethylsilyl or the ester group. Only twisted conformations such as *C* or *D* are satisfactory in this respect.

The joint use of NMR and chemical transformations, as well as the examination of molecular models, support the assignment to compounds **9** and **10** of the structure *C* (Fig. 2), where, curious at it might appear, the two Σ group are *trans* (see models) and pseudo equatorial. The *C* conformation is thermodynamically more favoured than *D*, as there are H–H transannular interactions instead of H–Σ interactions in *D*. As we will discuss later, these considerations on the stereochemistry of the final products have important consequences on the speculations which can be made as to the nature and structure of the reactive intermediates involved in the dimerization process.

TABLE 3

ASSIGNMENTS [a] OF ^{13}C NMR SIGNALS (ppm) FOR CYCLOOCTANE DERIVATIVES

	Carbon atoms					
	5,6	1,2	4,7	3,8	CH_3	C=O
 (**9**)	27.7	74.7	127.7	132.3	0.32	–
 (**11**)	26.3	76.4	23.9	32.0	–	–
 (**10**)	27.9	47.0	126.1	129.7	52.1	173.5
 (**12**)	26.28	44.4	26.46	27.11	51.7	175.7
 (**13**)	128.5	128.5	28.2	28.2	–	–

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[a] The assignment of the ^{13}C signals to the carbons in **9** and **10** involves a comparison with **13**; the deshielding effect of the trimethylsilyl group is: α +46.5, β +3.8, γ −0.8, while that of the carbomethoxy is: α +18.8, β +1.2, γ −2.4 ppm.

Influence of the diene structure

The data in Table 2 show that the dimerization reaction of functionalized dienes is not a general process. It depends on the electronic features of Σ, its position on the diene, and the general structure of the diene.

(i) Electronic nature of the Σ group

An electron-attracting group such as CO_2CH_3 increases the rate relative to an electron-donating group such as $OSi(CH_3)_3$. These specific substituents are needed to observe the dimerization; 1-acetoxy-1,3-butadiene, **3**, does not react in this way and is likely to be cleaved by the catalyst as shown by Yamamoto et al. with vinyl acetate [16]. Should a similar process occur with **3**, the nickel(0) catalyst would then be oxidized into inactive nickel(II) species.

The use of 1-diethylamino-1,3-butadiene as a substrate causes precipitation of the catalyst in metallic form. Obviously the presence of an equivalent of the ancillary phosphine associated with the nickel(0) is not sufficient to keep the catalyst homogeneous. The electron-donating properties of the nucleophilic enamines cleaves the metal from its organic ligands, thus giving rise to its precipitation as a colloidal, catalytically inactive species *. With dienes terminally substituted with an amide, no reactivity is observed, and the diene stays intact and the reduced catalyst remains in solution.

(ii) Influence of substitution in the diene

Previous observations have shown that the rate of cyclodimerization of conjugated dienes depends on the substituents on the diene [17]. The disubstituted dienes **2** and **8** (methyl sorbate) scarcely exhibit any reactivity. The latter remains completely untouched even under forcing reaction conditions (see Table 2, entries 18–20). For compound **2**, only a 1% conversion can be detected by vapor phase chromatography (OV17 column).

In order to get more insight on the influence of substitution, and on the effect of the position of the functional group in relation to the diene grouping, we have examined the chemical behaviour (Fig. 5 and Table 4) of compound **17**. This

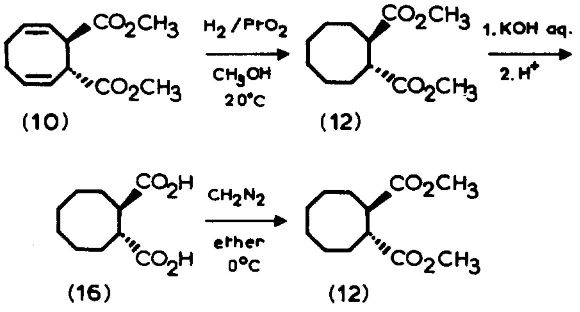

Fig. 3. Conversion of the diester **10** into 1,2-dicarbomethoxycyclooctane (**12**).

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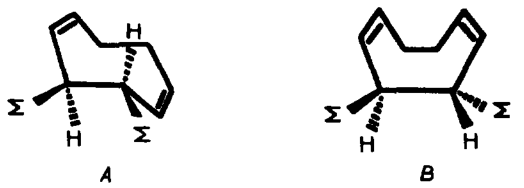
* It is quite interesting to note that this does not occur during the cooligomerization of conjugated imines with butadiene where we have postulated a dienamine type intermediate to explain the coupling of only one butadiene unit with the heterodiene (see Fig. 1).

derivative was obtained by the isomerization of methyl sorbate **8** using lithium diisopropylamide, followed by quenching in acidic medium [18].

The dimerization reaction yields a mixture of four major products, which are diesters of C_6 and C_8 rings, and which are not not separable by adsorption column chromatography. However one major compound, **18** was isolated, but its ^{13}C NMR



Tub conformation   Chair conformation

4 ^{13}C signals from the ring carbons

1 ^{13}C signal from the carbons of both Σ ($=OSi(CH_3)_3$) groups

2 ^{13}C signals from the carbons of both Σ($=CO_2CH_3$) groups

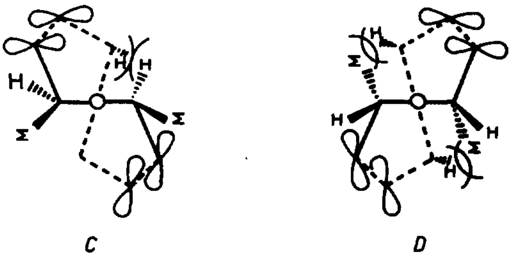


Fig. 4. Twist conformations of the cyclooctadiene with a *trans* orientation of the Σ groups.

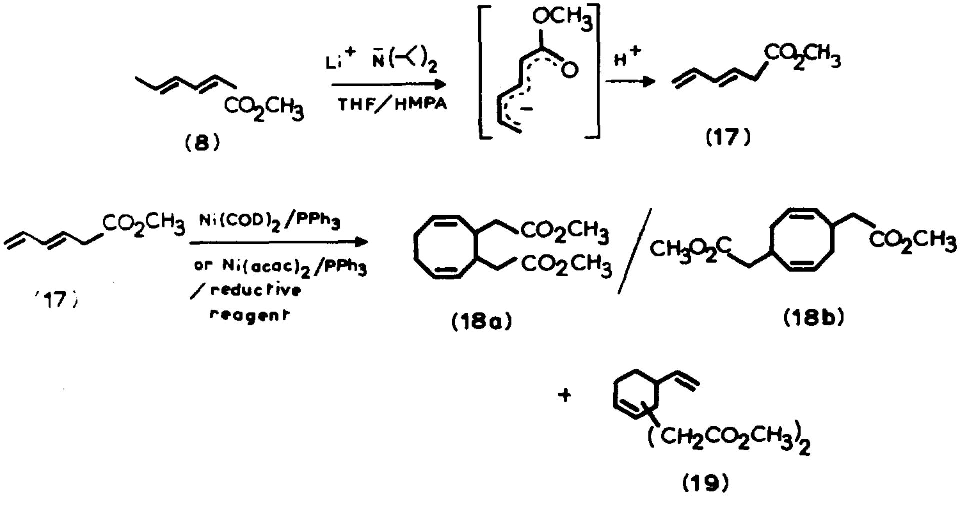


Fig. 5. Dimerization of methyl 3,5-hexanedioate (17).

spectrum does not allow one to decide between structures **18a** and **18b**. When Ni(acac)$_2$ is used as a the nickel source, the nature of reducing agent (compare entries 1 and 2) has an influence on the overall yields but not on the relative amounts of the components. Furthermore, when the chromatographic analysis is repeated on the reduction products of the dimerization derivatives ($H_2/PtO_2/MeOH$, 20°C, 18 h) four peaks are still observed. This indicates that the four corresponding components are structural isomers and consequently that the dimerization reaction completely loses its selectivity when the ester function is in the allylic position to the conjugated diene.

The intimate details of the process involved in the formation of the bis(π-allyl)nickel complexes obtained by the oxidative coupling of two diene units are a matter of current interest [19]. The regio- and stereo-selectivity of the cyclodimerization reaction of dienes **1** and **6**, as well as the unexpected stereochemistry of the cyclized compounds (see Fig. 2), provides useful information.

(a) Regioselectivity

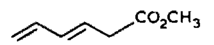
Three types of intermediate are likely to be involved in the dimerization. Tail-to-head coupling, giving rise to **20a**, can be ruled out immediately because of the structure of the dimer. In the case of a **20b** type of intermediate, formed by head-to-head coupling, the stereochemistry of the final product would be determined during the initial oxidative coupling. On the other hand, with intermediate **20c** the

(20a) (20b) (20c)

Fig. 6. Various types of intermediate which are likely to be involved in the cyclodimerization of functionalized dienes.

TABLE 4

NICKEL CATALYZED DIMERIZATION OF METHYL 3,5-HEXANEDIOATE (17) [a]

Entry	 (17)	Ni(acac)$_2$	PPh$_3$	Et$_2$AlOEt	Et$_3$Al	Dimerization product
1	10	1	1	2.25	–	39% (37.5 : 23.8 : 23.9 : 14.7) after reduction: (33 : 27,6 : 21,6 : 17,6)
2	10	1	1	–	2.25	66% (33.5 : 24.1 : 24.5 : 17.9) after reduction: (37.4 : 24.6 : 19.5 : 18.4)

[a] Reaction conditions: benzene, 65 h, 60°C. Reagent quantities are in mmol. The relative ratios of the four components of the products were determined GLC (column capillary OV1, 50 m).

stereochemistry would only be established during the final reductive elimination step.

In an attempt to decide between **20b** and **20c**, the dimerization reaction was carried out in presence of ethylene, in the hope of incorporating it. The separation of the Σ groups by two additional carbon atoms would have allowed a choice between **20b** and **20c**. Unfortunately only the cyclodimers were obtained.

When **6** is dimerized in presence of a palladium catalyst (Fig. 7), a linear product **21** is obtained with the two ester functions in the terminal positions. This result suggest that intermediate **20c**, with tail-to-tail coupling, is formed when a palladium catalyst is used. By analogy, the nickel catalyzed dimerization should proceed in a similar manner.

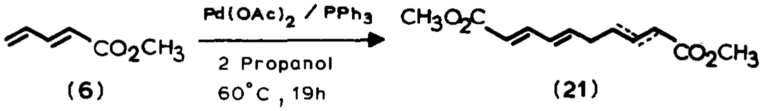


Fig. 7. Dimerization of the diene ester **6** in presence of a Pd catalyst.

(b) Stereoselectivity

The *trans* stereoselectivity can be explained by the reaction sequence shown in Fig. 8

The intermediate complex **21**, which has four *syn* substituents on the π-allyl ligands, is thermodynamically the most stable [20]. This is indeed the complex which

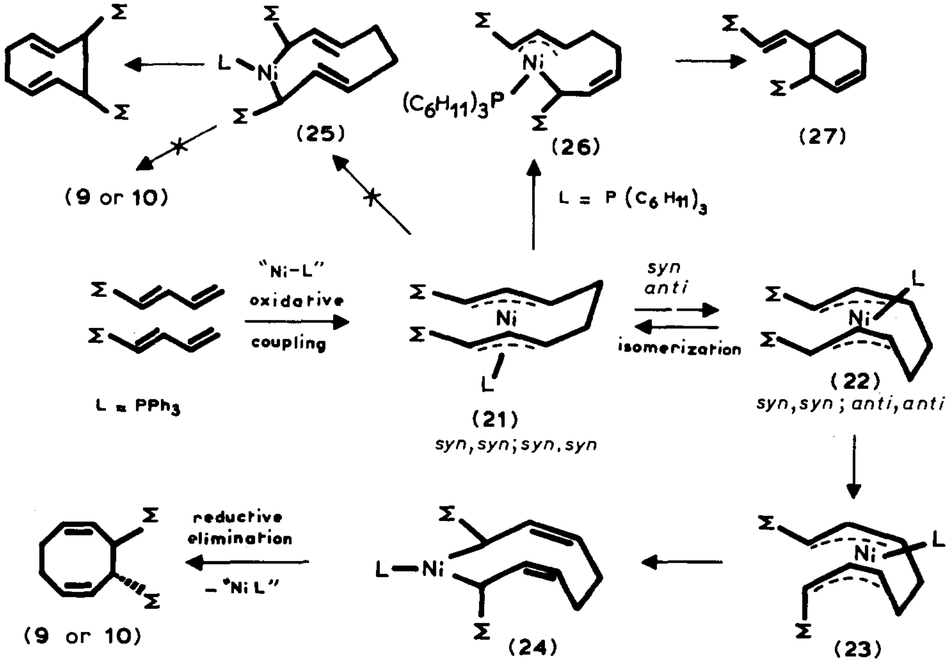


Fig. 8. Dimerization routes for functionalized butadienes.

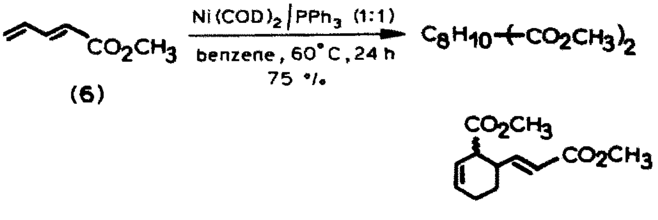
has been isolated by Binger * ($\Sigma = CO_2CH_3$, $L = PPh_3$) who used $Ni(COD)_2/P(C_6H_{11})_3$ as catalyst [21] instead of the $Ni(acac)_2/PPh_3/Et_2AlOEt$ employed in the present work. However Binger obtains five products (in the ratio of 2.5/67.3/2.3/17/6.9) with **10** present as only 2.5% of the mixture. His major compound (67.3%) is a vinylcyclohexene derivative, **27**, which is formed via a σ,π-allyl type intermediate, **26**, which is known to be stabilized by basic ligands such as tricyclohexylphosphine. Consequently intermediate **21** cannot be involved in the catalytic process of our reaction which gives, in high yields (83–90%), only *trans*-1,5-disubstituted cyclooctadienes. The cyclooctadiene structure of the compounds obtained, **9** and **10**, with two *cis* double bonds, requires a double *syn-anti* isomerization of **21** into **22**. The *trans* stereochemistry of the two Σ substituents implies a *syn-anti* isomerization of one of the Σ groups giving rise to **23**, where the interaction with the other Σ group is minimized. The formation of the metallacycle **24**, followed by the reductive elimination, can then be easily achieved.

A metallacycle **25** could be formed directly from **21**, but the steric interaction of the two Σ groups renders this pathway difficult; the reductive elimination of the Ni in **25** would lead to the formation of cyclooctadiene with two *cis* substituents and two *trans* double bonds. This does not seem reasonable.

The two last steps of the sequence illustrated in Fig. 8 (metallacycle formation and reductive elimination) are reported to occur with retention of configuration [22]. It appears difficult to make another assumption which would unreasonably impose retention on one carbon (bearing Σ) and inversion on the other.

Role of the organoaluminum reducing agent

In the above discussion, the comparison of our results with those of Binger called our attention to the role of the organoaluminum reducing agent, which in our experimental conditions remains in the reaction medium. Its role has been neglected until now; identical results have generally been obtained in oligomerisation reactions of conjugated dienes using $Ni^{II}/RR'R''Al$ catalysts and the aluminum-free nickel(0) catalyst ($Ni(COD)_2$). But with the functionalized diene **6**, mixtures are obtained with the latter catalyst (see Fig. 9) [21] whereas only the dimerization is observed with the former (Table 2, entries 15 and 16). It may be noted that the vinylcyclohexene derivative **27** is also obtained as a secondary product (5–10%) during the



(6)

(27)

Fig. 9. Dimerization of methyl 2,4-pentadien oate (6) with an aluminum-free nickel catalyst in the presence of triphenylphosphine.

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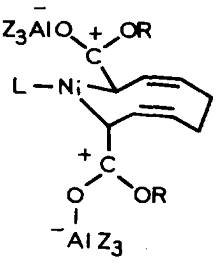
* We thank Dr. P. Binger, Max-Planck-Institut, Mülheim (R.F.A.) for sending us a preprint of his paper prior to publication.

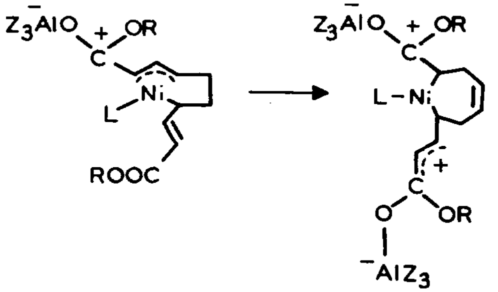
distillation of **6** through a conventional Diels-Alder reaction.

Obviously the organoaluminum reagent not only plays a role as the reducing reagent for nickel(II) species, but also as a Lewis acid which is able to form a complex with the ester group. These organoaluminum species AlZ_3 (Z = acac, EtO or Et) play a decisive role in the selectivity in the dimerization, probably during the nickel reductive elimination from the metallacycle **24**.



The positive and negative charges can be localized, respectively, on the ester carbon atoms and on the aluminum. This effect, and the fact that the triphenylphosphine bonded to the nickel is a π acceptor ligand, favour the reductive elimination process.

A similar explanation could be put forward in order to explain the formation of the vinylcyclohexene type derivatives observed by Binger and by us. But it should be noted that triphenylphosphine does not stabilize the σ,π-allyl complex. Furthermore, one positive charge is now delocalized over three carbon atoms, and its effect should be less important.



In the case of the trimethylsiloxy-1,3-butadiene the Lewis acid role of the organoaluminum reagent is less obvious. The cyclodimerization into **9** can also be achieved with $Ni(COD)_2/PPh_3$ catalysts, with a lower yield but with the same selectivity (see Table 2, entry 6).

Conclusion

The present work has shown that functionalized dienes are interesting substrates for cyclodimerization reactions involving nickel catalysts. The mechanism which we propose emphasizes the importance of the method of preparation of the catalyst, as well as the influence of the reducing organoaluminum species used to generate zerovalent nickel catalysts. We are currently investigating the synthetic potential of functionalized dienes in oligomerization and co-oligomerization reactions (with butadiene) in presence of nickel and palladium catalysts.

Experimental

General

All the reactions and manipulations were carried out under argon, using Schlenk type flasks.

The IR spectra were recorded on a Perkin–Elmer model 297, using NaCl windows. The NMR spectra were measured, using a VARIAN EM 360 or XL 200 spectrometer, in $CDCl_3$ solution. TMS was used as the internal reference and chemical shifts are given in ppm. GPC analyses were recorded on a INTERSMAT IGC 120 M or a CARLO ERBA, 2150 using OV 1 or OV 17 columns and hydrogen as the carrier gas. The microanalyses of carbon and hydrogen were performed at "Centre de microanalyses de la Faculté des Sciences de St. Jérôme".

The dienes **1** to **6** were prepared by known procedures (see Table 1). Diene **7** was prepared by treating the corresponding acid chloride with isopropylamine and the diene **8** was synthesized from sorbic acid by esterification in methanol.

Oligomerization reactions

$Ni(acac)_2$ (1 mmol), PPh_3 (1 mmol) and 25 ml of dry, degassed, toluene were introduced into a 100 ml Schlenck apparatus. The mixture was cooled to -10°C, and Et_2AlOEt (2 mmol) was added. The temperature was raised to 20°C over 30 min, when the colour changed from green to red. The functionalized diene (20 mmol) was then added and the reaction mixture heated under the conditions given in Table 2. The reaction mixture was then reduced in volume under vacuum and poured into hexane, in order to precipitate the nickel salts. These were filtered off and the oligomerization products were purified by column chromatography on SiO_2.

The same procedure was used with $Ni(COD)_2$.

Spectra of the oligomers

trans-1,2-Bis(trimethylsiloxy)-3,7-cyclooctadiene (9). Elution: hexane/ether 98/2. IR (neat): 3000, 2960, 1687, 1250, 1060, 880 and 840 cm^{-1}; ^1H NMR: 0.19 (s, 18 H), 2.30 (m, 4 H), 4.60 (m, 2 H), 5.56 (m, 4 H); ^{13}C NMR: 0.32 q, 27.7 t, 74.7 d, 127.7 d, 132.3 d. Anal. Found: C, 60.64; H 9.55. $C_{14}H_{28}O_2Si_2$ calcd.: C, 59.09; H, 9.91%.

trans-Dimethyl 3,7-cyclooctadiene-1,2-dicarboxylate (10). Elution: hexane/ether 80/20. IR (neat): 3025, 2950, 2895, 2835, 1735, 1655, 1430, 1195, 1115, 1025, 905, 860, 805 and 780 cm^{-1}; ^1H NMR: 1.7–2.56 (m, 2 H); 3.42 (s, 3 H); 3.93 (m, 1 H); 5.3 (m, 2 H); ^{13}C NMR: 27.9 t; 47.0 d; 52.1 q; 126.1 d; 129.7 d; 173.5 s. Anal. Found: C, 64.51; H, 7.01. $C_{12}H_{16}O_4$ calcd.: C, 64.32; H, 7.19%.

trans-Cyclooctane-1,2-diol (11). Hydrogenation of compound **14** catalysed by PtO_2 gives the cyclooctanediol in quantitative yield. IR (neat): 3380, 2925, 2855, 1465, 1445 and 1035 cm^{-1}; ^1H NMR: 1.4–1.9 (m, 6 H); 3.55 (m, 1 H); 3.9 (m, 1 H); ^{13}C NMR: 23.9 t; 26.3 t; 32.0 t; 76.4 d. Anal. Found: C, 66.95; H, 10.77. $C_8H_{16}O_2$ calcd.: C, 66.92; H, 11.18%.

trans-Dimethyl cyclooctane-1,2-dicarboxylate (12). The compound **10** was hydrogenated with PtO_2 as catalyst to give the diester in quantitative yield. IR (neat): 2960, 2850, 1735, 1430, 1190, 1105 and 1035 cm^{-1}; ^1H NMR: 1.4–2.18 (m, 6 H);

2.96 (m, 1 H); 3.67 (s, 3 H); ^{13}C NMR: 26.28 t; 26.46 t; 27.11 t; 44.4 d; 51.7 q; 175.7 s. Anal. Found: C, 63.12; H, 8.72. $C_{12}H_{20}O_4$ calcd.: C, 63.13; H, 8.83%.

*trans-1,2-Dihydroxy-3,7-cyclooctadiene (**14**).* The disiloxy compound **9** is added to a 1% solution of NaOH in MeOH and kept for 16 h at room temperature. After hydrolysis and the usual work up, the diol is recovered in a 70% yield. IR (neat): 3600, 3200, 2970, 1700, 1640, 1365 and 1220 cm^{-1}; ^{1}H NMR: 2.30 (m, 2 H); 4.33 (m, 1 H); 4.55 (m, 1 H); 5.6 (m, 2 H); ^{13}C NMR: 27.9 t, 73.9 d, 129.2 d, 130.8 d.

*trans-1,2-Cyclooctanedicarboxylic acid (**16**).* The diacid was obtained by saponification of the diester **12**. ^{1}H NMR: 1.07–2.4 (m, 12 H); 2.95 (m, 2 H); 10.7 (m, 2 H); ^{13}C NMR: 25.84 t; 26.57 t; 26.57 t; 44.14 d; 181.75 s.

*Dimethyl 2,4,7-decatriene-1,10-dicarboxylate, **21**.* This diester was obtained by the dimerization of **6** catalysed by $Pd(OAc)_2$ in the presence of 2 equivalents of PPh_3 in 2-propanol, yield 63%, b.p. 150°C at 0.05 mmHg. IR (neat): 3015, 2995, 2945, 1735, 1720, 1640, 1615, 1430, 1265, 1165, 995, 970 and 865 cm^{-1}; ^{1}H NMR: 2.8–3.15 (m, 4 H); 3.6 (s, 3 H); 3.65 (s, 3 H); 5.4–6.2 (m, 4 H); 5.84 (d, 1 H); 7.3 (dd, 1 H); ^{13}C NMR: 35.6 t; 37.7 t; 51.36 q; 51.70 q; 119.6 d; 124.1 d; 129.2 d; 130.6 d; 141.4 d; 144.7 d; 167.3 s; 172.0 s. Anal. Found: C, 64.39; H, 7.23. $C_{12}H_{16}O_4$ calcd.: C, 64.32; H, 7.19%.

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