

NICKEL-CATALYSED REACTIONS OF OLEFINS WITH
>C=N-DOUBLE BOND SYSTEMS

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Abstract - The reactions of Schiff's bases, hydrazones, 2,3-diazabutadienes and 2-azabutadienes with butadiene or activated monoenes in the presence of nickel catalysts lead to new classes of compounds, which are isolated as mixtures of isomers. The ratio of the isomer distribution can be controlled inside wide limits by variation of the nickel ligands and the reaction parameters. A comparison with the nickel-catalysed oligomerisation of butadiene or the cooligomerisation of butadiene with mono-olefins shows that the reaction products in the two cases are not analogous.

INTRODUCTION

In the last twenty years the chemistry of nickel-catalysed reactions of olefins and alkynes has undergone a vigorous upsurge. This interest is connected above all with the discovery of bis(cycloocta-1,5-diene) nickel(0) in the year 1960 (1).

In the following years the Mulheim group particularly occupied itself with possible new syntheses of cyclic and linear compounds from simple olefins and acetylenes.

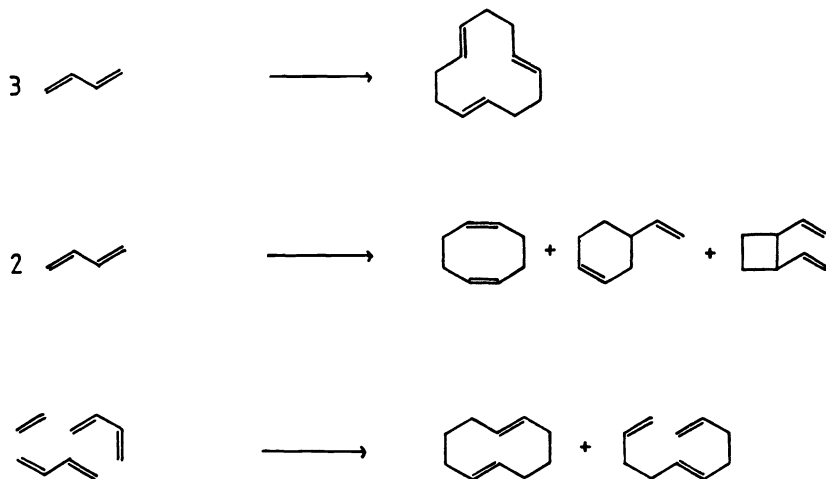


Fig. 1 Characteristic nickel-catalysed reactions

In spite of the multiplicity of reactions catalysed homogeneously by nickel and their simplicity and selectivity only very few have awakened the interest of the chemical industry.

In addition to the trimerisation of butadiene to 1,5,9-cyclododecatriene (2), the starting material for "Nylon 12" and dodecandicarboxylic acid, they are:

- The addition of HCN to butadiene giving adiponitrile, the starting material for hexamethylenediamine (3).
- The cooligomerisation of ethylene and butadiene to 1,4-hexadiene, an important comonomer for the polymerisation of ethylene and propylene with an unsymmetrical diene (4).

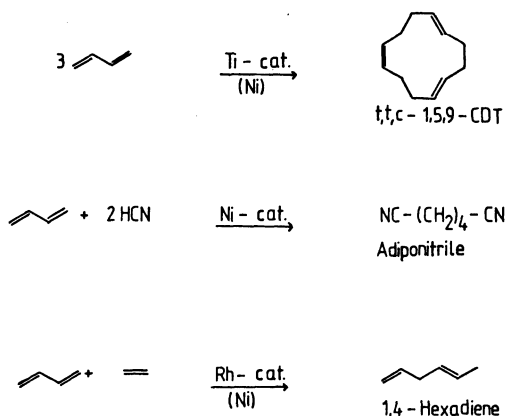


Fig. 2 Industrially important homogeneously-catalysed nickel reactions

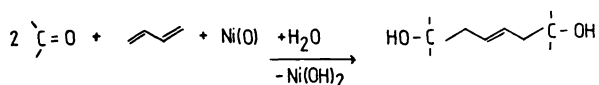
1,5,9-Cyclododecatriene is nevertheless also prepared in large quantities using a titanium catalyst, and 1,4-hexadiene by use of a rhodium catalyst.

The reason for industry showing little interest in these reactions is above all, that the cyclic or linear oligomers which can be built up from simple olefinic substrates can only be selectively functionalised with great difficulty.

For this reason, we have occupied ourselves for more than ten years with the cooligomerisation of olefins with hetero-double bond systems, particularly $>\text{C}=\text{N}$ -double bond systems.

It was known from the literature, that ketones react with butadiene in presence of stoichiometric amounts of nickel(0) catalysts to diols (5). In presence of a catalytic amount of a nickel-ligand catalyst octatrienyl-substituted alcohols are formed (6).

stoichiometric:



catalytic:

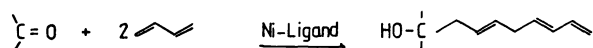


Fig. 3 Reactions of carbonyl compounds with butadiene

In the year 1971 J. Tsuji published the palladium-catalysed reaction of phenylisocyanate with butadiene (7). In 1974 the corresponding reaction with Schiff's bases was described by J. Furukawa (8). In both cases cyclic compounds are formed i.e. substituted piperidones or piperidines.

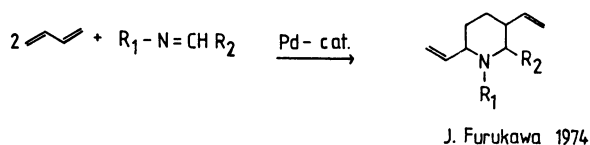
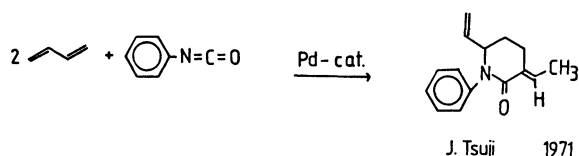


Fig. 4 Palladium-catalysed reactions of butadiene with $>\text{C}=\text{N}$ -double bond systems

REACTION OF SCHIFFS' BASES AND HYDRAZONES WITH 1,3-DIENES

Schiffs' bases

Ethylene reacts with butadiene under the conditions of the nickel(0) catalysis to a mixture of *cis*, *trans*-1,5-cyclododecadiene and 1-*trans*-4,9-decatriene. The ratio of cyclic to linear cooligomerisation products can be controlled within wide limits by varying the nickel ligands or the reaction conditions (9). If the monoolefin ethylene is replaced by a Schiffs' base, the corresponding reaction products A and B should be obtained.

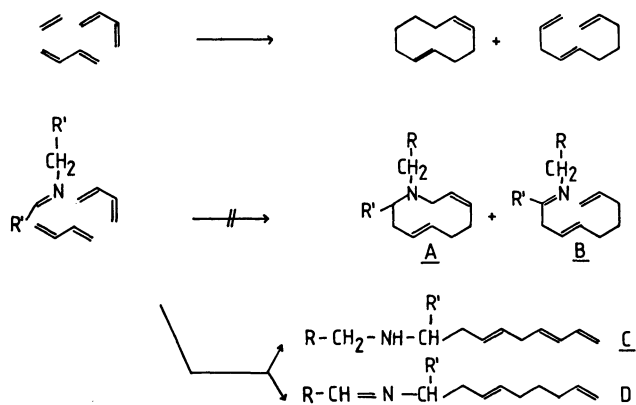
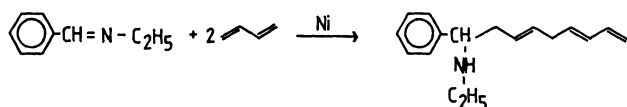


Fig. 5 Cooligomerisation of Schiff's bases with butadiene

The products A and B, analogues of the ethylene reaction, do not form as a rule. Only C and D or mixtures of C and D are isolated. The reaction can be controlled so that either C or D is the main product. For example, the addition of weakly protic compounds such as primary and secondary amines, phosphines, alcohols, weak organic acids and water leads to the octatrienyl-substituted amines C. Amines like morpholine possess not only the property of influencing the selectivity of the reaction, but also accelerate it.



Reaction-Time [h.]	Reaction-temperature [°C]	Solvent	Conversion	Yield
20	40	Toluene	77%	21%
2	40	Toluene : Morpholine = 6 : 1	86%	75%

Fig. 6 Effect of morpholine

The reaction achieves high conversions and yields in spite of the short reaction time. Octadienyl-substituted Schiffs' bases of type D (see Fig. 5) are formed at a temperature of 40° only when very pure reagents are used i.e. when amine impurities have been completely removed. If the reaction temperature is raised to > 75° D forms in high yields without the requirement for high purity reagents.

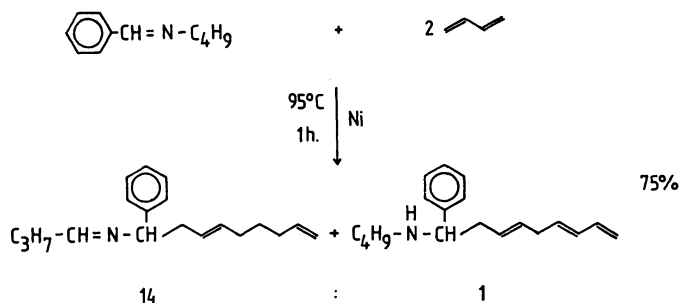


Fig. 7 Cooligomerisation of Schiffs' bases at high temperatures

In the reaction of N-benzylidene-butylamine with butadiene the desired product N-butylidene-(1-phenyl-octa-3,8-dienyl-amine) is formed to the extent of > 93%. The octadienyl-substituted Schiffs' bases of type D (see Fig. 5) can be cleaved hydrolytically to give aldehyde and a primary nonadienylamine, and the following scheme can be drawn.

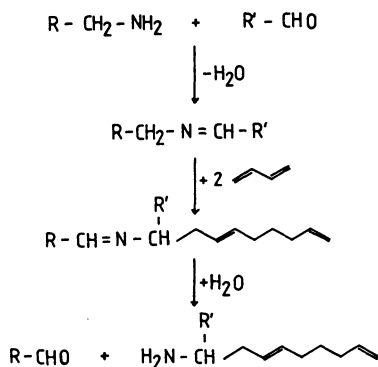


Fig. 8 General reaction scheme for the preparation of nonadienyamines

The starting amine is converted into the corresponding aldehyde, and the starting aldehyde into a primary doubly unsaturated amine eight carbon atoms longer. The scheme of Fig. 8 also shows a method of preparing aldehydes from primary amines or the corresponding nitriles which have a $-\text{CH}_2$ -group in the α -position. We have been able to establish that this method is generally applicable. We suggest the following mechanism for the reaction of Schiff's bases with butadiene.

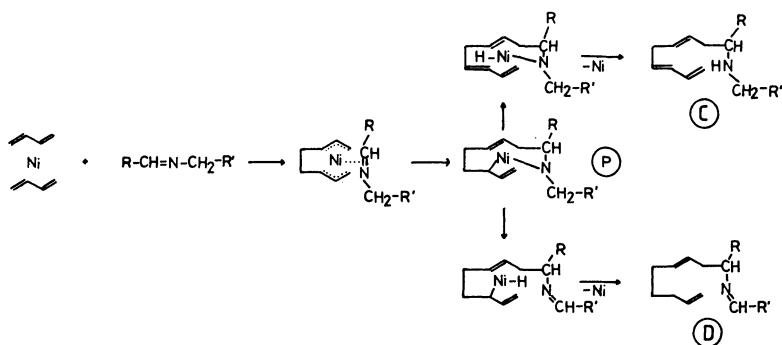


Fig. 9 Reaction mechanism for the cooligomerisation of Schiff's bases

We assume that (P) is an important intermediate on which basis the formation of the two isomers C and D can be explained by β -elimination and subsequent hydrogen-transfer to the C-3 atom of one of the allyl groups or to the nitrogen.

Hydrazones

Monoalkyl and monoaryl hydrazones react with butadiene in presence of a nickel(0) catalyst to give nitrogen compounds with branched (compound E) and linear (compound F) octadiene chains (11).

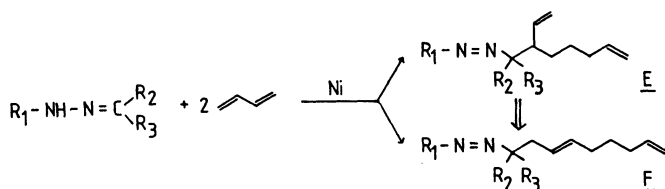


Fig. 10 Nickel-catalysed reaction of hydrazones with butadiene

The terminal double bonds of E and F can also be partially isomerised to internal double bonds.

We have found the ratio of E to F is only slightly dependent on the nickel ligand L. On the other hand, reaction temperature and time exert a strong influence on the product distribution. With extended reaction times the amount of the linear isomer F increases very strongly, which suggests an ensuing rearrangement E → F (12). Such a nickel-catalysed isomerisation of butadiene-oligomers has previously been described only for 1,2-divinylcyclobutane, which rearranges to 1,5-cyclooctadiene and 4-vinylcyclohexene (13). The influence of temperature and time on the nickel-catalysed rearrangement of E to F is shown in Fig. 11, where the initial mixture contains 75% E and 25% F, with $R_1 = C_6H_5$, $R_2 = H$ and $R_3 = CH_2-CH_3$

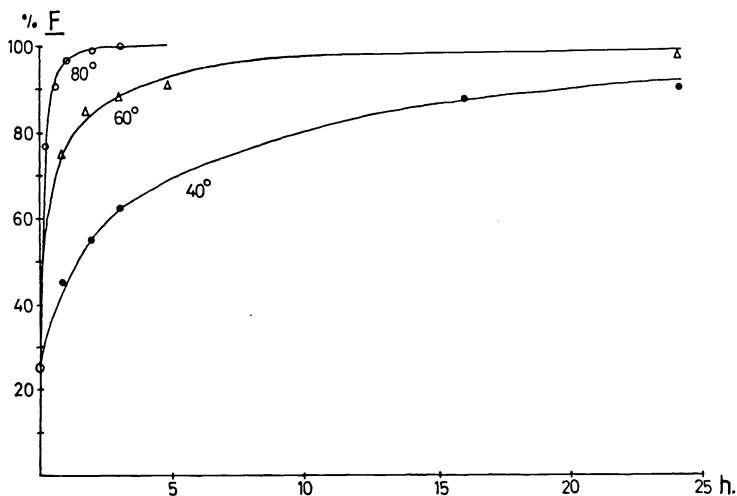


Fig. 11 Effect of temperature and time on the conversion E → F

The substituents (R_1 , R_2 , R_3) and the nickel ligands L have an important influence on the rate of isomerisation E → F. We found the following series of decreasing reactivity for the ligand L: $PPh_3 \sim P(\text{cyclohexyl})_3 > P(OEt)_3 \sim P(OPh)_3 > \text{no L}$. The formation of isomers E and F can be explained by the following scheme.

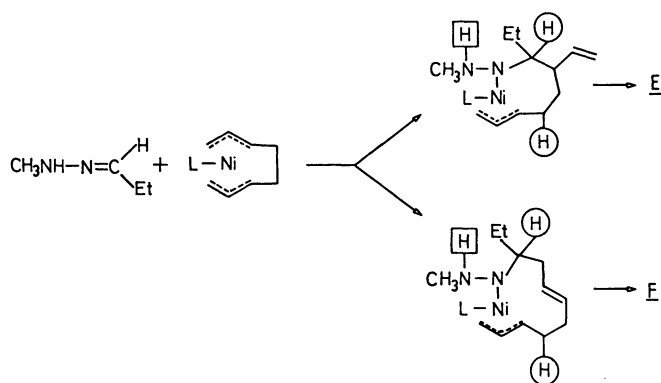


Fig. 12 Proposed reaction mechanism for the cooligomerisation of hydrazones

The $>\text{C}=\text{N}$ -double bond of the hydrazone can couple with one of the allyl groups of the nickel eight-carbon chain either at C-1 or at C-3. In the first case a straight-chain intermediate is formed and in the second a vinyl-branched one. It then appears, that of the three possible H-cleavage reactions only the H-atom bound to the nitrogen is transferred to the allyl group.

R. Baker found (11b), that the palladium-catalysed reaction of methyl- and phenyl-hydrazones with butadiene can proceed in a different manner contrary to the nickel-catalysed cooligomerisation. In addition to the C-alkylated products $\underline{\text{E}}$ and $\underline{\text{F}}$ one obtains an N-alkylated compound also.

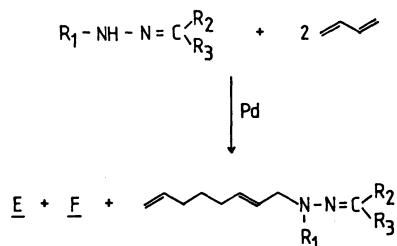


Fig. 13 Palladium-catalysed reaction of hydrazones with butadiene

This new product arises from the nucleophilic reaction of the N-H nitrogen with the π -allyl-palladium complex.

Isonornicotines

Schiffs' bases derived from 3- or 4-pyridinealdehyde react with butadiene to give 1:2 adducts. Substituted nonatrienyl amines or azomethines containing an additional C_8 unit are formed in yields of 60-80%.

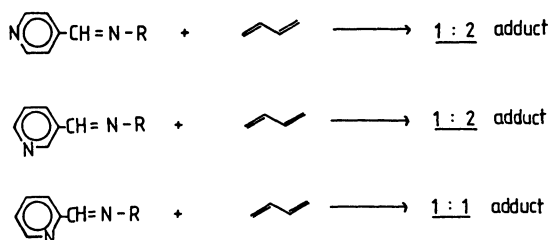


Fig. 14 Reaction of pyridine-aldehyde Schiff's bases with butadiene

On the other hand with Schiff's bases derived from 2-pyridine-aldehyde 1:1 adducts are surprisingly formed. These 1:1 adducts proved to be pyrrolidines or substituted α -nornicotines (14).

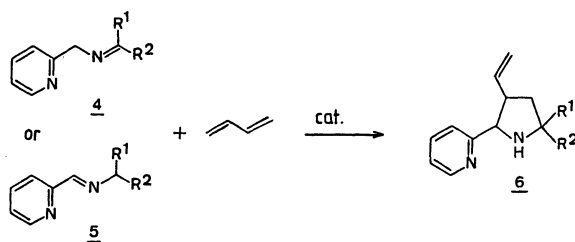


Fig. 15 Preparation of α -nornicotines

Thus 2-pyridylmethylene-methylamine 5 ($R^1 = R^2 = H$) reacts with butadiene at 40°C in presence of the nickel-triphenylphosphine catalyst to give the α -nornicotine 2-(2-pyridyl)-3-vinylpyrrolidine 6 in 45% yield. Variation of the nickel ligand L or the presence of morpholine produces no change in the composition of the final products. The vinyl-pyrrolidines are always the main components, even with excess of butadiene.

The azomethines 4 which are isomeric with 5, react with 1,3-dienes to give the analogous compounds 6. The reaction proceeds significantly faster and in higher yields: e.g. isobutylidene-2-picolyamine 4 ($R^1 = H$, $R^2 = -\text{CH}(\text{CH}_3)_2$) reacts with isoprene, which is less reactive than butadiene, at 40° in presence of 1% of a nickel-ligand catalyst ($\text{Ni}:\text{PPh}_3 = 1:1$) in 2 h. to give the corresponding α -nornicotine 6 in 78% yield.

A possible explanation for the formation of 1:1 adducts is given in Fig. 16.

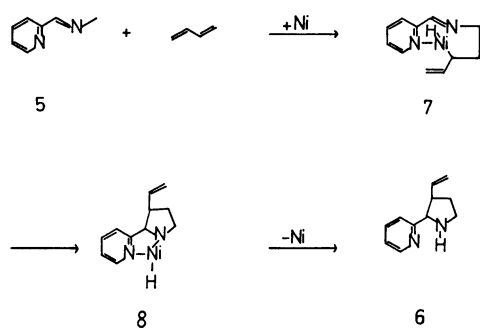


Fig. 16 Proposed reaction mechanism for the formation of α -nornicotines

Oxydative addition of C-H bond of the methyl group to nickel leads to a reactive intermediate. This reacts with butadiene to 7. Insertion of the $>\text{C}=\text{N}$ -function into the metal-carbon bond produces 8 and subsequent reductive elimination leads to the pyrrolidine derivative 6 and regeneration of the catalyst. Contrary to 4 the Schiff's bases 5, which are derived from 2-pyridine-aldehyde, react predominantly to the 2,3-trans isomers, i.e. the pyridyl- and vinyl group are in the trans configuration, whereas 4 forms preponderantly the 2,3-cis isomers.

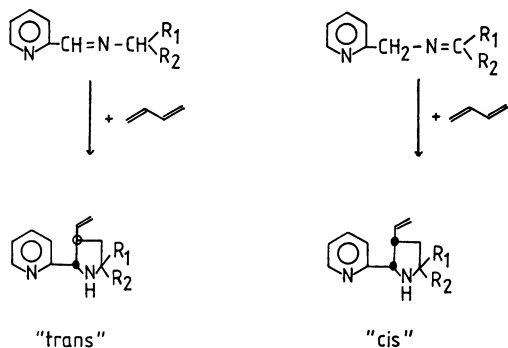


Fig. 17 Cis and trans isomers of α -nornicotines

Acrylonitrile and acrylate esters as well as sorbate esters react with the Schiff's bases 4 and 5 to give α -nornicotines, whereas acetylene and styrene gave negative results.

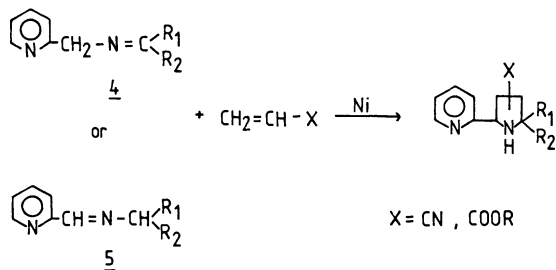


Fig. 18 Further synthetic routes to α -nornicotines

The reactions give high yields in relatively short reaction times. Thus isobutylidene-2-picolylamine 4 ($R_1 = \text{H}$, $R_2 = -\text{CH}(\text{CH}_3)_2$) reacts with ethyl acrylate at 40° in 1,5 h to give the substituted α -nornicotine in 92% yield. With acrylonitrile under the same reaction conditions the corresponding pyrrolidines are formed in 85% yield. These reactions are nevertheless not regioselective. The group X can be in position 3 as well as in position 4 of the reaction product. On the other hand in the reaction with butadiene the vinyl group is always in the 3-position.

Reactions of 2-azadienes with 1,3-dienes

2-Azadienes - In the nickel-catalysed reaction of 2-pyridine-aldehyde and 2-picolylamine azomethines giving α -nornicotines one can discuss the appearance of a 2-azadiene intermediate.

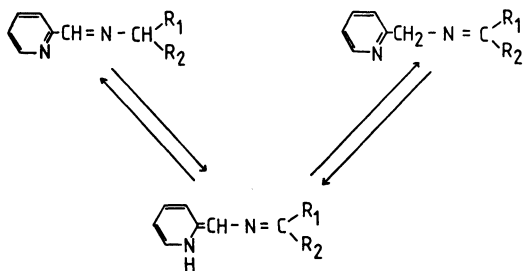


Fig. 19 Potential 2-azadiene intermediate

In order to investigate the mode of reaction of this possible intermediate and to obtain an indication of the reaction mechanism, we synthesized 2-azadienes in the following three ways.

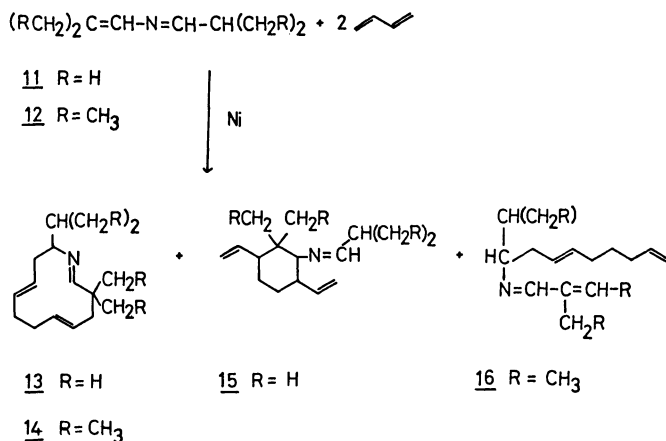


Fig. 22 Nickel(0)-catalysed reaction of 2-azadienes with butadiene

In addition to the open-chain product 16 a further open-chain compound having an octadienyl C₈-chain forms under certain reaction conditions.

Isobutylidene-2-methyl-propenylamine, which is easily prepared from isobutyraldehyde and ammonia reacts with butadiene on the nickel-ligand catalyst (Ni:L = 1:1) predominantly to the twelve-membered ring 13 and the six-membered ring 15. An open-chain product is as a rule not formed. The dependence of the product distribution on the phosphorus ligands is shown below.

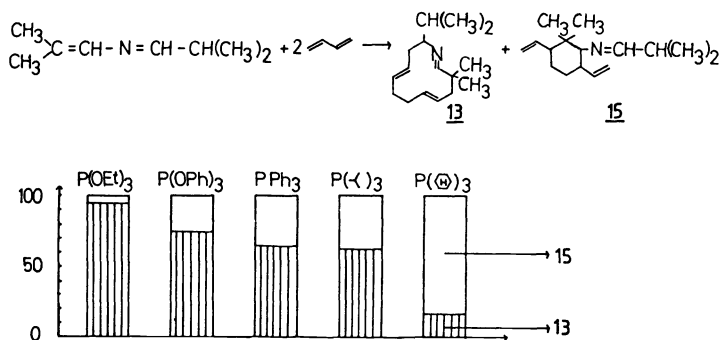


Fig. 23 Dependence of product distribution on phosphorus ligands (Ni:L = 1:1)

With the less basic ligands triethyl- and triphenylphosphite the twelve-membered ring 13 is formed mainly. Whereas ligands with strong donor character, such as triisopropyl- and tricyclohexyl-phosphine direct the reaction towards the six-membered ring.

The product distribution 13 : 15 is not only dependent on the nature of the nickel ligands, but also on the ratio of ligand to nickel.

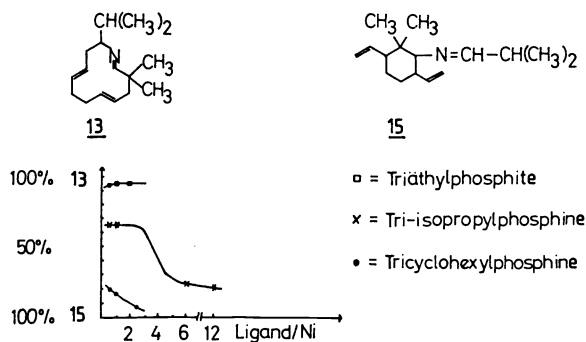


Fig. 24 Dependence of product distribution on phosphorus ligands and L:Ni ratio

With triethylphosphite or tricyclohexylphosphine variation is however relatively small. Thus the twelve-membered ring **13** forms with triethylphosphite at a ligand-nickel ratio between 0,5 : 1 and 2 : 1 to the extent of more than 90%, whereas with tricyclohexylphosphine the six-membered ring forms predominantly. With triisopropylphosphine as ligand an essentially more marked influence on the product distribution is seen. Thus at a ligand-nickel ratio 0,5 : 1 to 1 : 1 one obtains 65% of **13**, whereas the yield of **13** is reduced to about 20% at a ratio of 6 : 1 or 12 : 1. With aromatic substituted 2-azadienes, such as 1-phenyl-2-aza-penta-1,3-diene **17**, the product distribution can only be controlled to a limited extent.

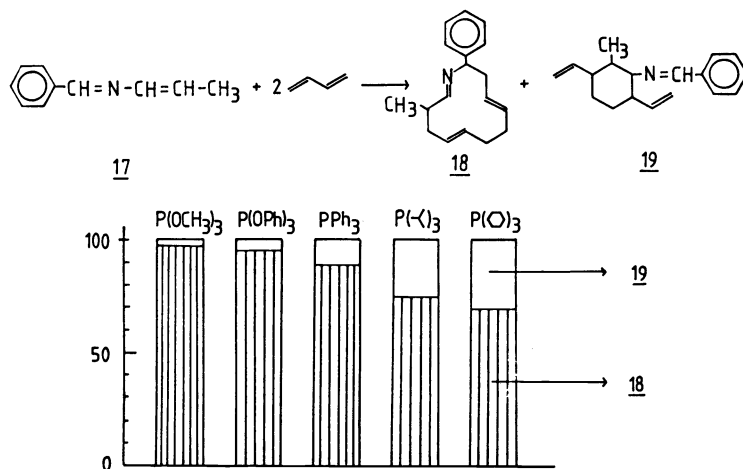


Fig. 25 Dependence of product distribution on phosphine ligand (Ni : L = 1 : 1)

The 1-aza-1,5,9-cyclododecatriene **18** is the main component in every case. The order of the phosphines, compared with Fig. 23 remains the same. The twelve-membered ring **18** consists of two isomers, the main isomer being the crystalline cis-compound, which is slowly (in presence of H^+ ions quickly) converted to the liquid trans-isomer. It was further found that with the 1-phenyl-2-aza-penta-1,3-diene, used in the above reaction, which is obtained from the preparation as a mixture of 54% **17** Z and 46% **17** E, the **17** E isomer reacts significantly more rapidly with butadiene. At a conversion of 61%, the unreacted 2-azabutadiene consisted of 95% of the **17** Z isomer.

Reaction temperature and solvent have a significant effect on the product distribution. For example if isobutyliden-2-methylpropenylamine is allowed to react with butadiene in tetrahydrofuran instead of toluene (catalyst = $\text{Ni}(\text{O}) \cdot (\text{cyclohexyl})_3\text{P}$) the yield of the six-membered ring increases from about 80% to > 96%.

Isoprene normally reacts with 2-azadienes in a very obscure way. A large number of 2 : 1 and 2 : 2 adducts are formed. Twelve-membered rings have so far not been isolated as reaction products.

1,2-Diaza-1,5,9-cyclododecatrienes

Contrary to the 2-azadienes, 2,3-diazabutadienes react with butadiene exclusively to twelve-membered rings, the 1,2-diaza-1,5,9-cyclododecatrienes (18).

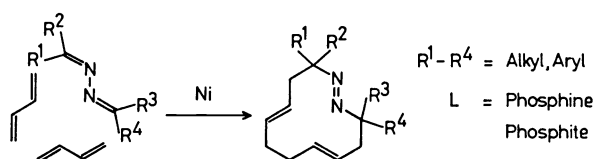


Fig. 26 1,2-Diaza-1,5,9-cyclododecatrienes

Six-membered rings and open-chain compounds are not formed in this case.

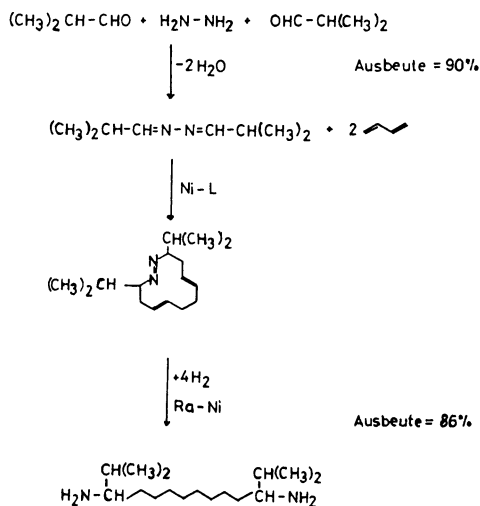


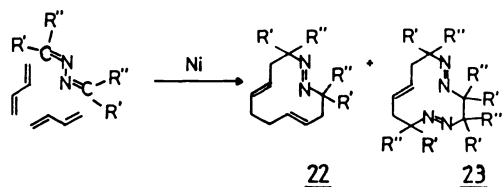
Fig. 27 Synthesis of a 1,10-substituted 1,10-diaminodecane

Isobutyraldazine, which is easily prepared from isobutyraldehyde and hydrazine reacts extremely selectively and in high yields to give 3,12-diisopropyl-1,2-diaza-1,5,9-cyclododecatriene. Dimers and trimers of butadiene only form after all of the 2,3-diazabutadiene has been used up. The twelve-membered ring can then be converted into the corresponding 1,10-diaminodecane in a simple manner.

The synthesis of 1,2-diaza-1,5,9-cyclododecatriene is best carried out in presence of a nickel-ligand catalyst, with ligands such as aromatic phosphines, such as triphenylphosphine. The reaction also occurs with trialkylphosphines and with phosphites, but the reaction rates are significantly slower however. In presence of an excess of butadiene only the diaza-twelve-membered ring

is formed.

If the amount of butadiene used is reduced more and more a new product, a 1,2,5,6-tetraaza-1,5,9-cyclododecatriene is formed, which finally becomes the main product at a butadiene-azine ratio of < 1.



Ratio Butadiene:Azine	Ratio 22:23
3 : 1	90 : 10
2 : 1	75 : 25
1 : 3	35 : 65

Fig. 28 1,2,5,6-tetraaza-1,5,9-cyclododecatrienes

In conclusion I would like to state that the extension of the nickel-catalysed cooligomerisation of butadiene with olefins to heteroolefins such as for example >C=N -double-bond systems has led to many surprises. Prediction of the products obtained on the basis of analogy could certainly only be achieved with great difficulty, as to some extent products were isolated for which there are no analogies in the nickel-catalysed olefin chemistry. Since all of the compounds can be prepared in high yields and with great selectivity and in addition possess functional groups, they may also be interesting intermediates for industrial requirements.

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