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

Dieter Reinehr

Zentrale Forschungslaboratorien, Ciba-Geigy AG,
CH- 4002 Basel, Switzerland

Abstract - The reactions of Schiffs' 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.
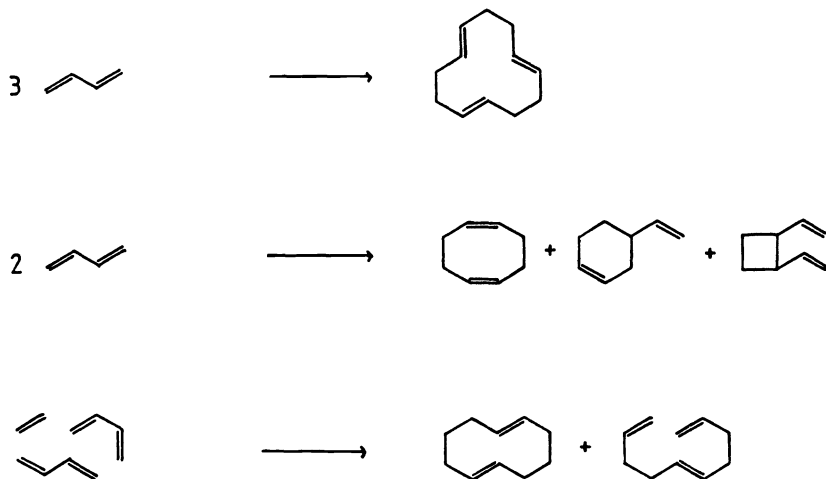

Fig. 1 Characteristic nickel-catalysed reactions

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:
   a) The addition of HCN to butadiene giving adiponitrile, the starting material for hexamethylenediamine (3).
   b) 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).
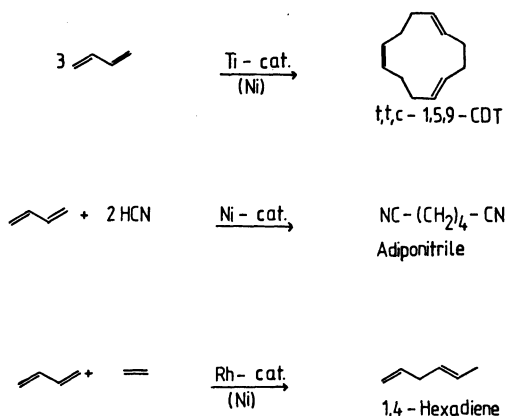
$$3 \diagup\diagdown \quad \xrightarrow[\text{(Ni)}]{\text{Ti - cat.}} \quad \text{t,t,c - 1,5,9 - CDT}$$

$$\diagup\diagdown\diagup + 2\,HCN \quad \xrightarrow{\text{Ni - cat.}} \quad NC-(CH_2)_4-CN \quad \text{Adiponitrile}$$

$$\diagup\diagdown\diagup + \; = \quad \xrightarrow[\text{(Ni)}]{\text{Rh- cat.}} \quad \diagup\diagdown\diagup\diagdown \quad \text{1,4 - Hexadiene}$$

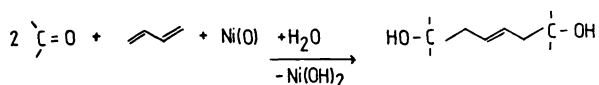Fig. 2   Industrially important homogeneously-catalysed nickel
         reactions

1,5,9-Cyclododecatriene is nevertheless also prepared in large quanti-
ties 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 functionali-
sed 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 $>$C=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:

$$2\; \underset{/}{\overset{\backslash}{C}}=0 \; + \; \diagup\diagdown\diagup \; + \; Ni(0) \; \xrightarrow[\text{- Ni(OH)}_2]{\text{+H}_2\text{O}} \quad HO-\underset{|}{\overset{|}{C}} \diagup\diagdown\diagup\diagdown \underset{|}{\overset{|}{C}}-OH$$

catalytic:

$$\underset{/}{\overset{\backslash}{C}}=0 \; + \; 2\diagup\diagdown\diagup \quad \xrightarrow{\text{Ni-Ligand}} \quad HO-\underset{|}{\overset{|}{C}} \diagup\diagdown\diagdown\diagup\diagdown$$
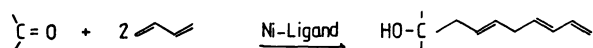
Fig. 3   Reactions of carbonyl compounds with butadiene

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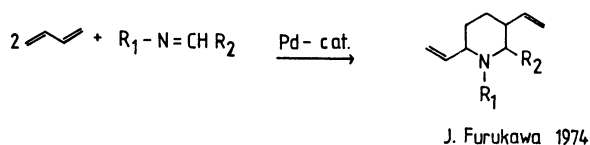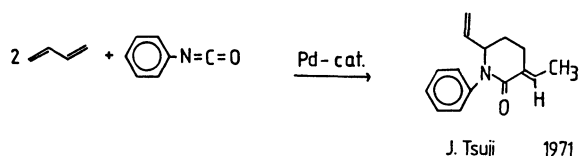or piperidines.

J. Tsuji   1971

J. Furukawa 1974

Fig. 4   Palladium-catalysed reactions of butadiene with >C=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-cyclodecadiene and 1-trans-
4,9-decatriene. The ratio of cyclic to linear cooligomerisation pro-
ducts can be controlled within wide limits by varying the nickel li-
gands or the reaction conditions (9). If the monoolefin ethylene is
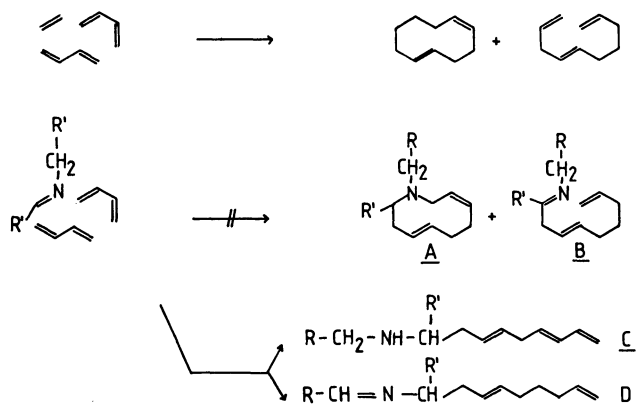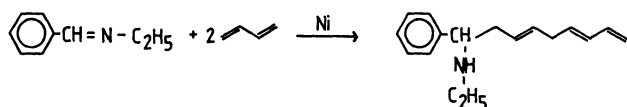replaced by a Schiffs' base, the corresponding reaction products $\underline{A}$
and $\underline{B}$ should be obtained.

Fig. 5   Cooligomerisation of Schiffs' bases with butadiene

The products $\underline{A}$ and $\underline{B}$, analogues of the ethylene reaction, do not
form as a rule. Only $\underline{C}$ and $\underline{D}$ or mixtures of $\underline{C}$ and $\underline{D}$ are isolated.
The reaction can be controlled so that either $\underline{C}$ or $\underline{D}$ 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 $\underline{C}$.
Amines like morpholine possess not only the property of influencing
the selectivity of the reaction, but also accelerate it.

$$\text{Ph-CH=N-C}_2\text{H}_5 + 2 \diagup\!\!\diagdown \xrightarrow{\text{Ni}} \text{Ph-CH}\diagup\!\!\diagdown\!\!\diagup\!\!\diagdown \text{ NH-C}_2\text{H}_5$$

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.

$$\text{Ph-CH=N-C}_4\text{H}_9 \quad + \quad 2 \diagup\!\!\diagdown$$

$$\xrightarrow[\text{1h.}]{\text{95°C} \quad \text{Ni}}$$

$$\text{C}_3\text{H}_7\text{-CH=N-CH}\diagup\!\!\diagdown\!\!\diagup\!\!\diagdown + \text{C}_4\text{H}_9\text{-N-CH}\diagup\!\!\diagdown\!\!\diagup\!\!\diagdown \qquad 75\%$$

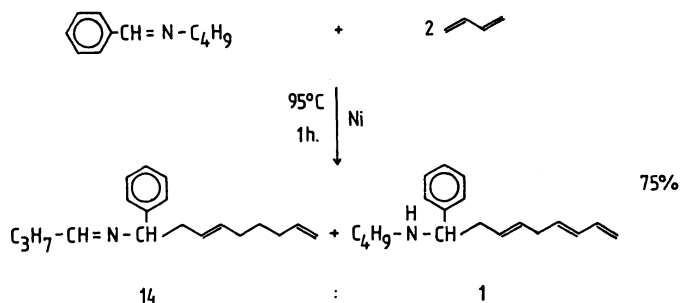$$14 \qquad\qquad : \qquad\qquad 1$$

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.
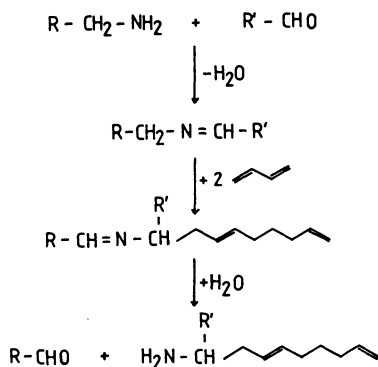
R-CH₂-NH₂ +   R'-CHO

$$\downarrow -H_2O$$

R-CH₂-N=CH-R'

$$\downarrow +2 \nearrow$$

R-CH=N-CH (R') ⌒⌒⌒⌒

$$\downarrow +H_2O$$

R-CHO +   H₂N-CH (R') ⌒⌒⌒⌒

Fig. 8   General reaction scheme for the preparation of
         nonadienylamines

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 -CH₂-group in the α-position. We have been able to esta-
blish that this method is generally applicable. We suggest the follo-
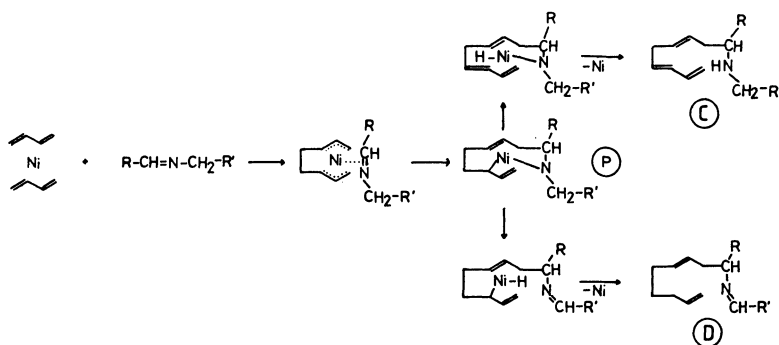wing mechanism for the reaction of Schiffs' bases with butadiene.

Fig. 9   Reaction mechanism for the cooligomerisation of
         Schiffs' bases

We assume that Ⓟ is an important intermediate on which basis the for-
mation of the two isomers C̲ and D̲ 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
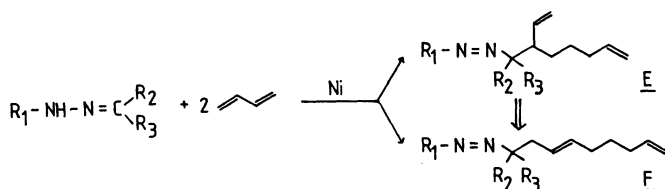(compound E̲) and linear (compound F̲) octadiene chains (11).

Fig. 10   Nickel-catalysed reaction of hydrazones with buta-
          diene

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 ensueing rearrangement E → F (12).
Such a nickel-catalysed isomerisation of butadiene-oligomers has pre-
viously been described only for 1,2-divinylcyclobutane, which rear-
ranges to 1,5-cyclooctadiene and 4-vinylcyclohexene (13). The influ-
ence of temperature and time on the nickel-catalysed rearrangement
of E to F is shown in Fig. 11, where the initial mixture contains
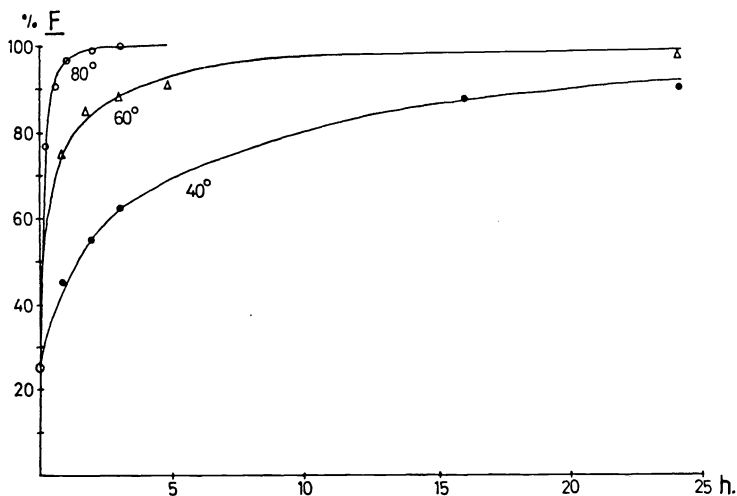75% E and 25% F, with $R_1 = C_6H_5$, $R_2 = H$ and $R_3 = CH_2-CH_3$

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 im-
portant influence on the rate of isomerisation E → F. We found the
following series of decreasing reactivity for the ligand L: PPh_3 ∿
P(cyclohexyl)$_3$ > P(OEt)$_3$ ∿ P(OPh)$_3$ > no L. The formation of
isomers E and F can be explained by the following scheme.
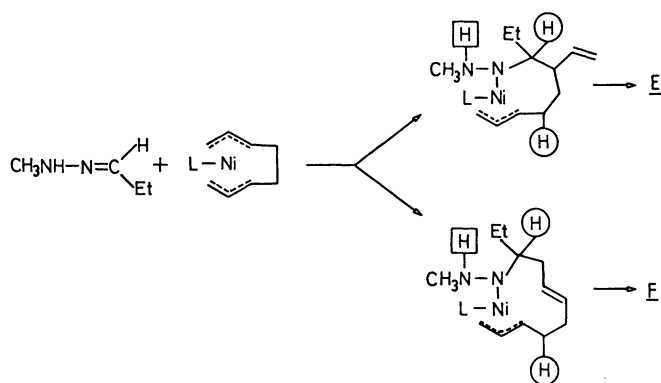
Fig. 12   Proposed reaction mechanism for the cooligomerisation
          of hydrazones

The $>$C=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 transfered to the allyl group.
R. Baker found (11b), that the palladium-catalysed reaction of me-
thyl- and phenyl-hydrazones with butadiene can proceed in a diffe-
rent manner contrary to the nickel-catalysed cooligomerisation. In
addition to the C-alkylated products E and F one obtains an N-alkyla-
ted compound also.

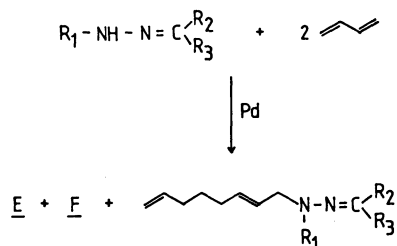Fig. 13   Palladium-catalysed reaction of hydrazones with
          butadiene

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 buta-
diene to give 1:2 adducts. Substituted nonatrienyl amines or azome-
thines containing an additional C_8 unit are formed in yields of
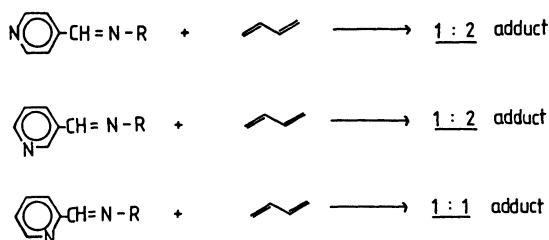60-80%.

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

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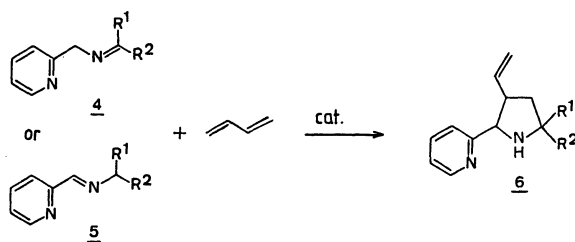to be pyrrolidines or substituted α-nornicotines (14).

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 signifi-
cantly faster and in higher yields: e.g. isobutylidene-2-picolyl-
amine 4 (R^1 = H, R^2 = -CH(CH$_3$)$_2$) reacts with isoprene, which is less
reactive than butadiene, at 40° in presence of 1% of a nickel-ligand
catalyst (Ni: PPh_3 = 1:1) in 2 h. to give the corresponding α-nor-
nicotine 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 ⊃C=N-function into the metal-carbon bond produces 8 and subse-
quent reductive elimination leads to the pyrrolidine derivative 6 and
regeneration of the catalyst. Contrary to 4 the Schiffs' 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 Schiffs' 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.
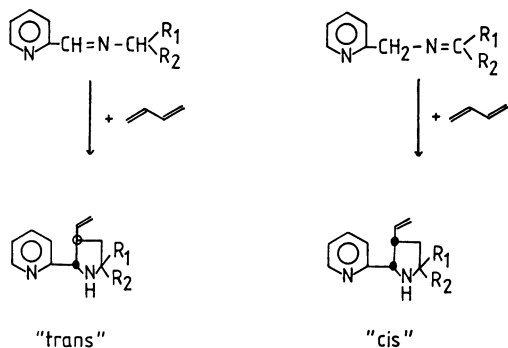Thus isobutylidene-2-picolylamine $\underline{4}$ (R_1 = H, R_3 = -CH(CH$_3$)$_2$) reacts
with ethyl acrylate at 40° in 1,5 h to give the substituted α-norni-
cotine in 92% yield. With acrylonitrile under the same reaction con-
ditions the corresponding pyrrolidines are formed in 85% yield.
These reactions 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 appearence of a 2-azadiene intermediate.

Fig. 19   Potential 2-azadiene intermediate

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

① $2\ \underset{R'}{\overset{R}{>}}CH-CHO\ +\ NH_3\ \xrightarrow{-2H_2O}\ \underset{R'}{\overset{R}{>}}C=CH-N=CH-CH\underset{R'}{\overset{R}{<}}$

② $\underset{R'}{\overset{R}{>}}C=O\ +\ H_2N-CH_2-CH=CH_2\ \xrightarrow{-H_2O}\ \underset{R'}{\overset{R}{>}}C=N-CH_2-CH=CH_2$
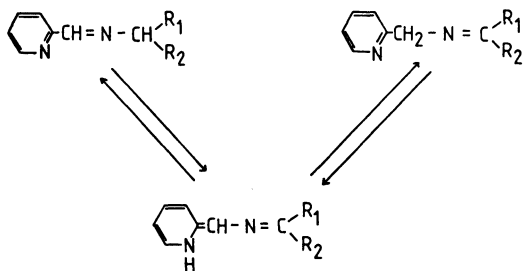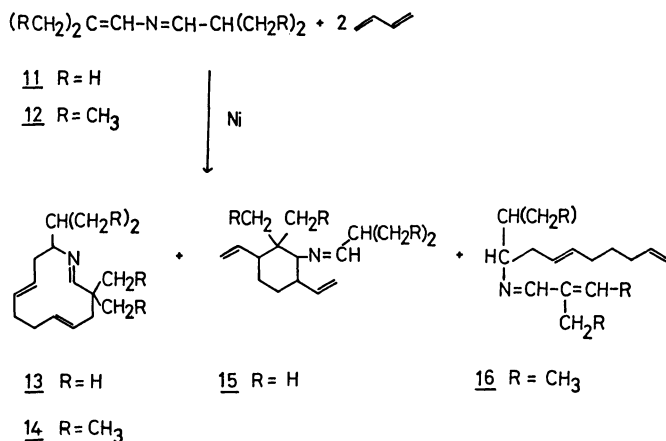
$\downarrow$ Cat.

$\underset{R'}{\overset{R}{>}}C=N-CH=CH-CH_3$

③ $\langle O\rangle-CH_2-NH_2\ +\ R-CH=\overset{R'}{\underset{|}{C}}-CHO\ \xrightarrow{-H_2O}\ \langle O\rangle-CH_2-N=CH-\overset{R'}{\underset{|}{C}}=CH-R$

$\downarrow$ Cat.

$\langle O\rangle-CH=N-CH=\overset{R'}{\underset{|}{C}}-CH_2-R$

Fig. 20   Preparation of 2-azadienes

The first method can be widely used for branched aldehydes (15).
The yields are between 70% and 95% depending on the aldehyde. The
second route leads to high yields of the desired 2-azadienes, espe-
cially with aromatic aldehydes (16).
The third method, starting from α,β-unsaturated aldehydes or ketones
and benzylamine, is however limited to the synthesis of 2-azadienes
with aromatic substituents.
Allylamine Schiffs' bases of α-branched aldehydes give the thermo-
dynamically stable product on isomerisation. For example in the
isomerisation of the isobutylidene-allylamine 9 with 2% potassium
t-butylate as catalyst one obtains after a reaction time of 20 h at 20°
> 85% of the 2-azadiene 11. The primary product 10 is formed to the
extent of < 5%.

$\underset{CH_3}{\overset{CH_3}{>}}CH-CHO + H_2N-CH_2-CH=CH_2\ \xrightarrow{-H_2O}\ \underset{CH_3}{\overset{CH_3}{>}}CH-CH=N-CH_2-CH=CH_2$ 9

$\downarrow$

$\underset{CH_3}{\overset{CH_3}{>}}C=CH-N=CH-CH_2-CH_3 \longleftarrow \underset{CH_3}{\overset{CH_3}{>}}CH-CH=N-CH=CH-CH_3$
$\quad\quad\quad 11 \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad 10$

Fig. 21   Preparation of propylidene-2-methylpropenyl-amine

2-Azadienes + 1,3-dienes
2-Azadienes react with butadiene as a rule to three different reaction
products: a twelve-membered ring, a six-membered ring and an open-chain
product (17).

$(RCH_2)_2 C=CH-N=CH-CH(CH_2R)_2$ + 2 ⟋⟍⟋

11 R = H

12 R = CH$_3$ | Ni

CH(CH$_2$R)$_2$ RCH$_2$ CH$_2$R CH(CH$_2$R)$_2$ CH(CH$_2$R)

[structure 13/14]   +   [structure 15]   +   HC⟋⟍⟋⟍⟋
N   N=CH   N=CH-C=CH-R
CH$_2$R   CH$_2$R
CH$_2$R

13 R = H   **15** R = H   **16** R = CH$_3$

14 R = CH$_3$

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

In addition to the open-chain product **16** a further open-chain compound
having an octadienyl C$_8$-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.

CH$_3$
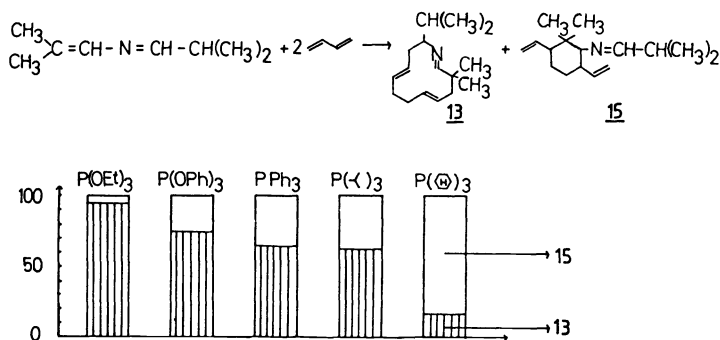   C =CH - N = CH - CH(CH$_3$)$_2$ + 2 ⟋⟍⟋ ⟶   [structures 13 and 15]
CH$_3$

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.

13   **15**

□ = Triäthylphosphite

x = Tri-isopropylphosphine
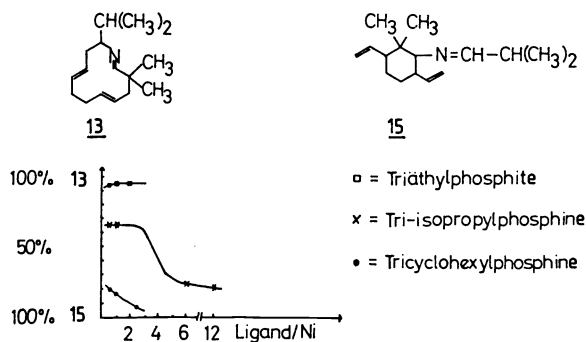
• = Tricyclohexylphosphine

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.

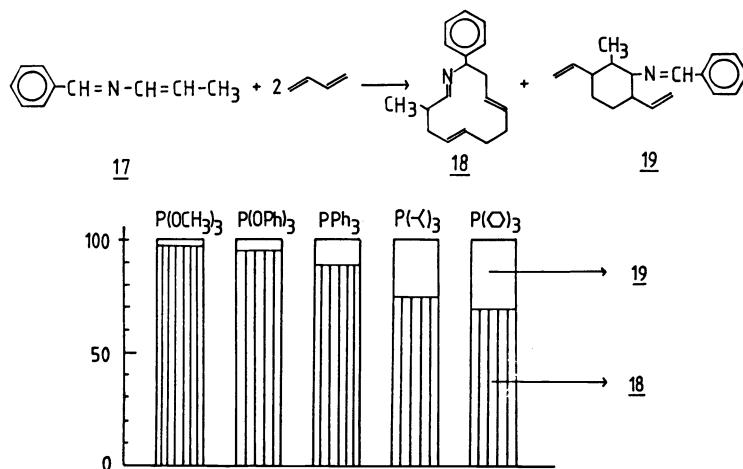17   18   19

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 cristalline 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 = Ni (O) · (cyclohexyl)$_3$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).
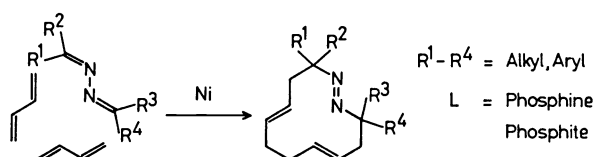

Fig. 26   1,2-Diaza-1,5,9-cyclododecatrienes

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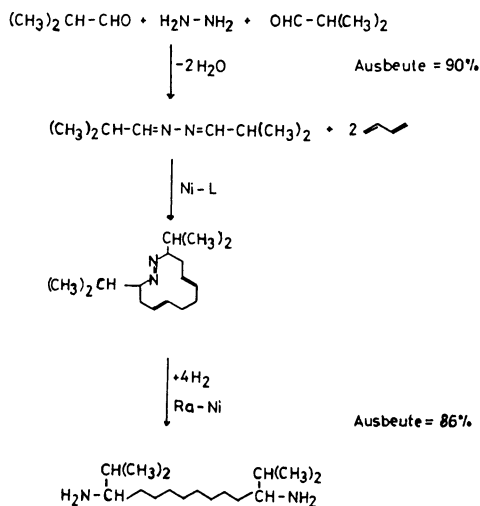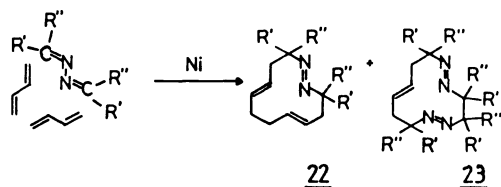

Fig. 27   Synthesis of a 1,10-substituted 1,10-diaminodecane

Isobutyraldazine, which is easily prepared from isobutyraldehyde and hydrazine reacts extremely selectivly 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-cata-
lysed cooligomerisation of butadiene with olefins to heteroolefins such as
for example $>C=N$-double-bond systems has lead 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 selecti-
vity and in addition possess functional groups, they may also be interesting
intermediates for industrial requirements.

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